

Fabrication and Characterization of CVD Graphene Based Hybrid Nanostructures for Photoconductive and Photocatalytic Applications

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Doctor of Philosophy*

By
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This Thesis Dedicated to
..... *My beloved Parents*





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STATEMENT

The work contained in the dissertation entitled “**Fabrication and Characterization of CVD Graphene based Hybrid Nanostructures for Photoconductive and Photocatalytic Applications**” has been carried out by me at Nanofabrication Lab, Centre for Nanotechnology, Indian Institute of Technology Guwahati under the supervision of **Prof. P. K. Giri**, *Professor*, Department of Physics and Centre for Nanotechnology, Indian Institute of Technology Guwahati. This work has not been submitted elsewhere for the award of any degree.

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CERTIFICATE

This is certify that the work contained in the dissertation entitled-**"Fabrication and Characterization of CVD graphene based Hybrid Nanostructures for Photoconductive and Photocatalytic Applications"** has been carried out by *Mr. Biroju Ravi Kumar* at Indian Institute of Technology Guwahati under my supervision. This work has not been submitted elsewhere for the award of any degree.

(P. K. Giri)

16/10/2015

Thesis Supervisor

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SYNOPSIS

Graphene, a two dimensional (2D) prototype carbon material, has revolutionized the nanomaterials research owing to its remarkable physical, chemical, mechanical and electronic properties. The huge carrier mobility, high optical transparency and high thermal conductivity make it a unique material to explore the 2D-physics for the fabrication of devices with wide range of electronic and optoelectronics applications. Interestingly, even in the absence of any band gap, the combination of its unique optical and electronic properties has been explored in the field of electronics and optoelectronics. Recently, graphene and graphene-based hybrid nanoassemblies have gained considerable attention in optoelectronic devices such as displays, light-emitting diodes and solar cells, which demands materials with low sheet resistivity and high transparency. Graphene can fulfil multiple functions in light-conversion systems as the transparent conductive window, photoactive material, channel for charge transport, and catalyst. For exploitation in electronics and photonics, graphene must be in close contact with other materials, which can influence its electrical and optical properties.

Various physical and chemical methods have been developed for the synthesis of graphene using top down and bottom-up processes. Among all the approaches, chemical vapour deposition (CVD) of graphene on different transition metal (TM) catalysts is the most promising, inexpensive and easily accessible method for the production of high quality single layer graphene (SLG). Graphene layers were first grown on Ni catalyst that was exposed to the hydrocarbons at high temperatures (~ 900 - 1000 °C), based on the dissolution of carbon atoms in Ni followed by rapid cooling. The basic disadvantages of graphene growth on Ni and other TMs is that the lack of grain size (few tens of microns) and less control over the number of layers. Interestingly, polycrystalline Cu foils are found to yield a better control over the large area growth and number of layers with low defects for the large scale production. Graphene grown on Cu foil and transferred on to the dielectric substrates exhibit exceptionally high mobility. On the other hand, various chemical exfoliation techniques have been advanced for the fabrication of chemically derived graphene (CDG) using graphite and carbon nanotubes as starting materials. CDG materials exhibit novel functional and optical properties due to the evolution of band gap from the size distribution of sp^2/sp^3 domains and in-plane/edge functionalization with oxygen functionalities. Raman spectroscopy is a versatile and non-destructive characterization tool to probe the crystalline quality, number of layers, defects, doping and functionalization of graphene.

Graphene with plasmonic metal nanoparticles (NPs), such as Au, Ag and Cu, offers a new perspective for the light conversion system by optimization of visible light absorption via the surface plasmon resonance (SPR) of the metal NPs, followed by electron exchange between graphene and metal NPs. The graphene-plasmonic metal hybrid catalyst is a very good candidate for the enhanced photocatalysis, SERS sensor and photoconductive applications. Understanding of various physical and

chemical functionalization approaches to enhance the interaction between metal NPs and graphene with defects and without defects is extremely important. Further, fabrication of integrated nanostructures (NSs) on 2D graphene with inorganic/organic NSs has triggered immense attention for the ensuing applications in the field of optoelectronic and photovoltaic devices, since pristine graphene does not possess a band gap. Integration of highly conductive graphene and extremely photosensitive semiconducting NSs enhances the optical and optoelectronic properties of the graphene–semiconductor hybrids as compared to the bare semiconducting NSs.

This thesis deals with the controlled growth of large area defect free graphene using CVD technique and synthesis of CDG functional materials for studies on their optoelectronic properties. Extensive investigations on number of graphene layers, uniformity, functionalization and defects were probed using μ -Raman spectroscopy and HRTEM analyses. Next, the fabrication of graphene–plasmonic hybrids with TM NPs such as Au, Ag, Cu, and organic molecules as well as the graphene–ZnO hybrid NSs and their SERS, photocatalytic and photoconductive applications were investigated. Significant new results have been achieved through systematic studies on the controlled growth and optoelectronic properties of the hybrid NSs.

At first, we have designed and developed a thermal CVD system in-house for the controlled growth of large area wafer scale SLG on a polycrystalline Cu foil. Next, we optimised the growth process and control the growth kinetics of CVD graphene by monitoring various growth parameters, such as ratio of precursor gases (Ar, H₂ and CH₄), temperature and pre-annealing of Cu foil using in-house developed CVD system. We found that the longer duration of pre-annealing of Cu foil in H₂ atmosphere at higher concentrations gives a large area coverage of SLG (> 90%, 1 cm² area of substrate), which is due to the formation of larger size Cu grains as well as very less nucleation sites of carbon adatoms in reduced environment. Detailed CVD reaction kinetics of graphene growth was investigated using electron microscopy and micro-Raman spectroscopy tools. Clean transfer of graphene from the Cu foil to insulating substrates without any damage and surface corrugation of graphene layers is a one of the challenging issues. Since graphene grows on either sides of the Cu foil, we have etched graphene on one side by two methods, namely i) diamond polishing and ii) reactive oxygen plasma etching techniques. Graphene grown on the other side was collected by conventional wet transfer process and transferred on to a Si/SiO₂, quartz and a free standing suspended graphene on a TEM Cu grid. Further, the residual PMMA and catalyst impurities along with the oxide traces that are present on the graphene substrate were removed by H₂ annealing treatment at 400 °C. After achieving the controlled growth, we have extensively studied the intrinsic defects such as point, line and multiple carbon vacancies on the basal plane and edges of graphene layer with resonance Raman and HRTEM analyses. Further, we have synthesized the CDGs, such as graphene oxide (GO), reduced GO (rGO), graphene oxide nanoribbons (GONR) and graphene quantum dots (GQD) by chemical

exfoliation technique and fabricated its thin films using simple spin coating technique. We have explored the identification of oxygenated functional groups at in-plane and edge sites that are responsible for the visible PL in the CDGs from oxygenation and hydrogenation studies using steady state and time resolved PL, micro-Raman, FTIR, XPS analyses, further corroborated by thermogravimetric analysis (TGA).

Next, we carried out physical functionalization of graphene with TM thin films/NPs such as Au, Ag, Cu and organic molecules (CoPc) grown by sputter deposition/ thermal evaporation on graphene and made extensive studies on the nature of interactions and their applications using resonance Raman spectroscopy, spatial Raman imaging, HRTEM and SPR absorption. The quantitative evolution of defects and defect mediated interaction of graphene-TM metal plasmonic hybrids preserving its sp^2 crystallinity were studied extensively from the physical functionalization of graphene with Au NPs. Defect mediated efficient physical functionalization of graphene was demonstrated for the first time. We further demonstrate the plasmon enhanced visible photocatalysis and SERS detection of organic molecules using graphene-Au plasmonic hybrids as a catalyst substrate. Next, we have demonstrated the fabrication of 1D semiconductor nanostructures on single (SLG) and few layer graphene (FLG) that serve as a versatile 2D platform for growing various ZnO nanorods (NRs), nanowires (NWs) and nanoribbons (NRBs) using low temperature (540 °C) physical vapor deposition (PVD) technique. We propose a new growth strategy based on the vapor-liquid-solid (VLS) and vapor-solid (VS) mechanism in the presence and absence of Au catalyst. An artificial epitaxial relation between wurtzite ZnO and a hexagonal crystalline graphene was proposed based on experimental observations. A systematic investigation on morphological evolution and crystalline structure of the graphene-ZnO NRs, NWs and NRBs was carried out from FESEM, HRTEM, XRD, micro-Raman and XPS techniques. Graphene enhanced UV-vis-NIR absorption and UV-visible PL studies were carried out for as-grown ZnO NRs, NWs and NRBs and origin of various visible and NIR PL emissions were investigated under different annealing conditions. Graphene enhanced UV photodetector (PD) based on graphene-ZnO NW hybrids was demonstrated and various device parameters such as photoresponse time, decay time, responsivity and photocurrent (PC) gain in the self catalytically grown graphene-ZnO NWs and bare ZnO NWs were evaluated. The explicit role of underlying graphene in the enhancement of UV PC was evaluated from the cyclic PC and photoresponse measurements in graphene-ZnO thin film in comparison with bare ZnO based PD.

The entire thesis comprises of **9 chapters**, in which at first the fabrication of millimetre area defect free SLG was demonstrated by the in-house developed CVD technique. We found shape evolution of various graphene grains (circular, star, hexagonal and square type) on the Cu foil during the optimization of CVD process. Large area SLG was achieved by the longer duration (>1 hr)

preannealing of Cu foil in 500 SCCM H_2 flow. An efficient functionalization of graphene with TM NPs was revealed from the striking enhancement of D and D' Raman bands without deteriorating its sp^2 crystallinity. A quantitative and qualitative evaluation of defects and defect mediated interaction of TM NPs with graphene was elucidated experimentally. Further, plasmon enhanced visible light photocatalysis and SERS of organic dye molecules were demonstrated from the graphene-Au plasmonic hybrids. Novel graphene-ZnO NRs, NWs and NRBs were fabricated at a relatively low temperature and established a new growth strategy based on the combination of VLS and VS mechanisms, for the first time. Enhanced UV-visible-NIR PL properties were demonstrated from these novel graphene-ZnO semiconductor nano hybrids. We have developed a graphene enhanced UV PD from ZnO NRs/NWs grown on graphene with enhanced UV sensitivity up to two orders higher than the bare ZnO NWs. The enhancement in UV responsivity was evaluated from the cyclic PC measurements of graphene-ZnO thin film hybrids. In addition, CDG thin films were fabricated by simple chemical approach and we achieved tunable PL through controlled hydrogenation and oxygenation of the in-plane and edge oxygenated functionalities, which are important for the optoelectronic, bioimaging and energy harvesting applications. The important outlines of each chapter are presented below.

Chapter 1 presents the evolution of graphene research since last few years and establishment of various synthesis approaches for graphene growth including chemical routes and its fascinating properties. Various growth strategies on CVD graphene on polycrystalline copper (Cu) foil for the production of large area and single layer defect free graphene is discussed. Further, the development of various transfer techniques of graphene from Cu foil on to the alien substrates and the challenges on a clean transfer of graphene is presented. A special focus on the extensive classification of intrinsic defects and identification of oxygen functional groups in graphene and its functional materials and their optical properties are discussed. Recent advances and the lacunae on the fabrication of graphene based 0D, 1D and 2D hybrid NSs for SERS, photocatalytic and photoconductive applications are presented. Fabrication and optoelectronic device applications on integrated graphene-semiconductor inorganic and organic NR/NW hybrids, especially for hybrid PDs, are discussed. The chapter ends with a motivation for the present work.

Chapter 2 describes the various in-house developed facilities for the controlled growth of graphene and fabrication of graphene-semiconductor heterostructures. It also provides a brief account of vapor deposition systems assembled/developed for the fabrication of TM and ZnO thin films over the graphene. Next, we discuss the working principle of various sophisticated characterization techniques used to explore the structural, optical, catalytic and optoelectronic properties of as-prepared graphene and graphene based hybrid NSs. Design and in-house development of microprobe based

photoconductivity setup to perform the photocurrent and photoresponse measurement on the graphene–ZnO hybrid nanostructures are presented at the end.

Chapter 3 presents the controlled growth of graphene on Cu foil using CVD technique. Optimization of various growth parameters such as flow rates of precursor gases (CH_4 , H_2 and Ar), growth temperature, pressure and effect of pretreatment conditions of the Cu foil on the grain size, shape and evolution of graphene layers are discussed. Next, clean transfer of graphene on the alien substrates followed by H_2 gas annealing is carried out. Morphological and structural features are estimated from optical microscopy, electron microscopy and excitation wavelength dependent Raman spectroscopy. Extensive characterization and classification of in-plane and edge defects on SLG using HRTEM and resonance Raman spectroscopy are presented.

In **Chapter 4**, we demonstrate the physical functionalization of graphene with the TM NPs and the role of intrinsic defects in graphene on the functionalization process. We have deposited various TMs, such as Au, Ag and Cu, on to the CVD graphene with/without defects in it and studied the SERS and SPR effects from the graphene–TM plasmonic hybrids. Wavelength dependent resonance Raman features were studied from the graphene–TM hybrids. A quantitative analysis of defects and defect mediated TM NPs interaction of graphene was studied by resonance Raman spectroscopy, SPR absorption, Raman imaging and HRTEM from the spatial distribution of TM NPs through the defects on a graphene layer.

Chapter 5 presents the application of graphene–Au NP hybrids for plasmon enhanced visible light photocatalysis and SERS sensing of organic dye molecules. We have achieved a strong 85% photodegradation of methylene blue (MB) dye molecules using graphene–Au and graphene oxide–Au hybrid photocatalysts. Extensive role of structural defects and oxygen functional groups was established in the enhanced visible light photocatalytic degradation of MB. Two organic dye molecules, rhodamine 6G (R6G) and fluorescein (FL) with high sensitivity in the visible light (absorption centers at 530 and 470 nm, respectively) were used for the detection of SERS from the graphene and graphene–Au plasmonic hybrids and corresponding enhancement factors were calculated from the standard Raman bands ranging between $600\text{--}1800\text{ cm}^{-1}$ for both the dye molecules on bare Si/SiO₂ substrate. We have achieved an impressive SERS enhancement factor in the order of $\sim 10^2\text{--}10^3$ from graphene–Au plasmonic hybrids.

Chapter 6 demonstrates the graphene assisted controlled growth of ZnO NRs, NWs and NRBs on few layer and single layer graphene using Au catalyst and ZnO seed layers with enhanced optical and optoelectronic properties. The pseudo-epitaxial growth mechanism of ZnO NSs on the graphene substrate was proposed based on the results on different pretreated substrates. Graphene–Au catalyst layer is shown to result in the formation of highly aligned hexagonal faceted ZnO NRs and NWs based

on VLS growth mechanism. Further, self-catalytic growth of vertically aligned ZnO NWs was demonstrated on graphene substrates, based on VS growth mechanism. Morphological, structural and optical properties of these graphene-ZnO NSs were investigated by electron microscopy, XRD, and micro-Raman.

In **Chapter 7**, a systematic study on the optoelectronic properties of graphene-ZnO NSs was carried out using UV-vis-NIR absorption, PL and photoconductivity measurements. Role of graphene on the enhanced UV-visible PL from as-grown and annealed (500 and 700 °C) ZnO NRs, NWs and NRBs in vacuum and Ar gas atmosphere was investigated to explore the origin of various visible and NIR PL emissions from graphene-ZnO hybrid NSs. A new NIR PL emission band is identified in the range between 815 nm–886 nm (1.52–1.40 eV) in the as-grown samples, and it is tentatively assigned to the oxygen interstitial (O_i) defects, detected experimentally for the first time. The local environment and nature of defects in graphene-ZnO hybrids were correlated from the XPS analysis. Graphene enhanced UV PD with graphene-ZnO NW hybrids was demonstrated that shows superior UV sensitivity of the order of 10^2 as compared to that of bare ZnO NWs. A graphene-ZnO thin film UV PD was fabricated to evaluate the enhancement of PC in ZnO film due to the underlying graphene layer. High responsivity (1100×10^3 A/W) was achieved from the cyclic photoresponse measurements at different bias voltages with UV ON/OFF conditions. We evaluated various device parameters such as response and recovery times, responsivity and PC gain in self-catalytically grown graphene-ZnO NWs and bare ZnO NWs as well graphene-ZnO thin film hybrids.

Chapter 8 describes the synthesis of chemically derived graphene (CDG) functional materials such as GO, rGO, GQD and GONRB by chemical exfoliation techniques and subsequent fabrication of CDG thin films using simple spin coating technique. Extensive study on the evolution of visible PL due to in-plane and edge functionalization of graphene with oxygenated functional groups and their identification was carried out through controlled experiments of oxygenation and hydrogenation treatment, for the first time. The origin of various PL peaks were investigated from TGA/DTG and FTIR analyses in the CDGs and are correlated with the Raman analysis. Our studies reveal that the blue and green PL emission can be tuned by controlled hydrogenation and oxygenation treatment of CDGs. Two green emissions in the range of ~ 497 – 502 nm and ~ 534 – 551 nm are assigned to the COOH and C=O sub-band energy states belonging to the edge sites, while the blue emission is attributed to the localised states of sp^2/sp^3 domains and epoxy related in-plane functional groups in the CDG materials.

Chapter 9 summarizes our important findings on the controlled growth of graphene, the fabrication of novel hybrid nanostructures with TMs, fabrication of inorganic/organic semiconductor nanowire/nanorods on graphene and its applications in UV photodetectors, visible light photocatalysis

and SERS. Future scope of work on graphene, related 2D materials and their heterostuctures for the energy harvesting and photosensitive devices are presented at the end.





List of Publications

The important findings of this thesis work have been published in several international peer reviewed journals and conference proceedings as listed below.

A. Publications in International Peer Reviewed Journals:

1. **Ravi K. Biroju** and P. K. Giri; Dhara, S.; Imakita, K.; Fujii, M. Graphene-Assisted Controlled Growth of Highly Aligned ZnO Nanorods and Nanoribbons: Growth Mechanism and Photoluminescence Properties. *ACS Appl. Mater. Interfaces* **2013**, *6* (1), 377-387.
2. **Ravi K. Biroju** and P. K. Giri, Controlled fabrication of graphene ZnO nanorod, nanowire and nanoribbon hybrid nanostructures. *J. Nanosci. Lett.* **2013**, *4*, 34.
3. **Ravi K. Biroju** and P. K. Giri, Defect Enhanced Efficient Physical Functionalization of Graphene with Gold Nanoparticles Probed by Resonance Raman Spectroscopy. *J. Phys. Chem. C* **2014**, *118* (25), 13833-13843.
4. **Ravi K. Biroju**, Nikhil Tilak, Rajender Gone, Dhara. S and P. K. Giri “Catalyst free growth of ZnO nanowires on graphene and graphene oxide and its enhanced photoluminescence and photoresponse” *Nanotechnology* **2015**, *26* (14), 145601.
5. **Ravi K. Biroju**, Rajender Gone and P. K. Giri “On the Origin and Tunability of Blue and Green Photoluminescence from Chemically Derived Graphene: Hydrogenation and Oxygenation Studies” *Carbon* **95** (2015) 228-238.
6. **Ravi K. Biroju** and P. K. Giri “UV Photodetector Based on Graphene–ZnO Nanowire Hybrid: Fabrication, Photoresponse and Photoluminescence Studies” *Advanced Science Letters* (2015, In Press).

B. Manuscripts under Review:

7. **Ravi K. Biroju** and P. K. Giri “Strong Visible and Near Infrared Photoluminescence from ZnO Nanorod/ Nanowires Grown on Graphene Studied Using Sub-band Gap Excitation” (*RSC Adv., Under Review*)

C. Manuscripts under Preparation:

8. **Ravi K. Biroju**, Biswajit Choudhury and P. K. Giri “Plasmon Enhanced Visible Light Photocatalysis in CVD Graphene and Graphene Oxide”
9. Rajender Gone, **Ravi K. Biroju** and P. K. Giri “Photoluminescence from Edge Functionalized Graphene Quantum Dots: Evidence for the Carboxyl (COOH)/Carbonyl (C=O) Sub-Band Emissions”
10. **Ravi K. Biroju**, P. K. Giri “Graphene-Transition Metal Plasmonic Hybrid Nanostructures: A Study on SERS, LSPR and Role of Intrinsic Defects”
11. **Ravi K. Biroju** and P. K. Giri “Fabrication of Graphene– CoPc Organic Molecule Hybrid Nanostructures, Their Structural and Optical Properties”
12. **Ravi K. Biroju** and P. K. Giri “Electron Microscopy and Raman Imaging Studies on CVD Graphene and its Structural Defects”
13. **Ravi K. Biroju** and P. K. Giri “Excitation Wavelength Dependent Raman Spectra in Single-Walled Carbon Nanotubes with Different Purities”

D. Conference Proceeding Papers

1. **Ravi K. Biroju** and P. K. Giri “Spectroscopic and Microscopic Imaging of Graphene-Plasmonic Interfaces” Microscopy Conference (**MC 2015**) Gottingen Sept 6-11, Gottingen, Germany
2. **Ravi K. Biroju** and P. K. Giri “Efficient Physical Functionalization of Graphene and Graphene Oxide for Photocatalytic and Photoconductive Applications” 6th International Conference on Advanced Nanomaterials (**ANM-2015**), July 20-22, 2015, Aveiro, Portugal.
3. Gone Rajender, **Ravi K. Biroju** and P. K. Giri, “On the Origin of Strong Blue and Green Emission from Edge Functionalized Graphene Quantum Dots”, 6th International Conference on Advanced Nanomaterials (**ANM-2015**), July 20-22, 2015, Aveiro, Portugal.
4. **Ravi K. Biroju** and P. K. Giri “Graphene Based 2D-0D Transition Metal Hybrids and Fabrication of 2D-1D Semiconducting Nanowire Heterostructures with Improved Optoelectronic Properties: A New Class of 2D-1D Hybrid Photodetectors”, **Reflux-2015**, The annual Chemical Engineering Symposium, Organized by Department of Chemical Engineering, IIT Guwahati, India, March 27-29, 2015. Received the [Certificate of Excellence \(1st prize\) for the Paper Presentations \(MST\)](#).
5. **Ravi K. Biroju** and P. K. Giri, “Graphene enhanced UV photodetector based on graphene-ZnO nanowires hybrid: fabrication, photoresponse and photoluminescence studies”, First International Conference on Emerging Materials: Characterization and Application (**EMCA-2014**), December 4-6th, 2014, Kolkata, India.
6. **Ravi K. Biroju** and P. K. Giri “Fabrication of graphene/ZnO and graphene/CoPc semiconducting nanowire hybrid structures and their optoelectronic properties”, International Conference on Nanoscience and Technology (**ICONSAT-2014**), Institute of Nanoscience and Technology (INST), Punjab University, Mohali, March 23-25, 2014. Received the [Best Poster Award, Sponsored by Nanoscale, Royal Society of Chemistry \(RSC\)](#).
7. P. K. Giri and **Ravi K. Biroju**, “Site Selective Physical Functionalization of Single Layer Graphene and Its Application in the Growth of 1-D Semiconductor Nanostructures on Graphene” First International Conference on Emerging Materials: Characterization & Application (**EMCA-2014**), CGCRI, Kolkata, Dec 4-6, 2014.
8. Gone Rajender, **Ravi K. Biroju** and P. K. Giri, “Effect of reduction and oxidation treatment on the photoluminescence of edge functionalized graphene quantum dots”, First International Conference on Emerging Materials: Characterization and Application (**EMCA-2014**), December 4-6, 2014, Kolkata, India.
9. Gone Rajender, **Ravi K. Biroju** and P. K. Giri, “Strong visible luminescence from edge functionalized 0-dimensional graphene quantum dots”, National Conference on Transport properties in low dimensional systems: Experiment and Simulation (TransLES-2014), December 11-13, 2014, Guwahati, India.
10. Gone Rajender, **Ravi K. Biroju** and P. K. Giri, “One step solvothermal synthesis of graphene quantum dots: structural and optical studies”, National Conference on Nanotechnology and Renewable Energy (**NCNRE-2014**), April 28-29, 2014, New Delhi, India.
11. **Ravi K. Biroju** and P. K. Giri “Controlled Fabrication of Graphene-ZnO Nanorod, Nanowire and Nanoribbon Hybrid Nanostructures”, International Conference on Nanotechnology Oct 23-25, (**ICNT-2013**), Haldia, Haldia Institute of Technology, Kolkata, India.
12. **Ravi K. Biroju** and P. K. Giri “Improved surface enhanced Raman scattering from copper nanoparticle decorated graphene layer” 6th India Singapore Joint Physics symposium (**ISJPS-2013**) on Physics and Advanced Materials, February 23-25, IIT Karaghpur, India.

13. **Ravi K. Biroju** and P. K. Giri “*Comparative Studies of Graphene, reduced graphene oxide and Graphene Oxide nano ribbons by Raman spectroscopy*” 21st International Symposium on Processing and Fabrication of Advanced materials (**PFAMXXI-2012**), December 10-13 2012, IIT Guwahati, Assam, India.
14. **Ravi K. Biroju** and P. K. Giri “*High quality, large area monolayer graphene synthesized by catalytic chemical vapor deposition for optoelectronic Applications*” 4th International Conference on Advance Nano materials (**ANM-2012**), Oct17-19, 2012, IIT Madras, Chennai, India.
15. **Ravi K. Biroju** and P. K. Giri, “*High quality few layer graphene synthesized by catalytic chemical vapor deposition*” 21st International Symposium on Processing and Fabrication of Advanced materials (**PFAMXXI-2012**), December 10-13, 2012, IIT Guwahati, Assam, India.
16. **Ravi K. Biroju** and P. K. Giri, “*Effect of purity and excitation energy on intermediate frequency Raman modes of Single-Walled Carbon Nanotubes*” International Conference on Nanoscience and Technology (**ICONSAT-2012**), January 20- 23, 2012, Hotel Taj Krishna, Hyderabad, India.
17. **Ravi K. Biroju** and P. K. Giri “*Excitation wavelength dependence of Raman spectra in single-walled carbon nanotubes with different Purities*” 2nd International Conference on Advanced Nano materials and Nanotechnology (**ICANN-2011**), December 8-10, 2011, IIT Guwahati, Assam, India.

E. Workshops Attended

1. **INUP-2012** “*Familiarization workshop on nanofabrication technologies, jointly organized by IISc Bangalore and IIT Guwahati*”, September 28–29, 2012, IIT Guwahati, Assam, India.
2. **NWNTD-2015** “*National Workshop on MEMS/NEMS and Theranostic Devices*” Organized by Centre for Excellence in Nanoelectronics and Theranostic Devices under the aegis of Centre for Nanotechnology, IIT Guwahati, India, March 16-17, 2015.
3. **RESEARCH CONCLAVE-2015** from 23rd–26th March, 2015 Organized by the PhD Council of the Students’ Academic Board (SAB), Indian Institute of Technology Guwahati, Assam, India-781039.

F. Received a Certificate from Central Instrument Facility, IIT Guwahati, for the Operation of Various Sophisticated Characterization Tools during the Period of July 2011–May 2015.



List of Abbreviations

<u>Abbreviation</u>	<u>Description</u>	<u>Abbreviation</u>	<u>Description</u>
2D	Two Dimensional	NS	Nanostructure
BLG	Bi Layer Graphene	NW	Nanowire
CDG	Chemically Derived Graphene	PC	Photocurrent
CVD	Chemical Vapor Deposition	PD	Photodetector
DGR	Defective Graphene	PL	Photoluminescence
FESEM	Field Scanning Electron Microscope	PVD	Physical Vapor Deposition
FFT	Fast Fourier Transform	rGO	Reduced Graphene Oxide
FLG	Few Layer Graphene	RTA	Rapid Thermal Annealing
FTIR	Fourier Transform Infrared Spectroscopy	SAED	Selective Area Electron Diffraction
FWHM	Full Width at Half Maxima	SCCM	Standard Cubic Centimetres per Minute
GO	Graphene Oxide	SEM	Scanning Electron Microscope
GONRB	Graphene Oxide Nanoribbon	SERS	Surface Enhanced Raman Scattering
GQD	Graphene Quantum Dot	SLG	Single Layer Graphene
GR	Graphene	SPR	Surface Plasmon Resonance
HRTEM	High Resolution Transmission Electron Microscope	TGA	Thermogravimetric Analysis
		DTG	Differential Thermogravimetry
MLG	Multi-Layer Graphene	TM	Transition Metal
NP	Nanoparticle	VLS	Vapor Liquid Solid
NR	Nanorod	VS	Vapor Solid
NRB	Nanoribbon	XPS	X-ray photo electron spectroscopy

Chapter 1

Introduction

The occurrence of carbon (C) in nature in many allotropic forms, and its fascinating properties make C a truly unique building block for next generation nanomaterials and nanotechnology. During the past, decades, the miracles of C nanostructures (NSs), such as fullerene, carbon nanotube, graphene have unfolded several aspects of the fascinating field of nanoscience and nanotechnology.¹

1.1. Graphene

The basic concept of sp^2 nanocarbons starts with a single layer graphene (SLG), the planar honeycomb lattice of sp^2 hybridized C atoms. It is considered as the fundamental building block of graphitic materials of all other C allotropes.² This thinnest (one atom thick $\sim 0.335\text{nm}$) and strongest crystalline graphitic material was first isolated by two Russian physicists, Konstantin Novoselov and Andrey Konstantin Geim from university of Manchester, U. K in 2004.³ Both of them received the Nobel Prize in 2010 for ground breaking experiments on graphene. Free standing graphene was first isolated from the repeated peeling of graphite using a simple scotch tape technique.³⁻⁴

In general, this system can be a sheet of infinite in-plane of nanocarbon with one atom thickness which is representing a two-dimensional (2D) sp^2 hybridization containing two atoms per unit cell, A and B. **Figure 1.1(a)** represents the unit cell and first Brillouine zone of SLG. The different allotropic forms of graphitic structures, which are associated with the graphene are shown in the **Fig. 1.1(b)**. It can be wrapped into 0D fullerene (C_{60}) and by stacking of two graphene sheets, bilayer graphene (BLG) is obtained. Below five sheets give few layer graphene (FLG) and stacking of number of graphene layers on top of each other with van der Waals interaction yield graphite (see **Fig. 1.1(b)**). A narrow strip of graphene (below 100 nm wide) is called a graphene nanoribbon. SLG can be rolled-up into narrow strip seamlessly to form single-wall carbon nanotube. Conceptually, nanoribbons and nanotubes could be infinitely long, which represents the 1D systems.⁵ A piece of graphite with small lateral dimensions ($< \text{one hundred nanometers}$) is called nanographite, which represents a 0D

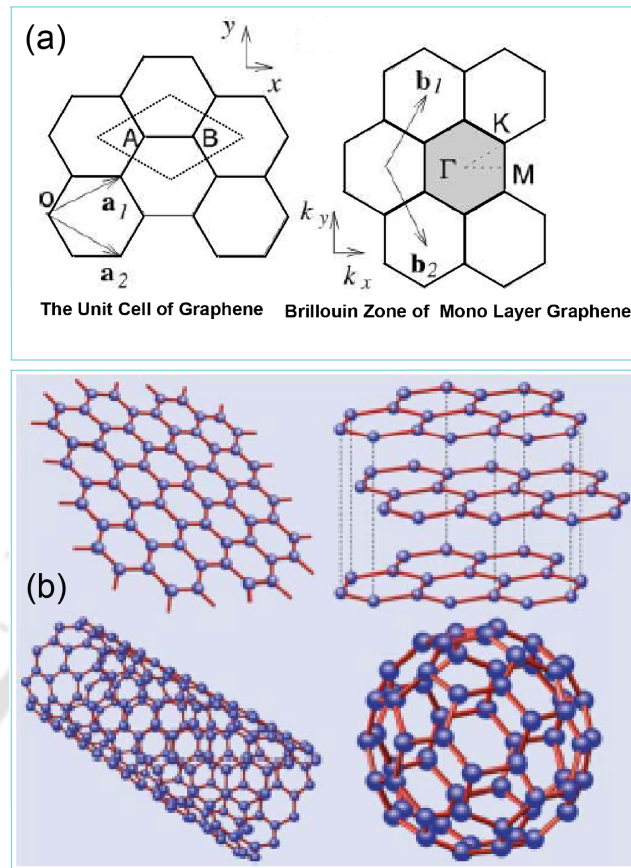


Figure 1.1: (a) The unit cell and first Brillouin Zone of SLG. (b) Graphene (top left) is a honeycomb lattice of carbon atoms. Graphite (top right) can be viewed as a stack of graphene layers. Carbon nanotubes are rolled-up cylinders of graphene (bottom left). Fullerenes (C_{60}) are molecules consisting of wrapped graphene by the introduction of pentagons on the hexagonal lattice. Adapted from **Ref. [7-8]**

system. Another form of the 0D system other than C_{60} is a graphene quantum dot (GQD), which consists of few layers of sp^2 nanocarbon with size varying from 5-50nm.⁶

1.2. Extraordinary Properties of Graphene

The lattice structure of the graphene can be characterized by two types of C–C bonds which are constructed by σ and π bonds. Basically the atomic number of C is 6 and its electronic configuration is $1s^2 2s^2 2p^2$; out of four valence orbitals, $2s$, $2p_x$, $2p_y$ are in-plane and $2p_z$ orbital will be out of plane (in z - direction), which is perpendicular to the sheet. Three σ -bonds join a C atom to its three neighbours. The optical-phonon frequencies are significantly higher as compared to the diamond like carbon due to very strong sp^2 hybridization. The fourth bond is associated with the overlapping of the $2p_z$ (π) orbital that will enhance the C-C bonding.¹⁰ The electronic properties of graphene can be determined by the bonding (π) and

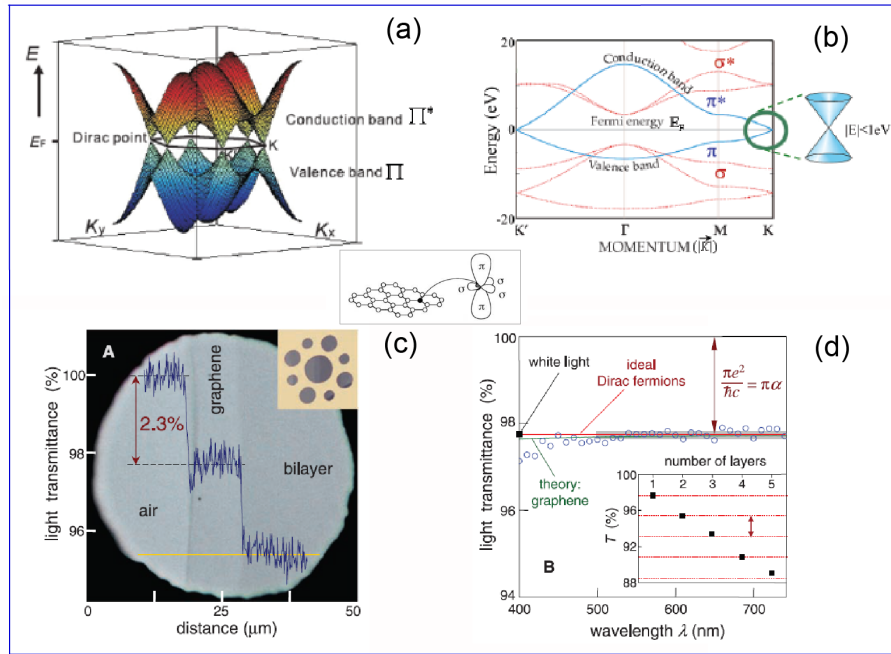


Figure 1.2: (a) Electronic structure of graphene in the first Brillouin zone, and (b) its corresponding energy band diagram. Adapted from **Ref. [7]** (c) Photograph of a 50 μm aperture partially covered single (SLG) and bilayer graphene (BLG), which shows the 97.7% transmission of white light. Note that, the line scan profile shows the intensity of transmitted white light along the yellow line. (d) Optical Transmittance spectrum of SLG (open circles). Adapted from **Ref. [9]**

antibonding (π^*) orbitals, that form electronic valence and conduction bands. The stereoscopic graph of the valence (π) and conduction (π^*) band of graphene in the first Brillouin zone is depicted by **Fig. 1.2(a)**, while **Fig. 1.2(b)** shows the energy of the π (π^*) and σ (σ^*) band along the high symmetry directions in the first Brillouin zone. Based on this band structure, graphene can be considered as a zero-gap semiconductor (semi metal). The π -band electronic dispersion for graphene at the six corners of the 2D hexagonal Brillouin zone is found to be linear,

$$E = \hbar v_F k \quad \dots\dots\dots (1.1)$$

where $\hbar$ is the reduced Planck's constant and v_F ($\approx 10^6$ m/s) is the electron Fermi velocity in graphene and k is the wave vector. The linear electronic dispersion of charge carriers leads to the description of carriers in graphene as “massless Dirac fermions”.⁷ The six points where the cones touch are referred to as the “Dirac” points, and Fermi energy crosses these points in neutral graphene. In addition, the optical transparency of graphene is 97.7% over the wide range of UV-visible-NIR wavelength. Nair *et al.* reported that the visual transparency of

graphene can be defined by its fine structure constant. Graphene is found to absorb a small fraction of incident white light ($\pi\alpha = 2.3\%$), which is a consequence of unique electronic structure of graphene. **Figure 1.1(c)** shows the light transmission from a suspended SLG and BLG on a metal scaffold and its corresponding optical spectrum is shown in the **Fig. 1.1(d)**, Optical transmittance from the SLG is found to be a 2.3% experimentally.⁹ In addition, high carrier mobility ($250,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature)³, very high thermal conductivity ($\sim 5000 \text{ W m}^{-1} \text{ K}^{-1}$)¹¹, huge mechanical strength ($\sim 1.0 \text{ TPa}$) of graphene are excellent for its application in transparent conducting electrodes over the large area, touch screens, flexible and bendable optoelectronic devices. Interestingly, even in the absence of any band gap, the combination of its unique optical and electronic properties has been explored in the field of optoelectronic applications by making graphene based integrated hybrid NSs.

1.3. Growth Techniques of Graphene

Numerous physical and chemical methods have been developed for the last ten years to synthesize the best quality of graphene.¹²⁻¹³ Depending upon the potential applications of graphene and its derivatives, the researchers have developed several methods for the production of graphene using top down and bottom-up processes. We discuss below some of the most common, simple and very low cost synthesis methods, which are summarised in this section.

1.3.1. Mechanical Exfoliation

The high quality graphene was first obtained from the mechanical exfoliation of HOPG³, although the yield is very small quantity using this method. However, it is widely used to probe the fundamental properties of graphene. Fabrication of SLG by repeated peeling of HOPG is shown in the **Fig. 1.3(a)**. Optical microscope (OM) image of the mechanically exfoliated graphene transferred on to a Si/SiO₂ substrate and graphene transistor are also shown in the same figure. Physicists have always highlighted the giant carrier mobility¹⁶ of graphene and its unusual Property arising from the linear energy dispersion.¹⁷ The mobilities of multilayer exfoliated graphene was achieved up to $60,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 4 K.³ Researchers have put more efforts on the large scale production of graphene using top down approaches also, which are known to be chemically derived graphene (CDG) and have the limitations for

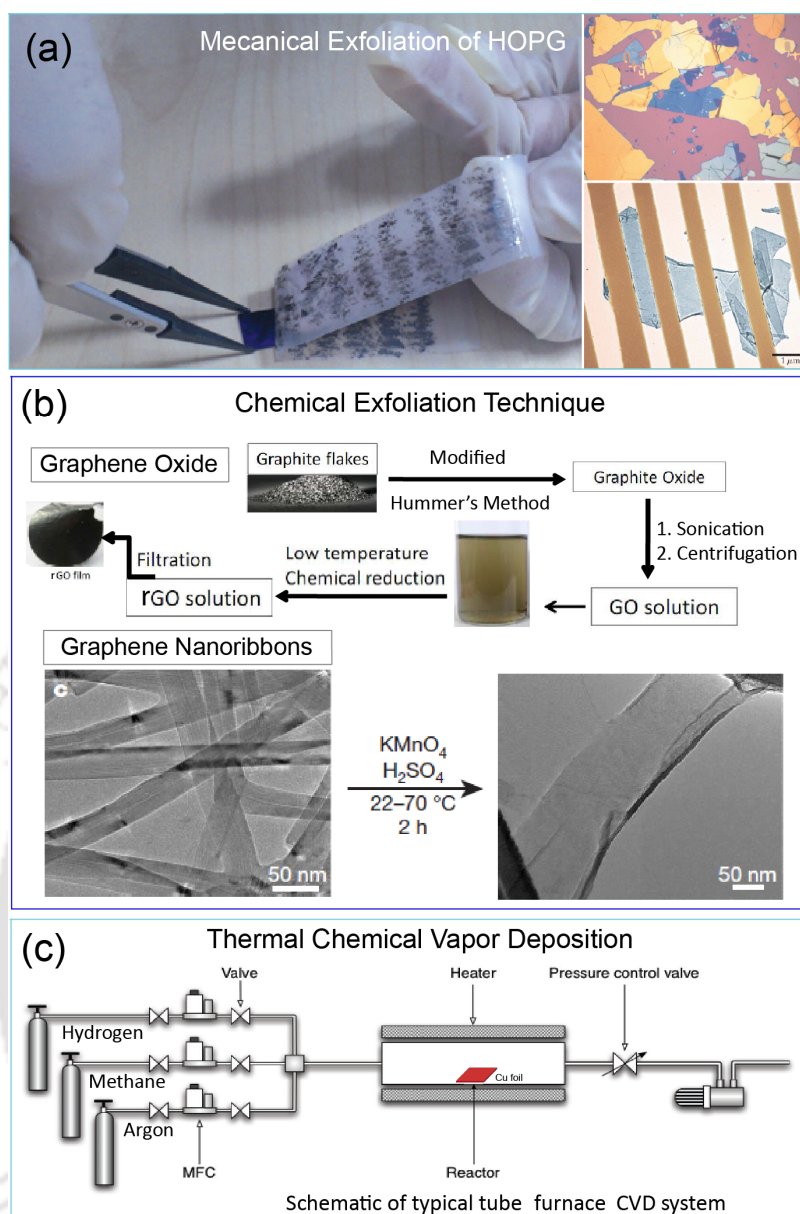


Figure 1.3: (a) Image showing repeated mechanical peeling of graphite to make graphene. Optical microscope image of the mechanically exfoliated graphene on Si/SiO₂ substrate and a graphene transistor. Adapted from **Ref. [4]** (b) A schematic shows the synthesis of chemically derived graphene such as graphene oxide and graphene nanoribbons. Adapted from **Ref. [14-15]** (c) A schematic of graphene growth using thermal CVD system Adapted from **Ref. [10]**.

the efficient electronic device applications due to the structural disorder and various oxygenated functional groups present on the basal plane of CDG.

1.3.2. Chemical Exfoliation

Various chemical exfoliation techniques have been advanced for the fabrication of CDG using graphite, CNTs and other carbon source materials. CDG is also a new kind of 2D form

carbon nanomaterial functionalized with oxygen moieties which shows new functionalities preserving its original properties in pristine form.¹⁴ The common CDG functional derivative of graphene is graphene oxide (GO), which is formed by the chemical synthesis of graphite oxide followed by chemical exfoliation into individual sheets of GO or reduction of GO into reduced GO (rGO).¹⁴ Similar kind of protocol is applicable for the fabrication of graphene oxide nanoribbons (GONRB) with CNTs as a starting material. **Figure. 1.3(b)** shows a schematic of process steps commonly used for the preparation of GO/rGO and GONRBs.^{15, 18} CDG materials exhibit novel functional and optical properties due to the evolution of band gap due to the size distribution of sp^2/sp^3 domains and in-plane/edge functionalization with oxygenated functionalities.^{15, 19} The major advantage of chemical exfoliation that is a very simple and straight forward method to synthesize CDGs which have exceptional optical properties, while there are other physical methods that have been developed for the large scale production of graphene and it focuses on the preservation of intrinsic properties of graphene.

1.3.3. Chemical Vapor Deposition

Chemical vapor deposition (CVD) is a widely used growth technique to fabricate the thin solid films on the various substrates from the vapor species through chemical reactions.¹⁰ The chemical reaction, plays a most prominent role in the formation of thin layers, which is one of the distinct features that CVD possess as compared to the physical vapor deposition (PVD) techniques.²⁰⁻²¹ In conventional CVD reaction gas precursors are utilized to decompose at relatively higher temperatures and deposited on to transition metal (TM) catalysts.²⁰ In most of the PVD processes, the source materials will be solid (powder) and vaporized on to the substrates by transporting through the inert and ambient carrier gases or vacuum.²¹ **Figure. 1.3(c)** shows a schematic of the typical tube-furnace CVD system used for the graphene growth. Note that the full details of our in-house developed CVD system and the growth parameters are discussed in **Chapter 2**. Among all the approaches, CVD growth of graphene on different transition metal (TM) catalysts is most promising, inexpensive and easily accessible method for the production of high quality graphene.¹² The crucial issues in the controlled growth of CVD graphene that are still debating in the graphene research community are: 1. Selection of a proper TM catalyst which have low solid carbon solubility to control the grain size, number of layers, defects etc.,²² 2. Thermodynamic parameters and 3. A clean transfer of graphene onto the alien substrates since direct growth is infeasible.¹²

TM assisted CVD syntheses of graphene using different TMs such as polycrystalline nickel (Ni), copper (Cu) including other TMs have progressed extensively for the last few years.²³⁻²⁵ In these techniques, carbonaceous gaseous species are reacted at high temperatures (900-1100 °C) in the presence of metal thin films/foils, which serve both in the decomposition of the carbon species and in the nucleation of the graphene lattice. The mechanism of graphene growth on a metal catalyst is influenced by several factors, including the carbon solubility limit in the metal, its crystal structure, lattice parameter, and thermodynamic parameters such as the temperature and partial pressures of the reactive system. Most of the growth mechanisms primarily attribute it to the carbon solubility in the TMs: In the case of very low carbon solubility catalysts (<0.001 atomic %) such as Cu, the synthesis of graphene is limited to the surface of the catalyst, and in the case of intermediate-high solubility (>0.1 atom %) metal catalysts, including Co and Ni, graphene synthesis is suggested to proceed via a combination of diffusion into the metal thin film at the growth temperature, and a precipitation of carbon from bulk to the surface of the metal upon cooling after CVD growth.²⁵⁻²⁶ However, large area graphene synthesis using a Cu catalyst in a low and atmospheric pressure CVD process has received much attention, since it was first reported in 2009.²³ The basic disadvantages of graphene growth on Ni and other TMs is that the lack of grain size (few tens of microns) and less control over the number of layers. In particular, polycrystalline Cu foils are found to yield a better control over the large area growth and number of layers with low defects for the large scale production. Graphene grown on Cu foil and transferred on to the dielectric substrates exhibit exceptional mobilities up to $\sim 10,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.¹²

According to the report of Bhaviripudi *et al.*,²² the schematic of the CVD process involved in the growth of graphene is shown in the **Fig. 1.4(a, b)**. A steady state flow of a mixture of methane, hydrogen, and argon gases are sent on the surface of a Cu catalyst at a growth temperature typically 1000 °C during the CVD growth. It is assumed that the boundary layer due to steady state gas flow is stagnant and its thickness is δ . The carbon species first (1) diffuse through the boundary layer and reach the surface, and at the surface they get (2) adsorbed on the surface, (3) decompose to form active carbon species, (4) diffuse on the surface of the catalyst or into the catalyst close to the surface and form the graphene lattice, (5) inactive species (such as hydrogen) get desorbed from the surface, form molecular hydrogen, and (6) diffuse away from the surface through the boundary layer and are

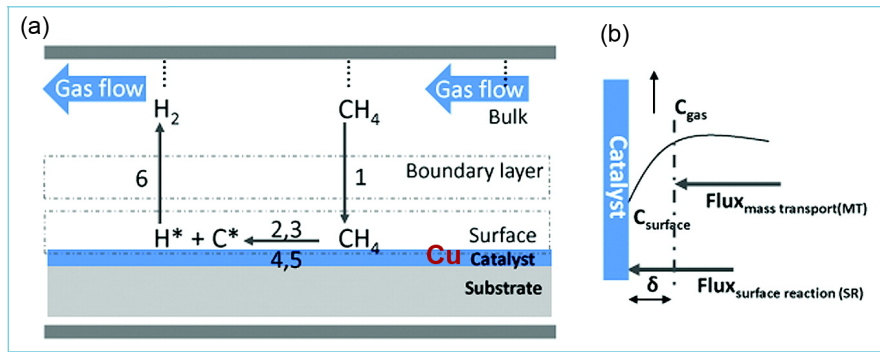


Figure 1.4: (a) Schematic of the CVD process during the graphene growth on copper catalyst. (b) The mass transport and surface fluxes under the steady state conditions. Adapted from **Ref. [22]**

eventually swept away by the bulk gas flow. Depending upon whether the processes take place in the boundary layer (1, 6) or near or closer to the surface (2-4), they can be classified into two regimes: mass transport region, primarily involving diffusion through the boundary layer, and surface reaction region. Processes that take place on or close to the surface are largely affected by the temperature of the substrate. Over all, there are two fluxes of the active species that coexist: flux of active species through the boundary layer and the rate at which the active species are consumed at the surface of the catalyst to form the graphene lattice (**Fig 1.4(b)**). Manipulation of these two species near the catalyst substrate will decide the growth of graphene.^{10, 27} On the other hand the pre-annealing of Cu also plays major role in the segregation of C adatoms to form the monolayer coverage over the large area depending upon the grain size and grain boundary of the Cu.²⁷ However, as long as the temperature along the length and breadth across the Cu substrate maintained uniform, thickness of graphene will be uniform. An important instruction for the CVD processes is that, all the reported values of the growth parameters for a CVD system may not be applicable to another CVD systems, it varies system to system. Keeping the kinetic processes in mind, it is necessary that one must have to perform the test runs of their own CVD system and calibrate it to optimise the thermodynamic parameters for the controlled growth of graphene.

1.4. Raman Spectroscopy of Carbon Nanomaterials

Raman spectroscopy has played a vital role in characterizing various forms of graphitic nanomaterials, historically.²⁸ It has been widely investigated over the last half century to characterize different forms of C species, including graphene.²⁸⁻³⁴ It gives the information

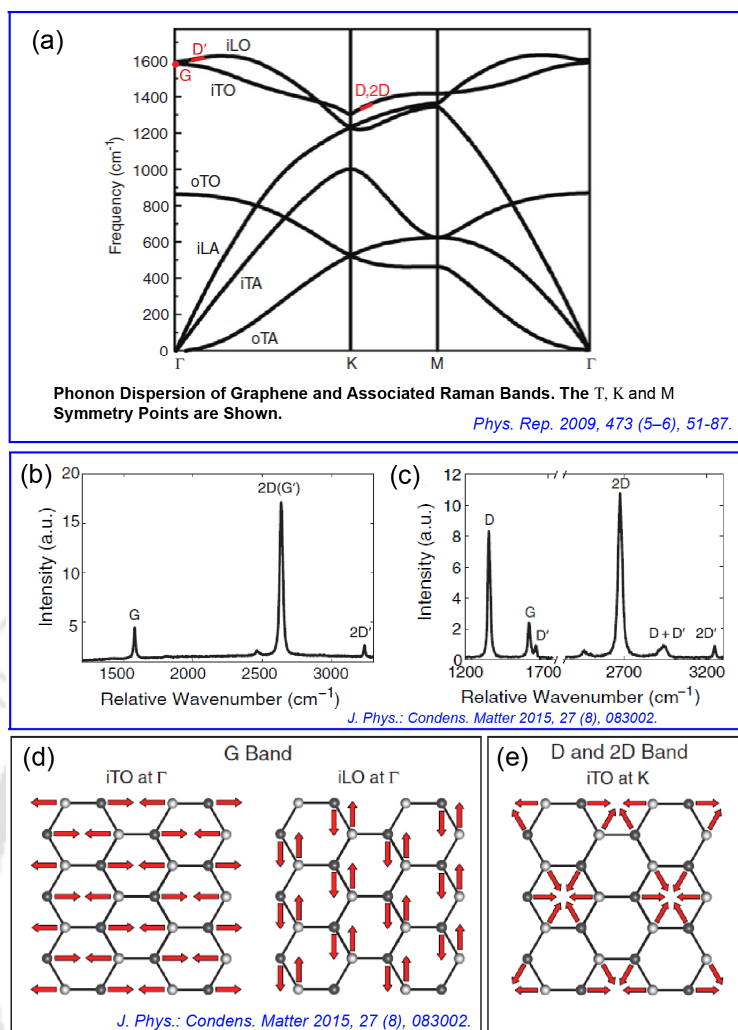


Figure 1.5: (a) Phonon dispersion of graphene. The phonons associated with important Raman bands are highlighted. The Γ , K and M symmetry points are shown. Adapted from Ref. [8]. (b, c) Typical Raman spectra of defect free and defective single layer graphene (SLG). Sketch of the phonon vibrations contributing to the main Raman bands in graphene. Adapted from Ref. [8].

about crystallite size, clustering of the sp^2 phase, the presence of sp^2 - sp^3 hybridization and the introduction of chemical impurities and functionalization,^{15, 35} optical band gap, elastic constants, doping, defects and other crystal disorder, edge structure, strain, number and orientation of the graphene layers.⁸

1.4.1. Overview of Raman Spectrum in Graphene

To understand the Raman modes in graphene, it is important to start with the phonon dispersion, which is shown in **Figure 1.5(a)**. Since the graphene unit cell has two atoms, there are six phonon branches, three acoustic (A) and three optical (O) phonons. Four of the phonon branches are in-plane (i): two acoustic and two optical. The other two branches are

out-of-plane (O). Depending on the direction of the zone-center mode along the carbon–carbon (C–C) bonds or perpendicular, the modes are known as transverse (T) or longitudinal (L). The six phonon branches are labelled in the **Fig 1.5(a)**. The iLO and iTO phonons are responsible for the main Raman bands observed in graphene. It is important to note that the iTO and iLO phonon energies are highly dispersive at the end of K points. **Figure 1.5(b, c)** shows a Raman spectrum of a pristine and defective graphene showing the primary bands, G and 2D, are labeled and there are several other second order Raman bands appearing, such as D, D', D+D' and their combination D+D and 2D'. The physical origin of these important Raman bands are discussed below. **Figure 1.5(d, e)** depicts the contribution of the important phonon vibrations in SLG.

1.4.1.1. Graphitic band (G-band)

The main first order Raman band in graphene, known as the G-band ($\sim 1580\text{ cm}^{-1}$), is a doubly-degenerate (iTO or an iLO zone centre phonon mode) and originates from the in-plane sp^2 C–C stretching vibrations, which belongs to the E_{2g} representation.³⁶ This band exists for all sp^2 carbon systems, including amorphous carbon, CNTs, graphite, and except the line shape, its position varies based on the sample quality.²⁸ The G-band originates from phonons at the point in the centre of the first Brillouin zone. Ideally, the width of the G-band is used to measure the deformation and strain on a sample.³⁷ When the bond lengths and bond angles are modified by strain caused by substrate interaction or with other graphene layers or due to external perturbations, the hexagonal symmetry is broken, therefore G-band is highly sensitive to the strain effects in sp^2 nanocarbons.

1.4.1.2. 2D-band (G')

The strongest peak in graphene is the 2D, or G' band at $\sim 2700\text{ cm}^{-1}$, which is a second order Raman mode originating from the in-plane breathing-like mode of the carbon rings (**Fig. 1.5(b)**). Basically 2D-band is the most distinguishing signature of graphene, which occurs from the double resonance (DR) process, and is created by an incident photon near the K-point resulting into a inelastic scattering of electron by a iTO phonon to the K' point. The conservation of energy and momentum must be satisfied in the Raman process; the electron must be scattered back to K before recombining with the hole. In the case of the 2D band the

electron is back-scattered by a second iTO phonon. The same process can also occur for the hole instead of the electron, consecutively. This process is known as double resonance. The line shape of 2D-band, particularly a Lorentzian shape, is used to determine the number of layers in graphene, experimentally.³⁴ In case of SLG, the 2D band is a single Lorentzian. However, the 2D band splits into four peaks in bilayer graphene (BLG).^{34, 38}

1.4.1.3. Disorder-induced band (D- band)

Another important band in graphene is the disorder-induced or defect band, D-band, which occurs near 1350 cm^{-1} for laser excitation of 514.5 nm .³⁶ This band involves an iTO phonon around the K-point like the 2D-band. However, unlike the G or 2D bands, the D-band requires a defect for the momentum conservation. In this case, the electron is inelastically scattered by an iTO phonon to the K' point and then is elastically back-scattered to the K point by a defect.³⁹ Since only one phonon is involved in the process, the energy shift for the D-band is half that of the 2D-band. For the momentum conservation, a defect causes breaking of the symmetry of the graphene lattice, such as sp^3 -defects⁴⁰, C vacancy sites⁴¹⁻⁴², grain boundaries and edges.⁴³ The defect density can be controllably increased using ion bombardment⁴¹⁻⁴², electron beam irradiation⁴⁴, or plasma functionalization.^{35, 45} Apart from the D-band there may be several other Raman bands, which are called combination modes arising from the edge reconstruction, interlayer coupling, layer stacking etc. They are commonly observed as D' ($\sim 1620\text{ cm}^{-1}$), D+D' ($\sim 2930\text{ cm}^{-1}$), 2D' ($\sim 3240\text{ cm}^{-1}$) and other second order weak modes in the range of $1700\text{--}2300\text{ cm}^{-1}$. It is well-known that, except for the G-band, all second order DR Raman modes D, D', 2D, D+D', and 2D' including weak combinational modes in the range of $1700\text{ and }2300\text{ cm}^{-1}$ of graphene are strongly dispersive in nature with respect to excitation wavelength.⁴⁶⁻⁴⁷

1.5. Graphene based Hybrid Nanostructures

Graphene-based hybrid nanoassemblies have gained considerable attention in optoelectronic devices such as displays, light-emitting diodes (LEDs) and solar cells, which demands materials with low sheet resistivity and high optical transparency.⁴⁸⁻⁵⁰ Graphene can fulfil multiple functions in light-conversion systems as the transparent conductive window, photoactive material, channel for charge transport, and catalyst.⁵⁰⁻⁵¹ For exploitation in electronics and photonics, graphene must be in close contact with other materials, which can

change its electrical and optical properties. Different kind of graphene based inorganic NSs can be built according to the desired functionalities. Depending upon the dimensionalities of the NSs grown on graphene 2D layers, they were categorized into three distinct subgroups: (i) 0D–2D such as nanoparticles(NPs)^{35, 50, 52}; and (ii) 1D–2D hybrids such as nanorods(NRs)/nanowires(NWs)⁵³⁻⁵⁷, nanoneedles⁵⁸, and nanotubes; (iii) 2D–2D hybrids such as nanowalls(NWL)⁵⁸⁻⁶¹, 2D semiconducting transition metal dichalcogenides (TMDC).^{1, 62} These kind of hybrid NSs provide tremendous opportunities to fabricate various electronic, optoelectronic and sensor applications, which are emerging as a new avenue of 2D materials research. In the next sections, we present the fabrication of each type of graphene based hybrid systems and their important applications reported in the literature.

1.5.1. Nanoparticles on Graphene Layers and their Applications

Several kinds of inorganic NPs including TM NPs have been grown on graphene layers.^{50, 63} Most of the inorganic NPs and quantumdots (QDs) were decorated on the graphene using chemical approaches and produced the graphene-0D hybrids. Chemical approaches yield high production rate of graphene-0D hybrids.^{50, 52} Different types of TM, inorganic QDs and graphitic hybrid structures have been categorized based on the covalent and noncovalent interactions.⁵⁰ Inorganic NPs and graphitic interfaces are divided into four categories, based on different surface functionalities on graphitic surfaces (pristine or nonpristine), which appear to be most influential on the system, as shown in the schematic **Fig. 1.6**. Based on this illustration, the interaction of foreign materials with pristine and defect free CVD graphene is very weak due to its inert nature of covalently bonded sp^2 carbon (C) atoms on the basal plane, as compared to CDG having surface functionalities. It is generally believed that the covalent interface between graphene and inorganic NPs starts from the defects such as nonhexagonal rings, vacancies, oxygenated defect sites.⁵⁰ It is important to understand the possible approaches to enhance the interaction between metal and graphene with defect and defect free graphene for ensuing applications. We present some of the important applications of the graphene-0D hybrids below.

1.5.1.1. Solar cells

As an example of inorganic NPs on graphene layers, a CdSe QDs array was prepared on the graphene sheet using an electrochemical synthesis method by Kim *et al.*⁶⁴ **Figure 1.7(a)** shows the schematic illustration of the fabrication method, where a mesoporous silica film

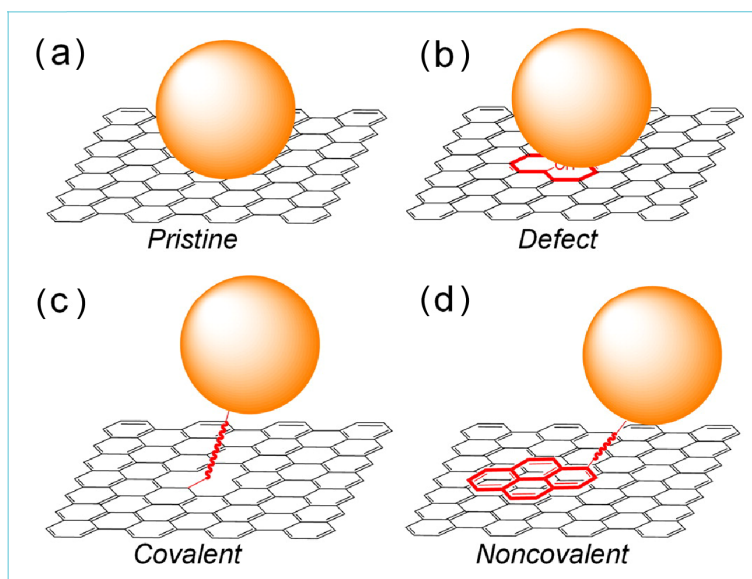


Figure 1.6: Schematic illustrations of four different types of transition metal– graphitic interfaces. (a) The pristine interface where TM NPs and pristine graphitic surfaces are in direct contact. (b) Metal–defect interface where atoms of TM NPs are bonded to the defect sites of the graphitic surfaces. (c) Covalent interface where covalent bonding between organic linkers and the graphitic surfaces is formed. (d) Noncovalent interface where organic linkers are attached to the graphitic surface through noncovalent interactions. Adapted from **Ref. [50]**

was employed as a hexagonal lattice mask for the selective formation of the NPs. Because CdSe was deposited only through the vertical pore channels under a constant potential of -0.7 V, the hexagonal array of CdSe NPs was formed on graphene layers as shown in **Fig. 1.7(b, c)**. **Figure 1.7(d)** shows the HRTEM image of the CdSe-graphene hybrid NSs. The resultant CdSe-graphene hybrids showed a red shift in the G and 2D-bandsbands of Raman spectra, which indicate the doping of graphene. In addition, the large shift of Raman peaks suggests a strong interfacial charge coupling between CdSe nanocrystals and the graphene sheet. Followed by this report, CdSe NPs on graphene layers was used as a QD sensitized solar cell applications.⁶⁵ According to the photovoltaic measurements of the QD sensitized solar cell, the optimal weight ratio of CdSe to graphene was found to be 4.5: 1. It has been suggested that graphene plays an important role in capturing and carrying photoinduced electrons by the CdSe NPs. Other factors determining the solar cell performance may include NP size, resistance between CdSe–graphene film and the substrate, and choice of electrolyte. There are other reports which have worked on the dye sensitized solarcells using graphene as a transparent conducting electrode due to its low sheet resistance and high optical transmittance over the wide range of UV-visible-NIR spectrum.⁶⁶

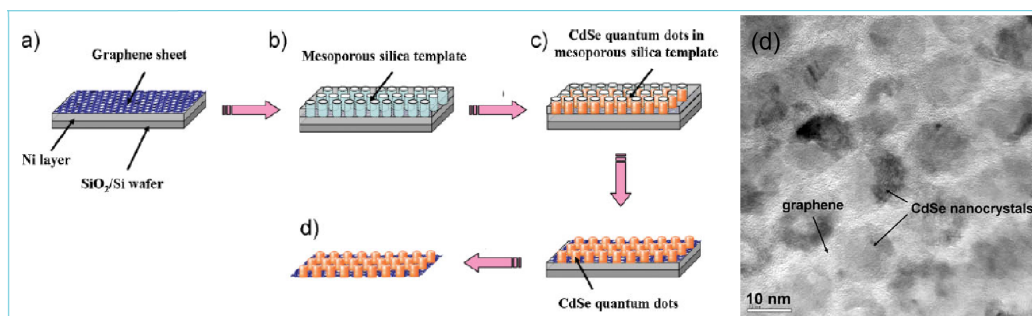


Figure 1.7: (a-c) Schematic process steps of the fabrication of CdSe-graphene hybrid structure on the basal plane of a graphene sheet using a mesoporous silica thin film as a template. (d) HRTEM image of the CdSe-graphene interface. Adapted from Ref. [64]

1.5.1.2. Photocatalysis

In addition to II–VI compound semiconductor NPs, many kinds of metal oxide NPs and conventional photocatalytic nanomaterials have been grown on graphene layers for energy and environmental applications.⁶⁷ As a representative photocatalytic material, TiO₂ nanocrystals were prepared on GO sheets for photocatalytic applications using a two-step method of TiO₂ coating by hydrolysis and subsequent hydrothermal crystallization.⁶⁸ **Figure 1.8(a-b)** represents the SEM and HRTEM images of the GO-TiO₂ hybrids. The TiO₂ and GO hybrid structures showed strong interactions between nanocrystals and graphene sheets. **Figure 1.8(c-e)** represents a schematic of the photodegradation experiment using Rhodamine B as a reference pollutant and their activities in comparison to the commercial photocatalyst P25. As a result of graphene the photocatalytic activity was three times higher than that of the commercial TiO₂ catalyst P25 (Degussa). There are several other reports exploiting graphene by fabricating the graphene-TM NPs hybrids and incorporating with the conventional photocatalysts to enhance the UV and visible light photodegradation of various organic environmental pollutants.⁶⁹⁻⁷² However, the mechanism and photocatalysis process parameters need to be addressed clearly by using graphene based plasmonic hybrid photocatalysts in comparison with conventional ones.

1.5.1.3. Supercapacitors

Graphene based functional materials are very good candidates for the super capacitor applications.⁷³ Due to large surface area and various oxygenated functional groups on the basal plane, it will provide the large amount of charge accumulation during charge/discharge processes.⁷³ The anode materials for the efficient Li-ion batteries, TM oxides particles⁷⁴, such

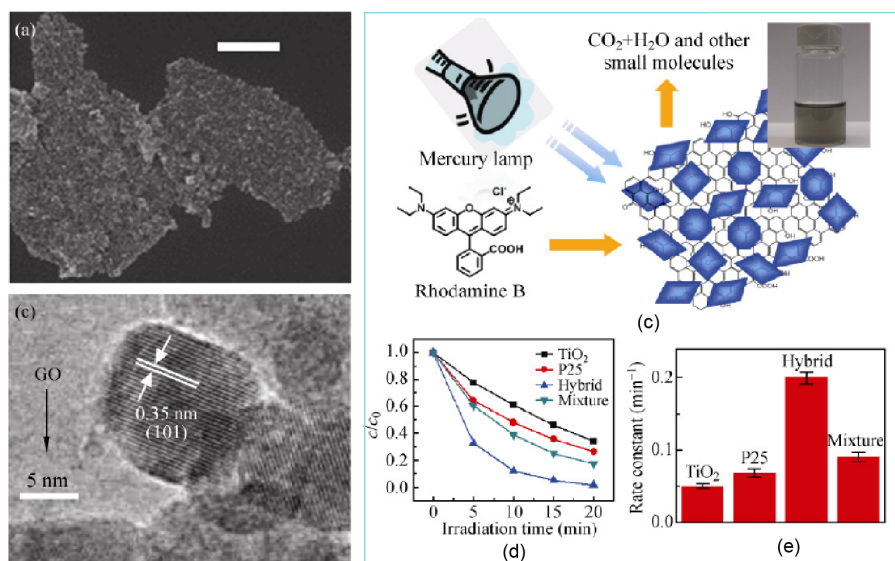


Figure 1.8: (a) SEM and (b) HRTEM images of TiO₂ nanocrystals grown on GO sheets (c) Schematic illustration of the photodegradation of rhodamine B molecules by the graphene/TiO₂ hybrid under irradiation by a mercury lamp. The inset shows the solution of the graphene/TiO₂ nanocrystals hybrid. (d) Photocatalytic degradation of rhodamine B monitored as normalized concentration change versus irradiation time in the presence of free TiO₂, P25, graphene/TiO₂ nanocrystals hybrid and a graphene/TiO₂ mixture. (e) Average reaction rate constant (min⁻¹) for the photodegradation of rhodamine B with free TiO₂, P25, graphene/TiO₂ nanocrystals hybrid, and the graphene/TiO₂ mixture. Adapted from **Ref. [68]**

as Co₃O₄⁷⁵⁻⁷⁶, Fe₃O₄⁷⁷, NiO⁷⁸, and Mn₃O₄⁷⁹ NPs, are promising alternatives for the graphite due to more efficient diffusion of Li ion and high specific capacities. However, due to their high reactivity and mechanical degradation caused by large volume swing associated with intercalation/deintercalation of Li-ions during charge/discharge cycling, it leads to the less usage and performance.⁸⁰⁻⁸¹ To overcome these issues, graphene or rGO sheets have been implemented as current collectors and mechanical supporters to host active nanomaterials by exploiting its high conductivity, large surface area, flexibility, and chemical stability.⁸²⁻⁸³ Based on the idea, Zhu *et al.* attempted to synthesize high lithium storage capacitor by using several metal oxide-rGO hybrids.⁷⁶ CoO/rGO hybrid was one of the examples for high specific charge capacitor. To fabricate the hybrids, ultrathin CoO nanowalls were attached on rGO sheets, which was derived from a-Co(OH)₂/rGO precursors by hydrothermal process. Through the optimization of the grain size of CoO nanoparticles by annealing under different gas environments and temperature, the CoO/rGO hybrid anode materials showed very promising performance with a high specific capacity of ~ 730 mAhg⁻¹ even after 100 cycles

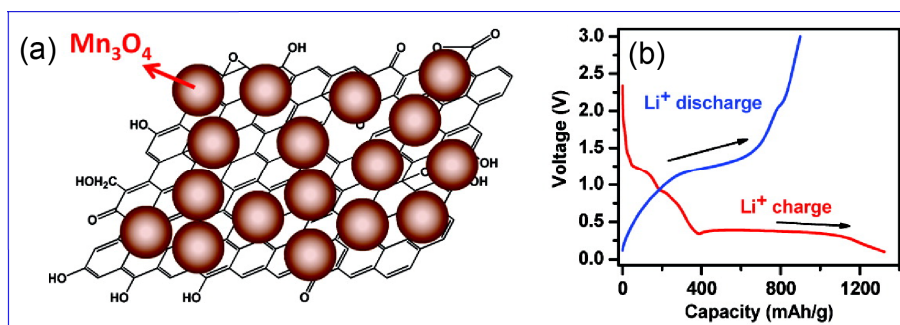


Figure 1.9: (a) Schematic of the $\text{Mn}_3\text{O}_4/\text{rGO}$ hybrid (b) Charge (red) and discharge (blue) curves of $\text{Mn}_3\text{O}_4/\text{rGO}$ for the first cycle at a current density of 40 mA/g. Adapted from Ref. [79]

at a discharge current density of 150 mA g^{-1} . TiO_2 -graphene hybrid nanomaterials have also been investigated as Li-ion battery anodes.⁸³ Compared with that of pure TiO_2 , the specific capacity of the TiO_2 -graphene hybrid nanomaterials was more than twice higher, even at high charge and discharge rates. This suggests that graphene provides enhancement in electrically connected channels and embedded metal-oxide supporting layers. In addition, Wang *et al.* reported that hybrid materials of Mn_3O_4 NPs on rGO sheets provide an enhanced high capacity, good rate capability and cycling stability.⁷⁹ **Figure 1.9(a)** shows a schematic of the $\text{Mn}_3\text{O}_4/\text{rGO}$ hybrid and **Fig. 1.9(b)** depicts the charge/discharge characteristics in the first cycle at a current density 40mA/g. It was found the superior charge capacity up to $\sim 900 \text{ mAh g}^{-1}$ based on the total mass of Mn_3O_4 . Although electrically insulating properties of Mn_3O_4 generally limit their use as an anode material, the Mn_3O_4 particles in the hybrid structure are electrically wired to underlying graphene layers, thereby increasing the capacity of Mn_3O_4 relative to its theoretical value of $\sim 936 \text{ mAh g}^{-1}$. Meanwhile, the charging capacity was reduced three-fold in the absence of the graphene layers, indicating enhanced charge transport due to close interactions between the Mn_3O_4 nanoparticles and the supporting graphene layers.

1.5.1.4. Surface Enhanced Raman Spectroscopy

Apart from the semiconductor QDs, metal and metal oxide NPs, various TM NPs, such as Ag ⁸⁴⁻⁸⁶, Au ^{35, 87-88}, Pd ⁸⁹⁻⁹⁰ and Pt ⁹¹⁻⁹² NPs, were also synthesized on graphene layers for surface enhanced Raman spectroscopy (SERS), bio-sensor, light energy conversion and fuel cells. Graphene with TM plasmonic NPs offers a new perspective for light conversion systems by optimization of visible-light absorption via the SPR of the NPs, followed by electron exchange between graphene and NPs and charge transport through graphene.⁹³ For

example, Ag nanoparticles were grown by heating the rGO substrate in aqueous silver nitrate solution under N₂ without using any surfactant or reducing agent.⁸⁵ Additionally, the graphene–Ag hybrid film was also obtained through the silver mirror reaction on graphene oxide layers.⁸⁶ The resulting Ag NPs on graphene layers show a high optical reflectivity, and a SERS activity leading to the signal increase of the graphene vibration modes. In graphene–Au NPs systems⁸⁷, Au nanoparticles were decorated on the surface of octadecylamine functionalized graphene suspended in a watermiscible organic solvent (THF). It was found that the presence of graphene sheets can prevent the Au NPs from aggregating, and Au NPs were attached on the surface of graphene by physisorption without any chemical bonds. The SPR effect from Au nanoparticles remains largely unaffected by the underlying graphene, and thus the metal–graphene hybrids may find potential uses in photocatalysis, plasmonic and optoelectronic applications. In addition to Ag and Au nanoparticles, other catalytic metals such as Pd, Pt, and magnetic particles can be immobilized on graphene which are useful in sensor, battery, solar cell, and fuel cell applications.⁸⁷ On the other hand, recent studies on CVD graphene have focused on the interaction of TM NPs with graphene in atomic scale and various experimental tools have been exploited.^{44, 84, 94-98} One of the important tools to probe the resonant effects between graphene and TM NPs is SERS. Significant Raman enhancements due to near field plasmonic effects in the vicinity of metal NPs and graphene were reported for different laser excitations.^{88, 99} Urich *et al.* reported the enhanced electron–phonon interaction by monitoring SPR effect in the Ag–graphene hybrid structure.⁸⁴ Park *et al.* studied the Au NPs–graphene–Au film junction hybrid system to identify the layer breathing mode and other out of plane phonon modes of few layer graphene through SERS.¹⁰⁰

1.5.2. Semiconductor Nanorods/Nanowires Grown on Graphene and their Applications

The absence of band gap in graphene and its remarkable electronic and optical properties foster the fabrication of plenty of 2D–1D integrated semiconductor hybrid NSs.⁶³ In such kind of graphene based hybrid structures, graphene acts as the 2D substrate onto which several 1D semiconducting nanomaterials can be grown and superior properties may be expected. Graphene mediated growth of semiconducting NWs and NRs heterostructures has received enormous attention for possible integration of 1D and 2D nanomaterials yielding

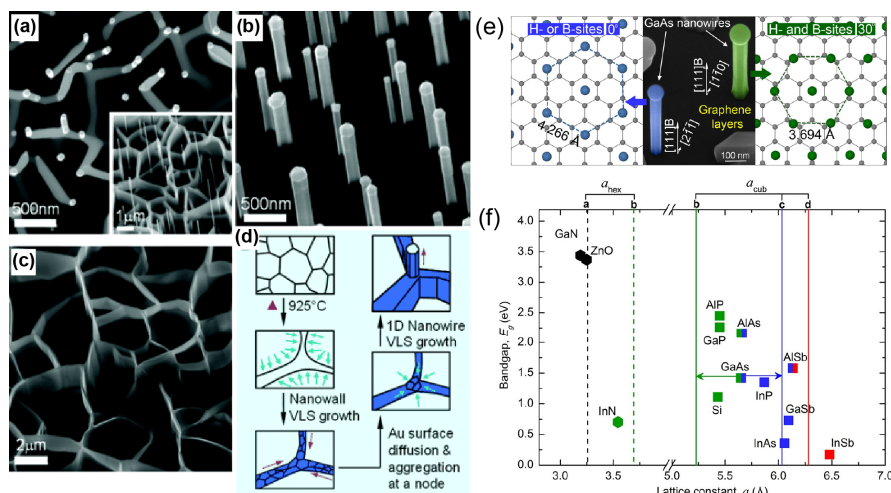


Figure 1.10: (a) SEM image of quasi-3D ZnO nanostructures grown on sapphire using 40 to 50 Å Au thin film as the catalyst. The inset shows a SEM perspective view. (b) 2D ZnO nanowalls (NWL) on a sapphire with a height 15 nm. (c) An array of free-standing 1D ZnO NWs on a HOPG substrate using 15 Å Au film as the catalyst. (d) Schematic illustration showing the growth mechanism of ZnO NWs and NWs. (e) Relative orientation and arrangement when semiconductor atoms are adsorbed on 'H- or B-sites' and 'H- and B-sites' and FESEM image of GaAs NWs grown on graphene layer. (f) Generic model describing the semiconductor bandgaps vs. lattice constants together with lattice constants for the lattice-matched atom arrangements on graphene. Dashed and solid lines correspond to the hexagonal (a_{hex}) and cubic ($a_{\text{cub}} = a_{\text{hex}} \times 2$) crystal phases of these lattices, respectively. The square (■) and the hexagon (●) represent the cubic and the hexagonal phases, respectively. Adapted from Ref. [53, 111]

superior electronic and optoelectronic functionalities. The presence of graphene layer over a dielectric surface may catalyze the growth of well aligned NWs. The extraordinary properties of graphene, such as the presence of 2D hexagonal sheet like structure having one atom thick sp^2 hybridized carbon,¹⁰¹ high carrier mobility, excellent optical transparency (97.7 %) over the entire visible region,⁹ mechanical flexibility¹⁰² and high thermal conductivity,^{11, 103} make it an attractive candidate to integrate it with semiconducting NWs, NRs and nanoribbons (NRBs) that may exhibit exceptional properties. It is expected that integration of the highly conductive graphene and extreme photosensitivity of the semiconducting NWs could improve the optical characteristics of graphene–semiconducting NWs based hybrid structures as compared to the semiconducting NWs only.¹⁰⁴⁻¹⁰⁵ Thus, it can serve as an exciting active material in the field of photovoltaic and optoelectronic device applications. In the process of fabrication of NW heterostructure, researchers utilized different kinds of heterostructure architectures using various suitable external materials including graphene.^{104, 106-110}

Ng *et al.*⁵⁹ reported the fabrication of vertically aligned 2D and 1D ZnO NWs and nanowalls (NWs) on electrically conducting HOPG and on insulating (1120) sapphire substrates for the first time using a carbothermal reduction process and Au as a catalyst as shown in the **Fig 1.10(a-c)**. **Figure 1.10(d)** represents a schematic of the growth mechanism of the ZnO NW/nanowalls on HOPG surface. This process involved reaction at relatively high temperature (900°C). Vertical growth of ZnO NWs on conducting substrates, e.g., Cu, stainless steel alloys¹¹² and improved electrical and thermal conductivity for resistive-switching random access memory device applications were also reported.¹¹³

The epitaxial growth of vertical semiconductor NRs/NWs on graphitic substrates has been demonstrated recently by Munshi *et al.*⁵³. According to this study, the possible adsorption sites for the semiconductor atoms on graphene can be identified as 1) above the center of the hexagonal carbon rings (H-site), 2) above the bridge between the carbon atoms (B-site), and 3) above the top of a carbon atom (T-site), as indicated in the **Fig. 1.10(e)**. From the pioneering work done by Hiruma *et al.*¹¹⁴, it is known that semiconductor NWs mostly grow along the [111] direction in the case of a cubic semiconductor and along the [0001] direction in the case of a hexagonal one¹¹⁴. Therefore, in the (111) plane of the cubic semiconductor (and (0001) for the hexagonal semiconductor), the atoms have a hexagonal symmetry as the carbon atoms in graphene. It was shown that depending on the preferential adsorption sites and the type of semiconductor atoms, different lattice mismatch of the semiconductor with graphene will result in different atomic arrangements⁵³. **Figure 1.10(e)** illustrates such arrangements when the atoms are adsorbed on either H- or B-sites, and on both H and B-sites. The adsorption energies for most of the semiconductor atoms are lower on the T-sites. The lattice constants, calculated for the four different atomic arrangements in **Fig. 1.10(f)**, are plotted together with the band gap vs. lattice constant diagram for some conventional semiconductors in **Fig. 1.10(f)**. Therefore, **Fig. 1.10(f)** represents an overview of the lattice mismatch conditions to achieve non-van der Waals epitaxial growth in the (111)/(0001) direction for cubic (hexagonal) semiconductors on graphene. It says that due to close lattice matching of hexagonal ZnO with certain atomic configurations of graphene, epitaxial growth of ZnO NRs/NWs on graphene is quite likely. However, further experimental evidences are needed to support of this hypothesis. In some of the works, the graphene layer was transferred onto an array of the NRs/NWs where it is acting as transparent and highly conducting window for the enhanced light transmission as well as

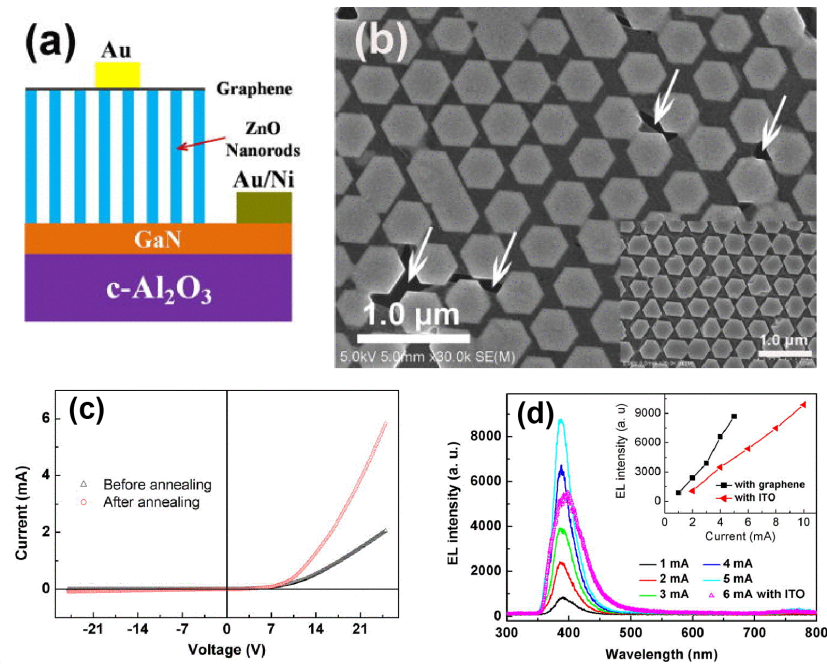


Figure 1.11: (a) Schematic diagram of the n-ZnO nanorods/p-GaN LED using graphene as a current spreading layer. (b) Top-view SEM image of the ordered ZnO nanorods with and without (inset) graphene. (c) I-V characteristics of the n-ZnO nanorods/p-GaN heterojunction LEDs before and after thermal annealing. (d) EL spectra of the ZnO nanorods-based LED with graphene under various injection currents ranging from 1 to 5 mA, together with the EL spectrum of the ZnO NRs-based LED with ITO at 6 mA¹¹⁶. The inset shows the EL intensity as a function of the injection current for the LEDs with graphene and ITO, respectively. Adapted from **Ref. [49]**

current spreading layer at the heterojunction for the generation of multiple excitons.^{49, 105, 115} For example, Zhang *et al.* fabricated the ordered ZnO NRs-based heterojunction light-emitting diodes (LEDs) by adopting FLG as a current spreading layer. **Figure 1.11(a-b)** shows the schematic of the graphene-ZnO NR based LED and corresponding FESEM image with and without graphene. The strong emission at low currents infers the high interfacial quality between GaN and ordered ZnO NRs, and the current spreading effect resulting from graphene. The improved electroluminescence performance was achieved compared to the ZnO NRs-based LED with a conventional indium-tin-oxide electrode, as shown in the **Fig. 1.11(c-d)**. These results demonstrate the feasibility of using graphene as electrodes for high-efficiency ZnO NR-based LEDs.⁴⁹

In this regard, graphene based 2D–1D hybrid structures, fabrication of vertically aligned semiconductor NRs and NWs onto graphene layer have received considerable attention^{53-54, 58, 60, 63} in order to develop unconventional sophisticated optoelectronic and photonic devices in the form of flexible, bendable and transparent electronic devices. Among

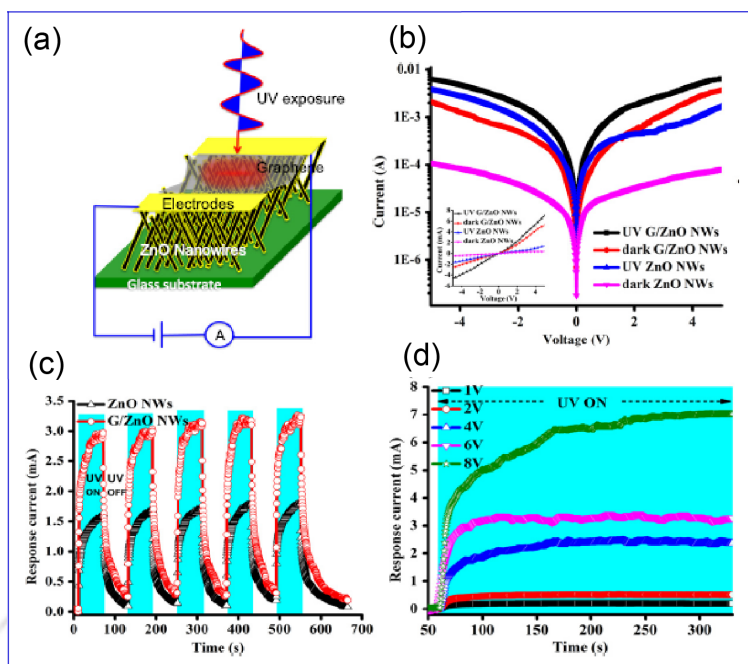


Figure 1.12: (a) Schematic of the graphene-ZnO (GR/ZnO) NWs device. (b) I–V characteristics of the ZnO NWs and GR/ZnO NWs device, where the current is plotted on a log scale and the inset plot shows the current on a linear scale with the applied bias voltage in both the absence and presence of UV illumination; (c) cyclical photoresponses of ZnO NWs and GR/ZnO NWs devices upon UV illumination; and (d) photocurrent saturation performance of GR/ZnO NWs device at different bias. Adapted from Ref. [120]

all, the graphene mediated growth of vertically aligned ZnO hybrid NSs has received much attention⁵⁵, since ZnO is a wide direct band gap (3.3 eV) semiconductor and has large exciton binding energy (60 meV) which can possess fast photo response upon illumination of UV light in the graphene based photodetectors (PDs)¹¹⁷ and gas sensing capability.¹⁰⁵ Kim *et al.*¹¹⁸ demonstrated the synthesis of vertically aligned ZnO nanoneedles and NWs on a few layer graphene sheets by sophisticated metal oxide CVD and studied its photoluminescence (PL) characteristics.

Recently, vertically aligned growth of ZnO NRs/NWs by vapor liquid solid (VLS) and vapor solid (VS) mechanisms have been reported on SLG and FLG graphene in the presence and absence of gold (Au) catalyst by vapor phase growth.^{55, 60–61} Fabrication of vertically aligned ZnO NRs/NWs with high aspect ratio and extremely large surface-to-volume ratio, specifically on graphene substrates without the aid of metal catalyst is still challenging. With the excellent electrical, mechanical and thermal characteristics of graphene layers, growing ZnO NSs and thin films on graphene layers would enable their

novel physical properties to be exploited in the diverse range of sophisticated device applications.² Therefore, several graphene–semiconductor nanocrystal hybrids have been successfully synthesized that show elegant combinations of properties not found in the individual components.¹¹⁹

Table 1.1: Comparison of responsivity (R_s) and photocurrent gain (G) of different ZnO nanostructure based photodetectors including our work are shown.

Sl. No	Photodetector	λ (nm)	P_o (mW cm ⁻²)	Bias (V)	R_s (A/W)	G
1.	Graphene/ZnO NW/graphene [122]	325	5×10^6	3	0.42	1.6
2.	ZnO NR/graphene heterostructure [104]	370	1.084	20	22.7	76.19
3.	ZnO NP–graphene core–shell structure [123]	375		20	640	2119.36
4.	Monolayer graphene film on ZnO NRs array [124]	365	0.1	–1	113	385
5.	Colloidal ZnO NPs [125]	370	1.06	120	61	204.73
6.	Graphene–ZnO NWs [120]	365	1.3	5	3.2×10^4	1.1×10^5
				8	6.7×10^4	2.3×10^5

Very recently, Q Xu *et al.* developed a metal–semiconductor–metal PD using hydrothermally grown ZnO NWs and observed the existence of SPR arising from the underlying graphene layer, which exhibited a UV to visible rejection ratio of ~ 4 .¹²¹ More recently, Buddha Deka *et al.*¹²⁰ fabricated a graphene–ZnO NWs based UV PD exhibiting excellent responsivity and photocurrent (PC) gain with. Due to higher charge carrier transport/ high mobility in graphene it induces faster response to UV illumination at the interface between ZnO and graphene with improved response and decay times as compared to a ZnO NWs device alone. **Figure 1.12(a)** represents the schematic of the device structure of the ZnO NWs covered with the graphene layer on glass substrate and corresponding dark and photocurrent (PC) characteristics at different bias voltages are shown in the **Fig. 1.12(b)**. **Figure 1.12(c–d)** represents the cyclic PC measurements at UV ON/OFF conditions and PC growth at different bias voltages. A linear increase in the responsivity and PC gain was observed from the graphene–ZnO NWs device with the applied bias. A comparison of responsivity (R_s) and PC gain (G) is shown in the **Table 1.1**.

1.5.3. 2D Semiconducting Layers Grown on Graphene and their Applications

Apart from the 0D and 1D NSs, vertical 2D inorganic NWs were grown on graphene layers^{60, 126}, which are a new kind of hybrid NSs for fabricating optoelectronic devices. As

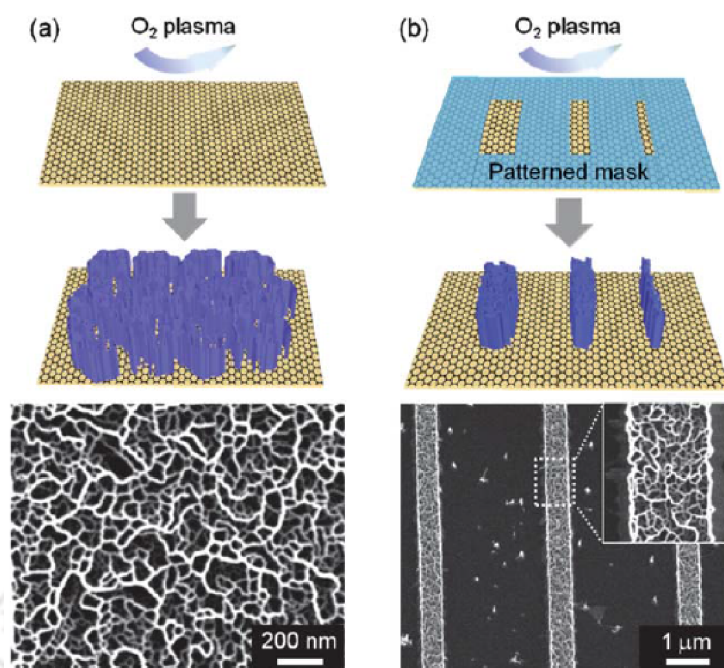


Figure 1.13: Schematic illustrations and corresponding SEM images of (a) ZnO nanowalls (NWs) grown on oxygen-plasma-treated graphene layers and (b) selectively-grown ZnO NWs on graphene layers. Adapted from **Ref. [63]**

previously mentioned in the section 3.3, for example, ZnO NWs as well as NRs can be formed preferentially along the step edges or boundaries that naturally exist on graphene layers, resulting presumably from the higher surface energy at the edges and boundaries than that on the basal plane.^{58, 60} Using this finding of enhanced nucleation and growth at the step edges, high-density ZnO NWs were grown on the rough graphene surface obtained by creating the artificial step edges using oxygen plasma treatment, as shown in **Fig. 1.13(a)**. Furthermore, selective-area growth of ZnO NWs was achieved by patterning a polymer mask layer on graphene layers and subsequently exposing it to oxygen plasma.⁶³ **Figure. 1.13(b)** shows the formation of high-density ZnO NWs inside the patterned area due to the enhanced growth at the large number of step edges created by the oxygen plasma, while ZnO NSs rarely grew on the bare graphene surface that had not been exposed to the oxygen plasma. This suggests that graphene layers with artificially formed step edges show great promise as a substrate for selective growth of NSs. Formation of ZnO NWs on rough surface and step edges of graphene was observed by Kumar *et al.*⁶⁰ and Kim *et al.*⁵⁸

It may be noted that in recent times, research on graphene based heterostructures with other 2D atomic crystals is intense and is likely to remain one of the challenging topics in

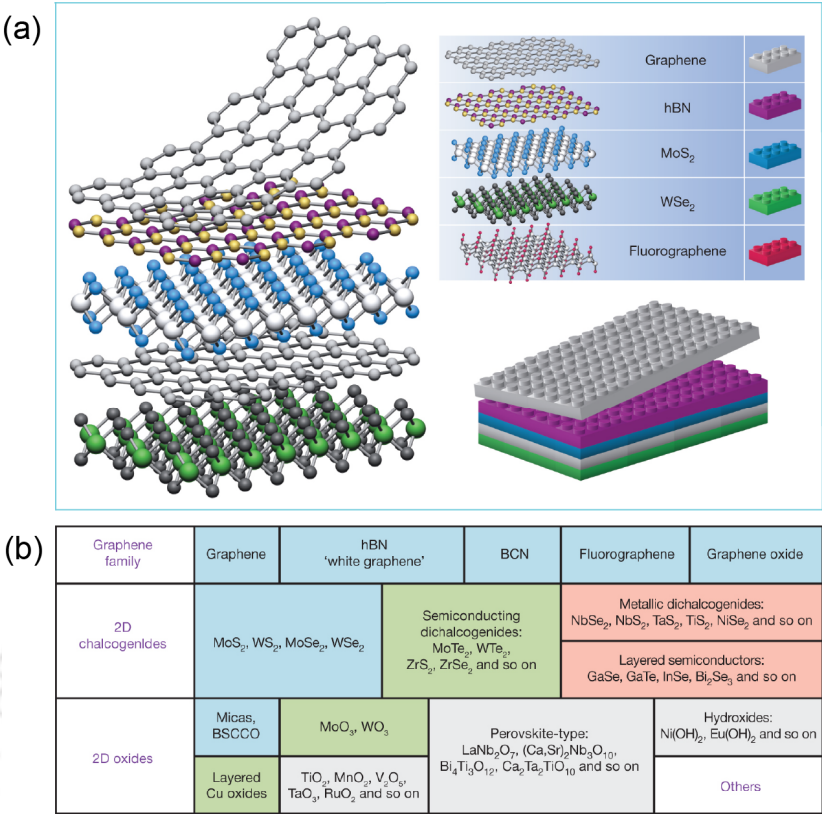


Figure 1.14: (a) Building van der Walls heterostructures with graphene, (b) Current 2D library of materials which have triggered the fabrication of novel graphene-semiconductor 2D heterostructures. Adapted from **Ref. [62]**.

condensed matter physics and materials science for many years.⁶² Taking into account of the recent perspective on the ‘van der Walls heterostucutures’ reported by A. K. Geim and his colleagues⁶², the individual isolated atomic planes can be reassembled into designer heterostructures made by layer by layer assembly in a desired sequence, which are known to be 2D quantum well NSs. **Figure 1.14(a)** shows various 2D van der Walls heterostructures which can be built using graphene as a transperant conducting window for the improved light matter interactions. **Figure 1.14(b)** shows a library of various 2D layered nanomaterials which are the members of the graphene family. Ideally, hexagonal boron nitride (hBN) is a 2D dielectric material usually called ‘white graphene’ most suitable to measure the field effect mobility of the graphene due to identical crystalline structure with graphene (sp^2 hybridization).

The conventional dielectric substrates such as SiO₂, HfO₂ do not give actual mobility of graphene. Due to its atomic layer thickness, most of the charge carriers are trapped at the

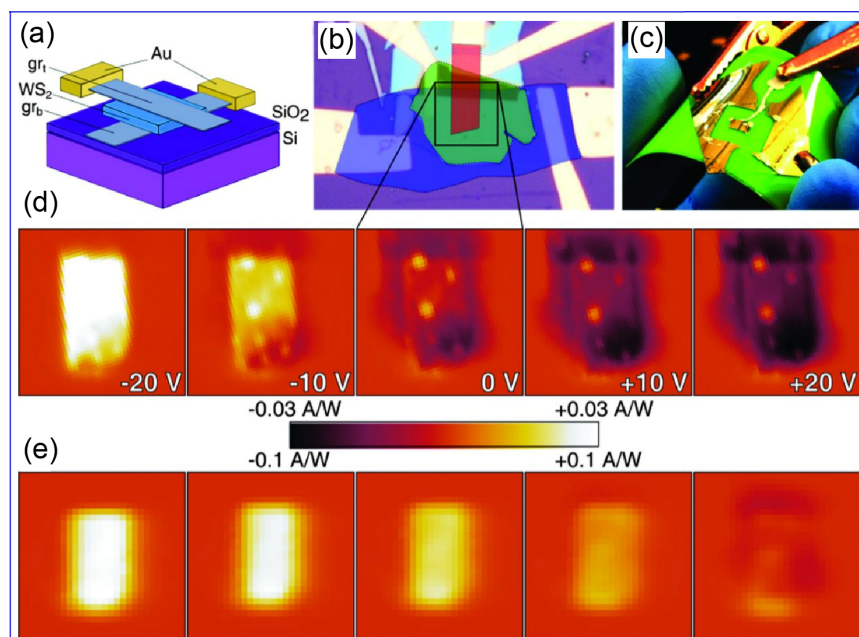


Figure 1.15: Graphene 2D-2D TMDC semiconductor hybrid device and photocurrent (PC) mapping. (a) A schematic of the device with the graphene-semiconducting 2D tungsten sulphide (WS_2) layers. (b) An optical micrograph of a devices. The shading of the three constituent layers denotes the regions of the respective materials—top and bottom graphene electrodes are shown in red and blue, and WS_2 is shown in green. (c) A photograph of one of the flexible devices placed on an electroluminescent mat. (d-e) photocurrent maps taken before (d) and after (e) doping the top graphene layer with water vapor. A signal is only seen in the area where all three layers overlap. The two graphene layers were connected via a 1 kW resistor, on which the PC was measured. No bias was applied, and for both (e) and (d), the maps were taken at gate voltages from -20 V to $+20\text{ V}$. The scale of the maps is given by their width, 20 mm. Adapted from the **Ref. [131]**.

thicker dielectric layer (usually the thickness ranges from $\sim 100\text{-}300\text{ nm}$). Improved properties were obtained when bulk hBN crystals¹²⁷. were shown to be an exceptional substrate for graphene, allowing a tenfold increase in its electronic quality¹²⁸. This advance attracted immediate attention and, shortly after, few-layer crystals and monolayers of hBN were used as gate dielectrics¹²⁹ and tunnel barriers (2D hBN can sustain biases up to about 0.8 V nm^{-1} and be free from pinholes)¹³⁰. Followed by this work, the first report on the fabrication of this kind of heterostructures with graphene was performed by Novoselov *et al.*¹³¹. They have combined the various 2D materials by vertical stacking using TMDCs/graphene heterostructures, which led to enhanced photon absorption and electron-hole creation that are collected from the transparent graphene electrode. Ideally, mono layer TMDCs show a striking visible PL due to the quantum confinement of electrons present in the d-orbitals.

Figure 1.15(a-c) shows the schematic of the graphene 2D-2D heterostructure device and corresponding photocurrent (PC) mappings are shown in the **Fig 1.15(d-e)**. Here TMDC (WS_2) is sandwiched between two graphene layers which is an atomic layer thick contact as well as a transparent window during the illumination. This work allowed for the development of extremely efficient flexible photovoltaic and photoconducting devices in the nanoregimes with photoresponsivity above 0.1 A/W and corresponding to an external quantum efficiency of above 30%.

1.6. Motivation and Focus of the Present Thesis

Achieving large area wafer scale SLG onto dielectric substrates without having any structural defects and layer non uniformity is still challenging. There is a lack of in-depth understanding on the role of defects in the interactions between graphene and foreign atoms and molecules. Investigating the various in-plane and edge defects including functional groups on the graphene using resonance Raman spectroscopy and HRTEM will provide the rich physics behind its electronic and optoelectronic applications. Physical and chemical functionalization of graphene preserving its sp^2 crystallinity can reveal the change in the electronic structure due to covalent and noncovalent foreign material interaction with graphene. It is anticipated that a proper understanding on the interaction of noble metal with defective graphene would pave the way for controlled functionalization of graphene for cutting edge applications. Functionalized graphene and its exploitation in integrated optoelectronics is least explored in the literature. Further, origin of solid state PL from CDG is not understood well with the help of controlled environments. Fabrication and characterization of graphene based semiconducting hybrid NSs for enhanced photodetection applications is imperative to develop various optoelectronic devices. Visible light photocatalysis of graphene and functionalized graphene incorporating TM plasmonic hybrids are little explored. Graphene based TM plasmonic hybrid NSs for SERS and mechanism of SERS are still challenging. Unlimited possibility of exploiting graphene based hybrid NSs for photoconductive, photocatalytic and SERS applications still remains.

This thesis focuses on the controlled growth of large area defect free graphene using CVD technique and synthesis of CDG functional materials. Extensive investigations on number of graphene layers, uniformity, functionalization and defects were probed using

micro-Raman spectroscopy and HRTEM. Next, the fabrication of graphene-plasmonic hybrids with TM NPs such as Au, Ag, Cu and organic molecules as well as the graphene-ZnO hybrid NSs and their SERS, photocatalytic and photoconductive applications were investigated.

At first, we have designed and developed an in-house thermal CVD system for the controlled growth of large area wafer scale SLG on a polycrystalline Cu foil. Next, we optimised the growth process and control the growth kinetics in CVD graphene by monitoring various growth parameters, such as ratio of precursor gases (Ar, H₂ and CH₄), temperature and pre-annealing of Cu foil using the CVD system. We found that the longer duration of pre-annealing of Cu foil in H₂ atmosphere at higher concentrations gives a large area coverage of SLG (> 90%, 1 cm² substrate), which is due to the formation of larger size Cu grains as well as very less nucleation sites of carbon adatoms in reduced environment. Detailed CVD reaction kinetics of graphene growth was investigated using electron microscopy and micro-Raman spectroscopy tools. Clean transfer of graphene from the Cu foil to insulating substrates without any damage and surface corrugation of graphene layers is a one of the challenging issues. Since graphene grows on either sides of the Cu foil, we have etched graphene on one side by two methods, namely i) diamond polishing and ii) reactive oxygen plasma etching techniques. Graphene grown on the other side was collected by conventional wet transfer process and transferred on to a Si/SiO₂, quartz and a free standing suspended graphene on a TEM Cu grid. Further, the residual PMMA and catalyst impurities along with the oxide traces that are present on the graphene substrate were removed by H₂ annealing treatment at 400 °C for the duration 1–3 hr. After achieving the controlled growth, we have extensively studied the intrinsic defects such as point, line and multiple carbon vacancies on the basal plane and edges of graphene layer with resonance Raman and HRTEM analyses. Further, we have synthesized various CDGs, such as graphene oxide (GO), reduced GO (rGO) and graphene oxide nanoribbons (GONRB) by chemical exfoliation technique and fabricated its thin films using simple spin coating technique. We have explored the identification of oxygenated functional groups at in-plane and edge sites that are responsible for the visible PL in the CDGs from oxygenation and hydrogenation studies using steady state and time resolved PL, micro-Raman, FTIR in association with thermogravimetric analysis (TGA) and differential TGA analyses.

Next, we carried out physical functionalization of graphene with TM thin films/NPs such as Au, Ag, Cu and organic molecules (CoPc) grown by sputter deposition/ thermal evaporation on graphene and made extensive studies on the nature of interactions and their applications using resonance Raman spectroscopy, spatial Raman imaging, HRTEM and SPR absorption. The quantitative evolution of defects and defect mediated interaction of graphene–TM metal plasmonic hybrids preserving its sp^2 crystallinity was studied from the physical functionalization of graphene with Au NPs extensively. Defect mediated efficient physical functionalization of graphene was demonstrated for the first time. We further demonstrate the plasmon enhanced visible photocatalysis and SERS detection of organic molecules using graphene–Au plasmonic hybrids as a catalyst substrate. Next, we demonstrate the fabrication of 1D semiconductor NSs on single (SLG) and few layer graphene (FLG) that serve as a versatile 2D platform for growing various ZnO nanorods (NRs), nanowires (NWs) and nanoribbons (NRBs) using low temperature (540 °C) physical vapor deposition (PVD) technique. We propose growth strategies based on the vapor–liquid–solid (VLS) and vapor–solid (VS) mechanism in the presence of Au catalyst and ZnO seed layer on graphene buffer layer, respectively. An artificial epitaxial relation between wurtzite ZnO and a hexagonal crystalline graphene was proposed based on experimental observations. A systematic investigation on morphological evolution and crystalline structure of the graphene–ZnO NRs, NWs and NRBs was carried out from FESEM, HRTEM, XRD, micro–Raman and XPS techniques. Graphene enhanced UV–vis absorption and UV–visible PL studies were carried out for as–grown ZnO NRs, NWs and NRBs and origin of various visible and NIR PL emissions were investigated under different annealing conditions. Graphene enhanced UV photodetector (PD) based on graphene–ZnO NW hybrids was demonstrated and various device parameters such as photoresponse time, decay time, responsivity and photocurrent (PC) gain in the self catalytically grown graphene–ZnO NWs and bare ZnO NWs were evaluated. The explicit role of underlying graphene in the enhancement of UV PC was evaluated from the cyclic PC and photoresponse measurements in graphene–ZnO thin film UV PD in comparison with bare ZnO PD.

1.7. Organization of the Thesis

The complete thesis work is presented in 9 chapters. This chapter has given an introduction to fabrication and characterization of graphene and graphene based hybrid NSs and their

important applications. Second chapter provides an account of the various in-house developed and commercial experimental setups that are used for the growth and fabrication of graphene and graphene-hybrid NSs. 3rd, 4th and 5th chapters present the preparation and characterization of large area defect free graphene and graphene-TM plasmonic hybrids and their application for the visible light photocatalysis and SERS, respectively. In 6th and 7th chapter, we demonstrate the fabrication of novel graphene-ZnO NRs, NWs and NRBs and their enhanced UV-visible-NIR PL properties followed by development of a graphene enhanced UV photodetector from ZnO NRs/NWs grown on graphene. In 8th chapter, we demonstrate synthesis of CDG and fabrication of their thin films with tunable optical properties. Last chapter summarizes the important findings and conclusions of the present thesis and future directions of work.



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Chapter 2

Experimental Techniques and Characterization

The present chapter deals with a brief outline of various experimental techniques used, the methodologies adopted for the controlled growth of graphene, and the fabrication of graphene based transition metal (TM) plamonic hybrids and semiconductor nanostructures (NSs). It also provides accounts of the design and development of the various experimental setups developed in the present work. Further, several microscopic, spectroscopic and electrical characterization techniques were used to probe the structural, optical and optoelectronic properties of graphene based integrated hybrid NSs systematically. The critical role of spectroscopic line shape analysis for resonance Raman spectra, PL, XPS and DTG spectra in the present study of defects and defect mediated interaction of foreign materials with graphene has been brought out. The suitability of different microscopic and spectroscopic techniques for understanding defects and functional groups in graphene functional nanomaterials has been discussed. Various data analysis techniques are used in different characterization tools for the interpretation of the experimental results to understand the physical phenomena of graphene based hybrid NSs.

2.1. Design and Development of Chemical Vapor Deposition System

The most promising and versatile approach for the growth of large area reasonably high quality single layer graphene is chemical vapour deposition (CVD) technique.¹⁻² For the graphene growth, we have designed and developed the thermal CVD system that is used to can produce large area defect free single layer graphene in our laboratory. **Figure 2.1(a)** shows a schematic of the typical thermal CVD setup and **Fig. 2.1(b)** shows a photograph of our CVD setup its arrangement. Primarily, the CVD system consists of a quartz chamber enclosed inside a tubular muffle furnace, mass flow controllers (MFCs from MKS systems, Type 247, Four channel readout) and a turbo molecular pump (TMP) (Pfeiffer, Germany, throughput $\sim 10^{-8}$ mbar) to create the base pressure inside the chamber, up to $\sim 10^{-5}$ mbar. A rotary pump (VT Vacuum, India, throughput $\sim 10^{-3}$ mbar) was used to eliminate the reactive

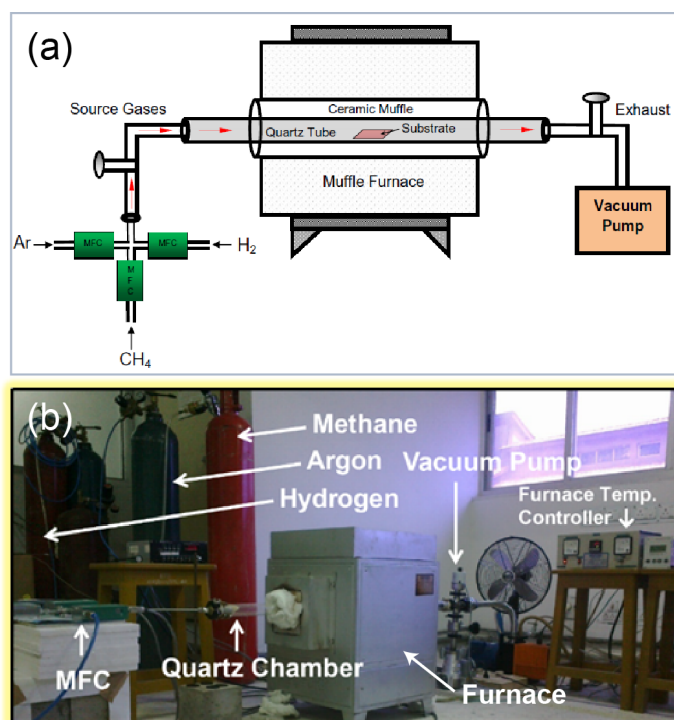


Figure 2.1: (a) A schematic of a typical thermal CVD system. (b) A photograph of the CVD system showing the various components that are assembled as a controlled system, which is developed in house for the growth of single layer graphene.

species during the CVD process. Typical dimensions of the quartz tube used for the graphene growth are 1.2 m long 32 mm inner diameter, which is placed inside a hot wall muffle furnace capable of reaching 1350°C with a heating zone of 15 cm at the centre. One end of the quartz chamber was connected to the MFCs to flow the precursor and carrier gases with high purity 99.999%, such as methane (CH₄), hydrogen (H₂) and argon (Ar). Note that the flow rates of the gases were monitored using a four channel mass flow readout (see **Fig. 2.1 (b)**). Other end of the quartz tube was connected to the vacuum system that is capable of controlling the growth pressure (atmospheric to low pressure~ 10⁻² mbar) as well as to remove the by-products of unwanted/excessive gas residual vapors during the CVD process.

2.1.1. Synthesis of Graphene using Thermal CVD

2.1.1.1. Preparation of Catalyst

A copper (Cu) foil of thickness 25 μm (Alfa-Aesar, Polycrystalline, 99.8%) was used as a catalyst for the growth of graphene. Initially the Cu foil was cut into 1x1 inch pieces and immersed in a dilute acetic acid for 10 minutes and rinsed in the acetone for two times. This will help to remove the oxide impurities on the Cu foil. This Cu foil was loaded into the quartz chamber. The CVD growth parameters, such as growth temperature (~ 1000-1045°C), vapor pressure, and flow rates of precursor gases such as methane (CH₄), Argon (Ar) and

Hydrogen (H_2) were monitored to control over the number of graphene layers and the grain size. Preannealing of the Cu foil in reduced environment before graphene growth plays an important role on the monolayer coverage of the graphene depending on the grain size of the polycrystalline Cu. We performed a set of experiments systematically to achieve the large area SLG and the results are presented in the later chapters.

2.1.1.2. Reactive Oxygen Plasma Etching

A clean transfer of graphene onto dielectric substrates is one of the challenging tasks without any damage of the SLG. Ideally, graphene is grown on the both sides of the Cu foil in CVD growth process. Removing bottom graphene from Cu foil is essential, otherwise it will adhere onto the top portion which lead to the formation of multilayers consisting plenty of metal catalyst NPs. In order to rectify this problem, we have done reactive oxygen plasma etching (RIE) for some of the GR samples. We exposed the bottom portion of the Cu foil containing the as-grown graphene for 5-10 min of duration in RF plasma of oxygen. A photograph of the



Figure 2.2: Photograph of the plasma cleaner (HARRICK PLASMA, PDC-32G-2, U.S.A) used for the removal of the bottom graphene deposited on the backside of the Cu foil in the CVD growth. Inset shows the exposure of oxygen plasma on graphene samples.

plasma cleaner (HARRICK PLASMA, PDC-32G-2, U.S.A) used in this work is shown in the Fig. 2.2.

2.2. Development of RF Magnetron Co-Sputtering System

The sputtering system is configured for the deposition onto round substrates from 2 targets (water cooled magnetron cathodes of 2" diameter each) in sputter up mode. The system consists of one process module with targets and a substrate holder cum heater. Substrate heating unto 500°C is possible with the substrate holder. It is capable of depositing uniform films of metals and metal oxides. The schematic of the custom made sputtering system is

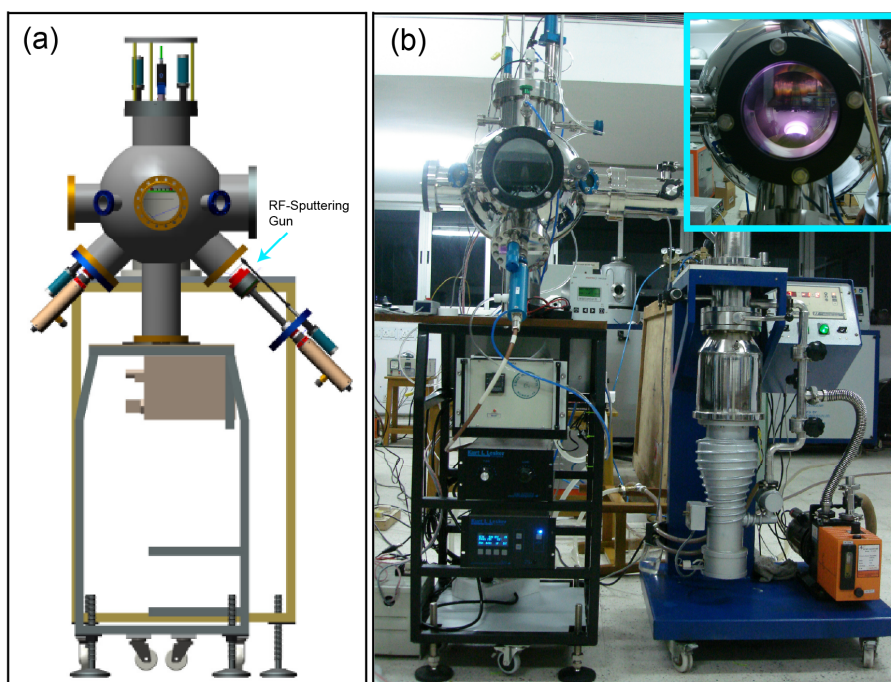


Figure 2.3: (a) Schematic design of the custom made RF magnetron co-sputtering system. (b) A photograph of the sputtering system showing the assembly of important components which are used to monitor the thin film growth. Inset shows the RF plasma during Au deposition.

shown in the **Fig. 2.3(a)**. **Figure 2.3(b)** is a photograph of the sputtering assembly in our laboratory and inset shows the gold (Au) plasma during the sputter deposition. The sputtering chamber was manufactured by Excel Instruments, India. Note that the other accessories, such as RF source (Kurt J Lusk, USA, input rating 25 KV), vacuum pumps (VT Vacuum, India) were assembled separately. This system was designed such that the sputtering gun is inclined at an angle of 45° with the substrate holder that have rotation during the deposition. The diameter of the sputtering target used here is 2" and 0.125" thickness. Due to high performance magnet pack design, the system is capable of giving great uniformity of films. Ultra-thin films were fabricated from TMs (Au, Ag, Cu & Ni etc.) and various commercial metal oxide sputter targets such as ZnO, TiO₂ (99.999%, Kurt J Lesker, USA). Fabrication of thin films has been carried out at a base pressure 6.7×10^{-6} mbar and during the sputtering it was maintained at 1×10^{-2} mbar.

2.2.1. Fabrication of Graphene-Transition Metal Plasmonic Nanostructures

We fabricated graphene-TM metal plasmonic hybrids and graphene-ZnO hybrids by depositing ultra-thin films of Au, Ag, Cu and ZnO on graphene substrates using this RF magnetron sputtering system with controlled growth parameters (Ar gas flow, RF power, Deposition pressure etc). We prepared the high purity TM targets were produced locally and

ZnO sputtering target was procured from Kurt J Lesker, USA, (99.999%) for the thin film fabrication. We fabricated the plasmonic NPs (Au, Ag and Cu) by depositing ultra-thin films with thickness 2-5 nm on graphene substrates. ZnO seed layers were fabricated by sputtering on graphene substrates for the fabrication of ZnO NWs.

2.3. Design and Development of Physical Vapor Deposition System

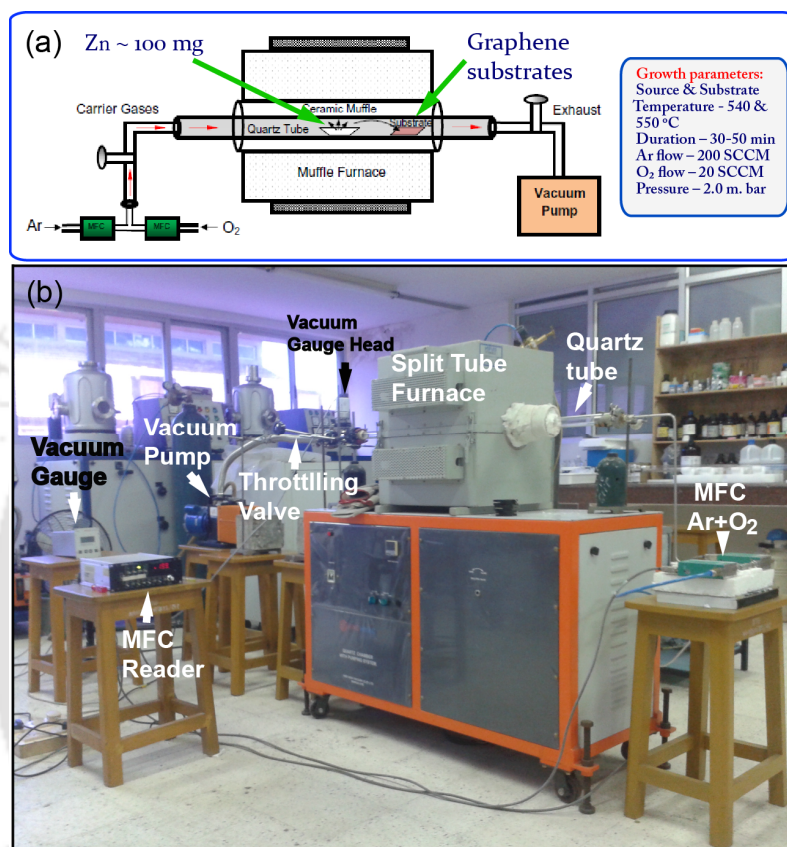


Figure 2.4: (a) Schematic design of the physical vapor deposition (PVD) system. (a) A photograph showing the arrangement of in-house developed PVD system that displays the important components used to monitor the growth parameters for the controlled fabrication of the various organic and inorganic semiconductor nanostructures on graphene substrates through vapor transport process.

Physical vapor deposition (PVD) is one of the versatile and simple fabrication techniques for the growth of 1D NSs. In our present study, graphene based ZnO hybrid NSs were fabricated using laboratory PVD system. Various ZnO NSs such as NRs, NWs and NRBs were fabricated over the different pre-treated graphene substrates. **Figure 2.4(a)** shows the schematic of the PVD system and **Fig. 2.4(b)** shows the arrangement of the PVD system developed in the laboratory. The schematic of the PVD system is shown in the **Fig. 2.4(b)**. It is similar to the CVD system, except it has a split type furnace and carrier gases are different. The precursors used for the ZnO growth are in the form of Zn powder and it vaporises at a

particular source temperature. The source vapors are transported by a carrier gas, (usually Ar gas) and deposited on the substrates at different substrate temperatures. Depending on the substrate temperature and pre-treatment conditions, various NSs were grown based on the VLS and VS growth mechanism. Here we fabricated the graphene-ZnO hybrid nanostructures from evaporation of Zn powder (99.999%, Sigma Aldrich) and transporting with high purity oxygen and Ar gases on to the required substrates. Various graphene substrates were kept towards the down-stream of the ZnO vapor at relatively low growth temperatures in the range of 540-550°C in controlled growth conditions (see **Fig. 2.4(a)**). Comprehensive study on various growth conditions of graphene-ZnO hybrid NSs are elucidated in detail in **Chapter 6**.

2.4. Other Experimental Setups

2.4.1. Rapid Thermal Annealing

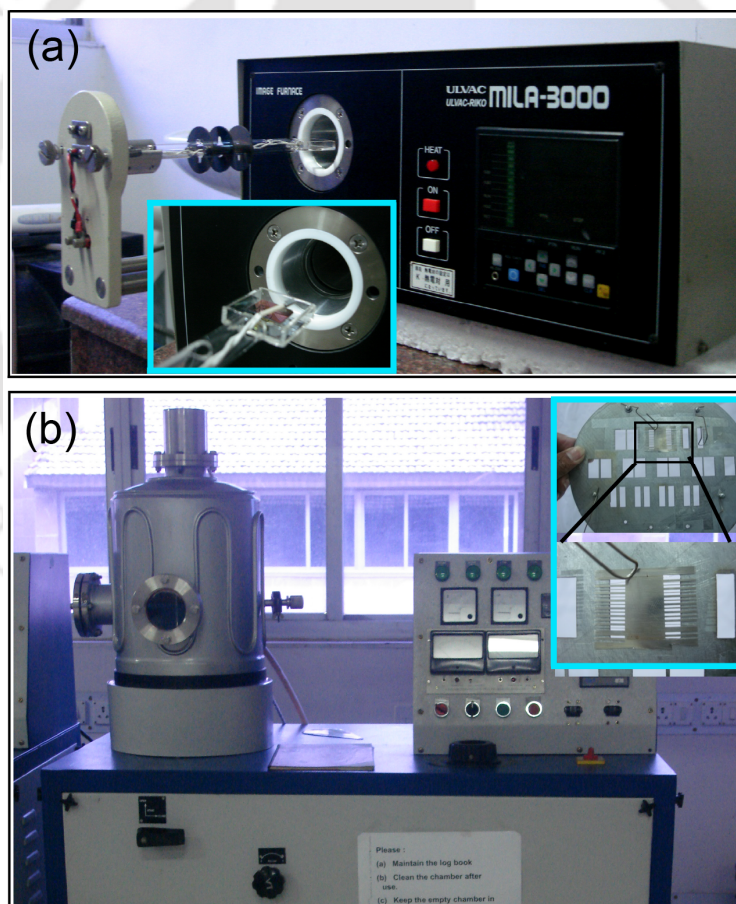


Figure 2.5: Photographs of (a) Rapid thermal annealing system (MILA 3000P, ULVAC, Japan) and inset shows the quartz sample holder and a thermocouple. (b) Vacuum thermal evaporation system used for the deposition of metal contacts; inset shows shadow mask designed to fabricate the metal contacts.

In order to fabricate the plasmonic NPs with controlled size over the graphene layer and to improve the structural quality of the ultra-thin ZnO films, we performed the rapid thermal

annealing (RTA) of our samples. RTA is a one of the important techniques to fabricate the plasmonic NPs and to improve the structural quality of as-grown ZnO films over the graphene.³ It functions with extremely high heating rates (few minutes) and annealing is performed for very small time to avoid deterioration the intrinsic crystalline property of the graphene. Therefore we have performed the RTA to fabricate the plasmonic NPs by using mini lamp annealer (MILA 3000P, ULVAC, Japan) and study the influence of RTA treatment on the structural and optical properties of graphene plasmonic hybrids. **Figure 2.5(a)** shows the photograph of the compact table top RTA system. This system is built around a gold reflector infrared lamp furnace and contains a high precision programmable temperature controller. This system can perform up to a maximum heating rate of 50°C/sec and has options for annealing in vacuum and gas feeding. Some of the Au and ZnO coated graphene substrates were treated by RTA at 600°C in Ar atmosphere to form Au and ZnO islands. The heating and cooling rate was fixed at a value of 40°C/sec.

2.4.2. Thermal Evaporation System

Thermal evaporation system was used to deposit the metal contacts over the graphene and graphene-ZnO hybrids for the electrical and photoconductivity measurements. The photograph of the coating system is shown in the **Fig. 2.5(b)**. Ag contacts were deposited by thermal evaporation under high vacuum (1×10^{-5} mbar) on top of the bunch of ZnO NWs surface by keeping a shadow mask with a channel dimension of $\sim 0.1 \times 0.1 \text{ mm}^2$. Tungsten resistive coils were used for the metal evaporation. The deposition rate was monitored with a water cooled quartz crystal microbalance. The deposition rate of the Ag metal was 0.5 to 3 Å/sec and the film thickness was typically ~ 100 nm.

2.4.3. Tip Sonicator

The Sonic Ruptor 250 Ultrasonic Homogenizer is used for the dispersion of chemically derived graphene in various polar solvents. Usually ultrasonic homogenizers generate the sound waves with frequency 20 KHz. The tip is fabricated from titanium (Ti). Different kinds of Ti micro tips are available depending on the volume and dispersion level of the solution. The photograph of the tip sonicator is shown in the **Fig. 2.6(a)**. We can monitor the various parameters such as output power, timer control and ultra sonic pulsar for the controlled dispersions of the graphene layers in the polar solvents.

2.4.4. Spin Coating

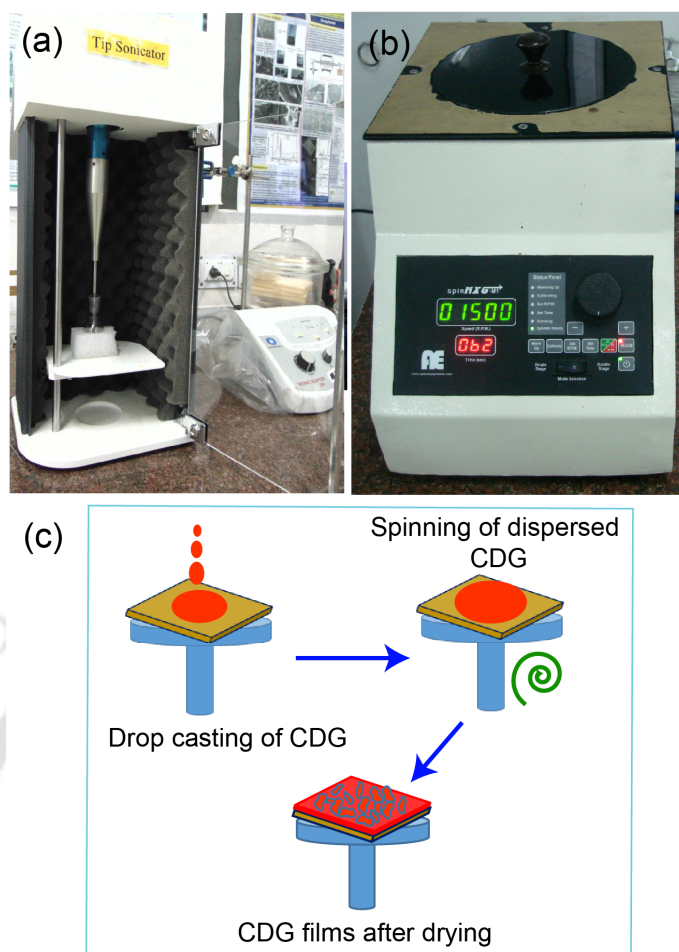


Figure 2.6: (a) Tip sonicator (Sonic Ruptor 250, Germany) used for the dispersion of chemically derived graphene (CDG) in various polar solvents. (b) Manual spincoater (APEX spin NXG-M₁) used for the fabrication of thin films of CDG. (c) Schematic of process steps for the CDG thin film fabrication using simple spin coating technique.

A manual spin coater is used for the fabrication of uniform thin films of the chemically derived graphene (CDG) on transparent and opaque substrates. The photograph of the spin coater unit (APEX spin NXG) used for the fabrication of CDG thin films is shown in the **Fig. 2.6(b)**. Usually, before spin coating of the CDGs, it is dispersed properly in polar solvents (dimethyl formamide (DMF)) using mild tip sonication for controlled dispersion of the graphene layers in the solvent as described above. The schematic in the **Fig.2.6(c)** shows the steps involved in the spin-coating process. The dispersed solution of the CDG will be drop casted using micro-pipette on a substrate fixed on a rotated vacuum chuck. The substrate is then rotated at an average speed in the range of 500-2000 rpm in the spin coater. The uniformity and thickness of the CDG layers depends on the spinning speed and concentration of the CDG solution. One can monitor the thickness and uniformity of the CDG films with suitable

spinning speed and time. We fabricated all the CDG thin films at room temperature and atmospheric pressure conditions.

2.5. Characterization Tools

2.5.1. Microscopy Techniques

In order to understand the surface morphology of as-grown CVD graphene having different number of layers, defects, disorder and its combination with foreign materials, various microscopic techniques are utilized from conventional optical microscopy to advanced microscopic techniques, such as high resolution transmission electron microscopy (HRTEM). In this section, we present a brief description of the microscopy tools used for the characterization of the graphene layers and graphene transition metal plasmonic and ZnO hybrids. Details of the sample preparation for imaging as well as for specific measurements are also discussed in detail.

2.5.1.1. Optical Microscopy

Optical microscopy is one of the best imaging techniques to investigate the 2D layered nanomaterials, especially graphene. Based on the colour contrast of the graphene sample transferred onto SiO₂, one can estimate the number of layers, grain size, shape and surface corrugation etc.⁴ We have performed estimated the optical microscopy of as-transferred graphene onto various alien substrates and checked the cleanliness of the surface after H₂ annealing.⁵ We have used the microscope which is attached to micro-Raman spectrometer. We have shown the optical microscope image analysis of the large area single and bi layer graphene that we have been grown by CVD technique and discussed later in **Chapter 3**.

2.5.1.2. Field Emission Scanning Electron microscopy

The Field emission scanning electron microscope (FESEM) is a very useful tool for the high resolution imaging in the fields of nanomaterial science. The use of electron has two main advantages over optical microscopes: much larger magnification are possible since electron wavelengths are much smaller than photon wavelengths and the depth of field is much higher. The electron wavelength λ_e depends on the electron velocity v or the accelerating voltage V as

$$\lambda_e = \frac{h}{mv} = \frac{h}{\sqrt{2qmv}} = \frac{1.22}{\sqrt{v}} \text{ nm} \quad \dots\dots\dots (2.1)$$

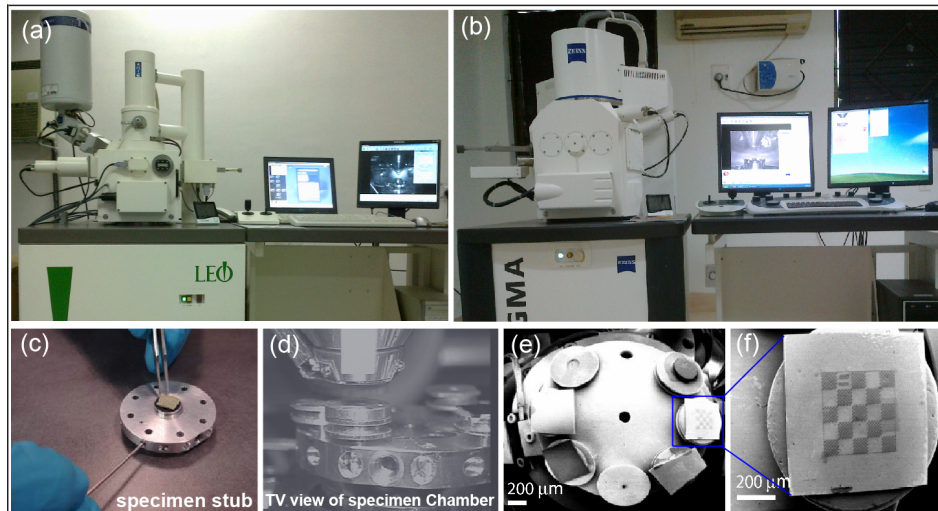


Figure 2.7: Photographs of (a) a scanning electron microscope (SEM) (LEO 1430 VP, UK) and (b) field emission scanning electron microscope (FESEM) (Sigma, Zeiss, Germany). (c) Specimen stub used to keep the sample with the support of conducting carbon tape. (d) A TV view of the specimen chamber and (e-f) a low resolution FESEM image of the specimen.

In the FESEM, field emission gun is used which utilizes field emission effect. Field emission is the emission of electrons from the surface of a conductor caused by a strong electric field. An extremely thin and sharp tungsten needle (tip diameter 10-100 nm) works as cathode. The FE source reasonably combines with conventional scanning electron microscope (SEM).

Figure. 2.7(a) is a photograph of the SEM used in the present study. The photograph of the FESEM (Sigma, Zeiss, Germany) extensively used for the present study is shown in **Fig. 2.7(b)**. The acceleration voltage between cathode and anode commonly varies between 0.5 to 30 kV, and the apparatus requires an extreme vacuum ($\sim 10^{-9}$ torr) in the column of the microscope. After the emission, the electrons are then accelerated off the source by two anodes. Because of the microscopic size of the electron source, the beam produced by this emitter about 1000 times smaller than that in a standard SEM, which markedly improves the image. The beam is collimated by electromagnetic condenser lenses, focused by an objective lens, and scanned across the surface of the sample by secondary electrons that are released by the sample. A secondary electron detector is placed near to the specimen. By correlating the sample scan position with the resulting signal and image is formed on the screen that is strikingly similar to what would be seen through an optical microscope. **Figure 2.7(c)** represents the specimen stub where the sample is kept and **Fig. 2.7(d)** shows the specimen chamber and an in-lens detector which collect the back scattered electrons from the sample surface. **Figure. 2.7(e-f)** represent the sample positions and FESEM image of the specimen. The FESEM is equipped with a special objective or focusing lens that projects the magnetic

field below the lens. Very high resolution is obtained by shortening the specimen-lens distance and using a specially designed in-lens. The distance is shortened by placing the specimen in the lens magnetic field. In this case, secondary electron detector is placed above the objective in-lens, which makes difference in the image compared to the conventional image of the secondary electron detector.

FESEM imaging has been carried out on as-grown graphene on Cu foil, wet transferred graphene on SiO₂, graphene plasmonic NPs hybrids and graphene-ZnO NWs/NRs hybrids, which were directly mounted on the FESEM stub using a carbon coated conducting tape (see **Fig. 2.7(e)**). Here the carbon tape is used as adhesive and also provide an electrical conduction to the sample.

2.5.1.3. High Resolution Transmission Electron Microscopy

Transmission Electron Microscope (TEM) is one of the best imaging technique of nanoscale materials with resolution close to atomic level. Combination of TEM with the selective area electron diffraction (SAED) pattern, a plethora of information, such as number of graphene layers, various in-plane and edge defects, sp^2 hybridization, interaction of foreign materials in nanoregime and lattice constants can be studied. A photograph of the TEM and its important components are shown in the **Fig. 2.8**. It works on the principle of optical projection; when an object is placed in front of a light source, its image is enlarged and shadow is created on the screen place far distance behind this object. Electrons emitted from the an electron gun area accelerated to high voltages ranging typically 100 to 400 kV and focused on the sample by the numbers of electromagnetic lenses. For the generation of a beam of electrons, a lanthanum hexaboride (LaB₆) crystal is connected between two electrodes at high accelerating voltages for thermionic emission of electrons. The emitted electrons pass through a series of lenses to be focused and scanned across the sample. The sample is placed on a small copper grid a few mm (~ 3 mm) in diameter. The static beam has a diameter of few microns. The sample must be sufficiently thin (a few tens to a few hundred nm) to be transparent to electrons. The transmitted and forward scattered electrons from a diffraction pattern in the back focal plane and a magnified image plane. With additional lenses, either the image or the diffraction pattern is projected onto a fluorescent screen for viewing or photographic recording. **Figure 2.9** shows a sample holder which is used for the loading of Cu TEM grid at the tip of the holder. High resolution TEM (HRTEM) gives structural information on the atomic size level, which is known as lattice imaging. We performed the

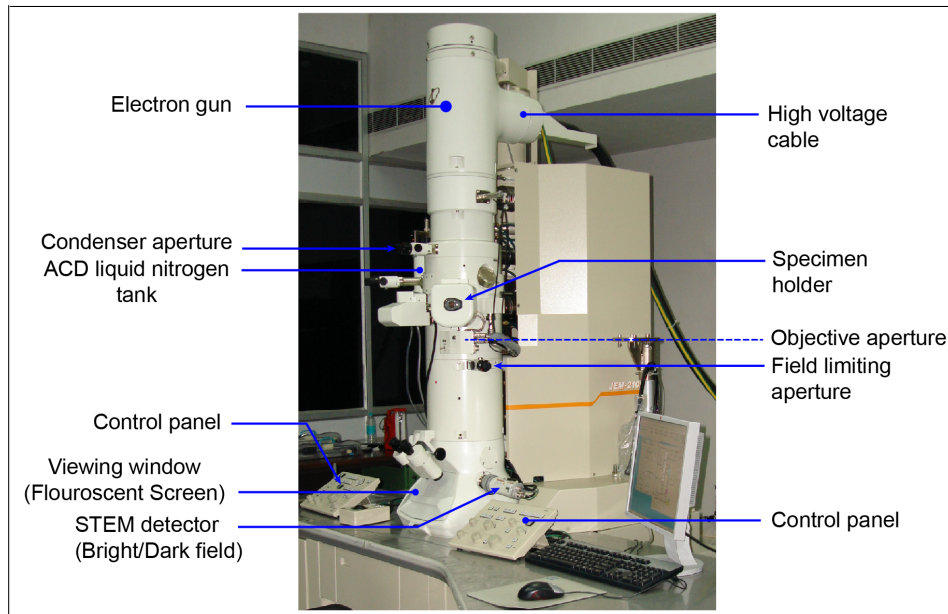


Figure 2.8: Photograph of HRTEM (JEOL-2100 F, Japan) used for the present study. Some of the important components are labelled in the image.

lattice imaging of monolayer graphene and various intrinsic defects on basal plane and edges of graphene using HRTEM. It is also useful to know the growth direction of the NWs and presence of defects/dislocations. In the present study, a 200kV TEM (JEM2100, JEOL, Japan) with high resolution CCD camera (Gatan, USA) is used for the normal TEM and HRTEM imaging. Sample for the TEM imaging was prepared by directly transferring the graphene on to Cu TEM grid. Plasmonic metals are directly deposited on the graphene layer on Cu TEM grid. In-case of graphene-ZnO NRs/NWs sample for TEM imaging was prepared by transferring by sonication and then drop casted on the carbon coated Cu TEM grid containing few hundreds of square shaped hollow meshes with dimension of 1 μm . Improved resolution of lattice image is obtained after processing of fast Fourier transformation (FFT) and inverse FFT using '*Digital Micrograph*' (Gatan, USA) image analysis software. In addition, we used SAED to get information about crystallinity and lattice structure of graphene plasmonic and ZnO hybrids.



Figure 2.9: Photograph of the TEM specimen grid holder.

2.5.2. Spectroscopic Techniques

In this section we present a brief account of the tools used for the spectroscopic characterization of the graphene and graphene based hybrid NSs with plasmonic NPs and ZnO NRs/NWs. The spectroscopic data analysis techniques used in the present study is also discussed.

2.5.2.1. Micro Raman Spectroscopy

Micro-Raman spectroscopy is a one of the most powerful popular non-destructive spectroscopic techniques to characterize many properties of carbon based nanomaterials and Raman spectrum of graphene was measured in 2006 for the first time.⁶ In case of graphene, Raman is a boon as it allows us to know its fascinating properties, such as number of graphene layers, disorder due to defects, crystallinity, strain, doping, functionalization etc. It is based on the Raman optical phonons. During Raman spectroscopy measurement, an intense laser beam is incident on the sample through a commercial optical microscope with spot size about few microns (2 μm). The weak back-scattered light or signal from the sample is passed through a double monochromator to reject the Raleigh scattered light and the Raman-shifted wavelengths are detected by a CCD detector. The lines become very broad for amorphous materials, allowing distinction to be made between single crystal, polycrystalline and amorphous material. Raman spectral profile contains information about the structure, crystallinity, strain and phonon confinement effects in graphene.

We used a high resolution micro-Raman spectrometer (Lab RAM HR 800, Jobin Yvon, USA) with a liquid nitrogen cooled CCD detector. The photograph of the micro-Raman setup used in the present study is shown in the **Fig. 2.10(a)**. We have carried out the Raman measurements of graphene for the determination of layers and uniformity over a large coverage at room temperature using three different excitation wavelengths: 488, 514.5 nm (Ar⁺ laser) and 632.8nm (He-Ne laser). Note that the optical microscopy of the as-transferred graphene on to SiO₂ substrates were investigated with the same equipment as mentioned in the previous section. We extensively investigated the plasmonic NPs interaction with graphene from the resonant Raman spectral line shape analysis. The spectral resolution of the Raman spectrometer is 0.3 cm^{-1} . The laser power at the sample side was fixed at approximately 1 mW to avoid laser heating effects.

Besides the Raman spectroscopic features of graphene and graphene based hybrids, we have performed spatial Raman mappings of the pristine and graphene plasmonic hybrids.

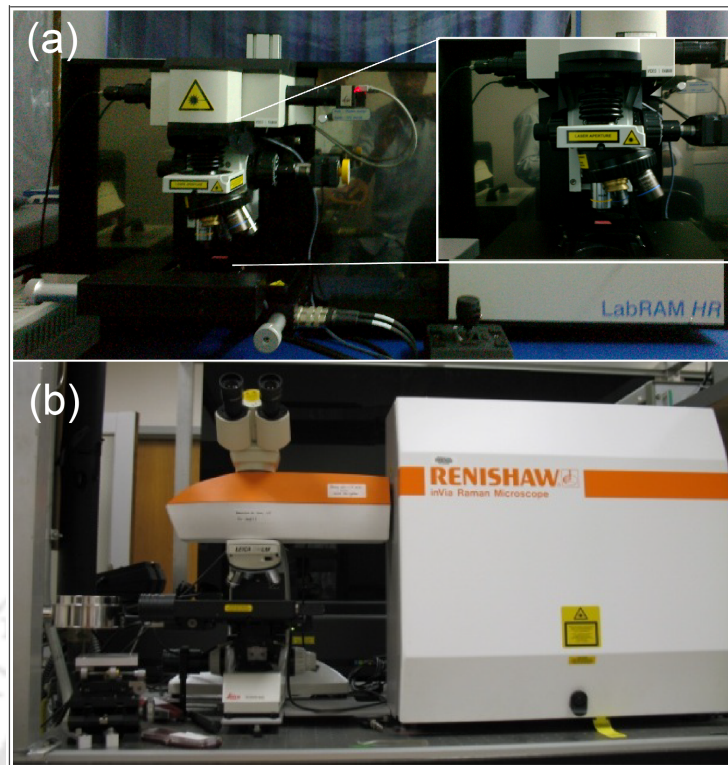


Figure 2.10: (a) Laser micro-Raman spectrometer (Horiba, Lab RAM HR) with back scattering geometry having four excitation wavelengths 488, 514.5, 632.8 and 785 nm. (b) Image of High resolution Raman spectrometer (inVia, Renishaw), with the excitation source 514.5 nm (Ar⁺ laser) and a thermoelectric cooled CCD detector in the backscattering configuration to examine the crystalline quality and number of layers in the graphene. Raman mapping was carried out with 10×10 μm² frame size on the samples at 514.5 nm laser excitation with a spatial resolution of 100×600 nm using a Streamline imaging facility for covering large area.

Figure. 2.10(b) shows the high resolution Raman spectrometer (inVia, Renishaw), used for the spatial Raman mappings with the excitation source 514.5 nm (Ar⁺ laser) and monochromator using 1800 grmm⁻¹ lines with a thermoelectric cooled CCD detector in the backscattering configuration to examine the layer uniformity, number of layers in the CVD graphene and defect mediated interaction of plasmonic NPs with it. Raman mapping was carried out with 10×10 μm² frame size on the samples at 514.5 nm laser excitation with a spatial resolution of 100×600 nm using a streamline imaging facility for covering large area.

A. Spectral Analysis of the Raman Features

The spectral line profile of the Raman feature is usually analysed by the Lorentzian line shape fitting and it is expressed as

$$y = a_0 \frac{1}{1 + \left(\frac{x - a_1}{a_2} \right)^2} \quad \dots\dots\dots (2.2)$$

Where, a_0 is the peak intensity, a_1 represents the centre for the Raman peak and $2a_2$ gives a measure of FWHM. In the present study, experimentally observed Raman spectra of graphene were deconvoluted using a multiple Lorentzian peaks. Usually, in case of graphene, 2D band profile is very sensitive to the number of graphene layers and it is perfectly fitted with a single Lorentzian for monolayer, while for bi-layer it will be 4 Lorentzians and more than 5 layers, 2D band will be identical that of graphite.⁶ However, the relative intensity of 2D band is higher than the G band for single and bi layer graphene samples.⁵ In the present work, Raman spectroscopy is extremely used to study the evolution of graphene layers, uniformity of the layers after clean transfer, finger prints of in-plane and edge defects in CVD grown graphene layers and Based on the resonant Raman line shape analysis we demonstrated the physical functionalization of graphene with plasmonic NPs through defects for the first time. Note that the Raman spectroscopy of graphene and its derivatives was discussed in details in the **Chapter 1**.

2.5.2.2. Optical Absorption Spectroscopy

This technique is used to study either reflection or absorption or transmission properties of thin films since the electronic band structure of semiconductors and metals can be determined by studying their optical properties. The optical absorption is a result of interaction between the material and light. In the present case, we have measured the absorption spectra of graphene, CDGs, graphene-plasmonic hybrids and graphene-ZnO hybrids directly fabricated on the quartz substrates. **Figure 2.11(a)** shows the photograph of the absorption spectrometer (PerkinElmer UV Win Lab, UV-3101PC).

2.5.2.3. Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) is one of the powerful spectroscopic tool used to determine the structural bonding information, impurities and chemical functional groups in the sample. The FTIR is based on the phenomena of Michelson interference combined with Fourier transformation of the source along with reflectance spectroscopy to confirm the various types of oxygenated covalent functional groups in the CDG. A FTIR spectrometer of Perkin Elmer (Spectrum BX) is used in this study, as shown in the **Fig. 2.11(b)**. We have performed the FTIR measurements in reflection and transmission mode in the range of 400-3000 cm^{-1} at a resolution of 2 cm^{-1} . The infrared transmission spectrum is acquired for the CDGs prepared from the standard KBr pallet. Thin circular KBr pellets of diameter 10 mm were prepared by using KBr pellet machine for the FTIR measurement.

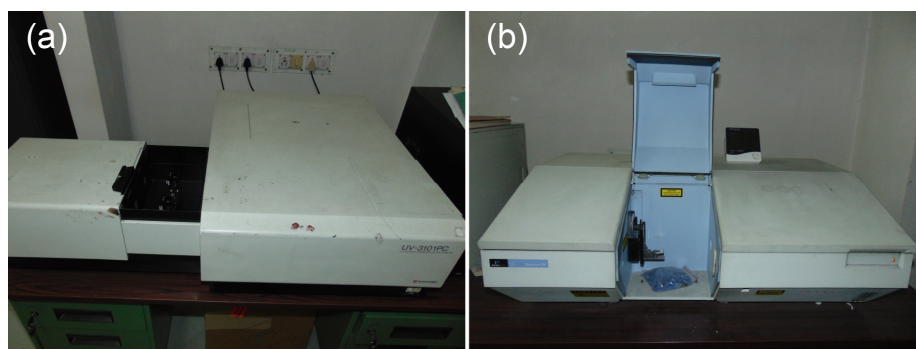


Figure 2.11: Photographs of the (a) UV-vis-NIR absorption spectrometer (Perkin Elmer UV Win Lab, UV-3101PC), (b) FTIR (Perkin Elmer, Spectrum BX).

We used FTIR reflectance spectroscopy to confirm the functional groups in CDG samples on SiO_2 substrates.

2.5.2.4. Photoluminescence (PL) Spectroscopy

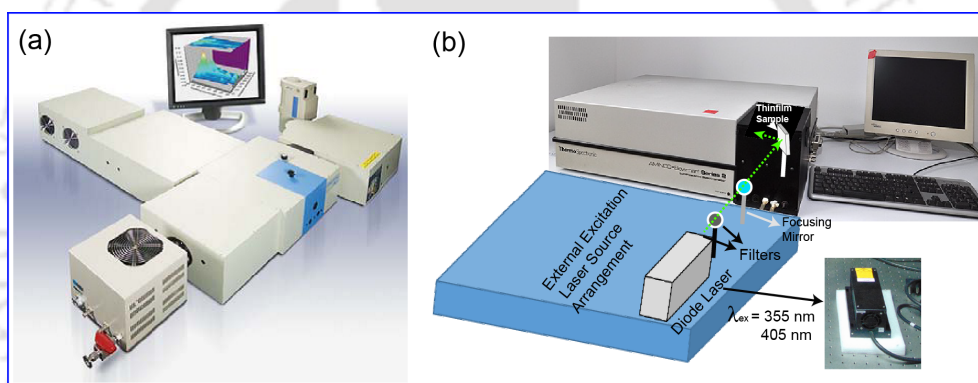


Figure 2.12: (a) Image of the commercial photoluminescence (PL) spectrometer (Fluorolog-3, Horiba, with light source Xe lamp and double monochromator). (b) Arrangement of external excitation source with 355 and 405 nm diode lasers to the PL spectrometer (AB2, Thermo Spectronic) for excitation wavelength dependent PL studies.

In PL spectroscopy, the optical properties of the materials can be probed by shining the photons which excite the electrons to higher energy levels and analysing the optical emission when these states relax. The spectral distributions of the emission energies are related to the electronic transition probabilities within the sample. Photoexcitation causes electrons-holes generation within the material and that electrons move into permissible excited states, the excess energy is released and electron and a hole can either recombine non-radiatively by emitting phonons (or transferring energy to other particles) or radiatively by emitting photons. The energy of the emitted light (PL) relates to the difference in energy levels between two electronic states involved in the transition between the excited state and the equilibrium state. The PL spectroscopy measures the count of emitted photons in a spectral

range. The PL spectroscopy provides the quantitative information like exciton transition, exciton binding energy, defect states, impurities states etc. From PL spectrum, information of the radiative defects present on the samples could be obtained.

We carried out the PL studies using two PL spectrometers one is Fluorolog3, Jobin Yvon with excitation light source of 325 nm He-Cd continuous laser and another one is AB2, Thermo spectronic with two external excitation sources (355 and 405 nm) of diode lasers. The PL spectrometers are depicted in the **Fig. 2.12(a)** and **(b)**. The steady state PL peaks are usually expressed as Gaussian line shape

$$y = y_0 + A \exp \left[- \left(\frac{(x - x_c)^2}{2w^2} \right) \right] \quad \dots\dots\dots (2.3)$$

Where y_0 is the offset constant, x_c , w and A are the peak position, width and peak amplitude, respectively. w multiplied by $\sqrt{2 \ln 2}$ give the exact values of the FWHM of the Gaussian profile. We measured the spectral profile of the PL spectrum using a Peakfit software.

2.5.2.5. X-ray Photo Electron Spectroscopy (XPS)

XPS utilizes photo-ionization by X-ray photons and analysis of the kinetic energy distribution of the emitted photoelectrons to study the composition and electronic state of the surface region of a sample.⁷ For each element, there is a characteristic binding energy, which is associated with the core atomic orbital, i.e., there will be a set of peaks in the photoelectron spectrum corresponding to each element with respect to their kinetic energies determined by the photon energy and the respective binding energies. The line shapes of the XPS peaks display the information about the chemical composition and local environment of defects and defect mediated interaction of the surface moieties up to 10 nm thickness. In case of graphene, one can estimate the surface information for monolayer and few layers based on the XPS peaks corresponds to sp^2 and sp^3 hybridization and their ratio of integrated area. For our measurements, we had used XPS- PHI-Xtool, Ulvac Phi, Japan, using an Al $K\alpha$ X-ray beam (1486.7 eV) as shown in the **Fig. 2.13**. Experimentally recorded spectra were deconvoluted using XPS peak 4.1 software with Shirley background. We have used XPS spectroscopy to study the physical functionalization of graphene with plasmonic NPs and various oxygenated functional groups covalently attached on the graphene surface.



Figure 2.13: Photograph of the XPS spectrometer (PHI-Xtool, UlvacPhi) using an Al K α X-ray beam (1486.7 eV).

2.5.3. Analytical Techniques

2.5.3.1. X-ray Diffraction (XRD)

XRD is the most important non-destructive characterization tool to probe the crystallinity of the materials. The crystalline phase, lattice parameters, strain and orientation of the ZnO NWs/NRs can be assessed from the XRD patterns. In XRD, a collimated beam of X-rays with wavelength $\lambda = 0.5\text{--}2.0\text{\AA}$, is incident on a specimen and is diffracted by the crystalline phases in the specimen according to 'Bragg's law',

$$2d \sin \theta = n\lambda \quad \dots\dots\dots (2.4)$$

Where d is the lattice spacing between atomic planes in the crystalline phase, θ is the angle of incidence of the X-ray beam with the atomic plane, n represent the order of diffraction (we consider only the first order diffraction). In the present study, the Bragg-Brentano geometry is used⁸, where the incident X-rays impinge on a fixed specimen at a small angle $1\text{--}5^\circ$ and the diffracted X-rays are recorded by a detector that moves along the focusing circle. This method provides good sensitivity for thin films, due to para focusing circle and large



Figure 2.14: Photograph of the X-ray Diffractometer (TTRAX II, RIGAKU 2500, 18kW)

diffraction volume. Owing to huge data bank available in the form of JCPDS Powder Diffraction Files⁹, covering practically every phase of every known material, crystal phase of the sample is identified from the peak position of the diffractogram. Homogeneous or uniform elastic strain in the (hkl) direction can also be calculated from the shift in the diffraction peak positions, and the d_{hkl} spacing of the unstrained crystal. X-ray diffraction patterns of the as-grown and annealed graphene based ZnO NSs were obtained using a commercial XRD (TTRAX III, RIGAKU 2500) using a $CuK\alpha_1$ ($\lambda = 1.5406\text{\AA}$) radiation or Mo X-ray radiation ($\lambda = 0.7093\text{\AA}$) with nickel filter. A photograph of the XRD machine is shown in the **Fig. 2.14**. All the data are taken at room temperature in thin film mode at a grazing angle of 3° .

2.5.3.2. Thermo Gravimetric Analyser (TGA)

TGA measures the weight loss of the sample with respect to temperature and difference in temperature between sample and reference that are exposed to the heating ramp via symmetric placement within the furnace. The reference material is a substance which has the same thermal mass as the sample and do not undergo any phase transformations during the heating ramp. There are two ceramic pans kept on a weight balance symmetrically which have the high degree of sensitivities of weight ($\sim$ micro gram) and temperature (0.001°C). The difference between the sample and reference is measured by a “differential thermocouple” in which one junction is in contact with the underside of the sample pan, and other side is in contact with the underside of the reference pan.

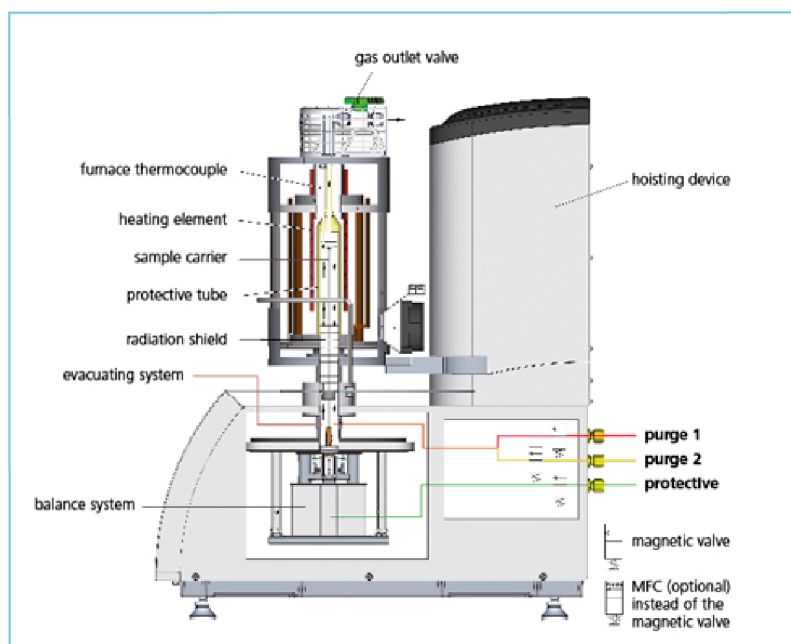


Figure 2.15: Schematic of the TGA analyser (STA 449 F3 Jupiter, Netzsch, Germany) equipped with high temperature tungsten furnace with temperature range from room temperature to 2400 °C.

Differential thermocouple signal amplifier is a critical component which amplifies minute voltages along with eliminating random noise. When the sample undergoes a transformation, it will either absorb (endothermic) or release (exothermic) heat. For example, the melting of a solid material will absorb heat, where that thermal energy is used to promote the phase transformation. Instrument detects the sample cooler than the reference and will indicate the transformation as “endotherm” on a plot of differential temperature (ΔT) versus time. It also determines the rate of change in the weight of the sample with respect to the temperature and temperature. In general, the derivative of the weight loss gives the information about the apparent weight loss at a particular point. The local environment inside the TGA is purged with an inert gas to prevent the unwanted reaction with oxygen atmosphere. A computer is used to control the instrument.

Figure 2.15 an image of the TGA instrument (STA 449 F3 Jupiter, Netzsch, Germany) built with high temperature tungsten heating element (2400°C) used for the present study. It consists of a furnace, microbalance, and temperature controller, sensor for temperature monitoring and electronics for control and data acquisition. Different forms of carbon show different oxidation rate and temperature for maximum oxidation temperature for a particular heating rate and gas flow rate. We recorded TGA and DTA spectra for the CDG materials in high oxygen gas environment. The maximum temperature chosen for TGA measurement was 900°C in a controlled flow (60 SCCM) of high purity oxygen (99.999%)

gas atmosphere with a heating rate $5^{\circ}\text{C min}^{-1}$. The initial weight of the CDG sample was taken as 2-3 mg in each measurement. Structural defects, sp^3 carbon associated with various oxygenated functional groups on the basal plane and edges of the graphene sheets can lower the thermal stability. Using TGA study we classify the epoxy/-OH, COOH and C=O functional groups on the basal plane and edges and the reactants are presented in the **Chapter 8**.

2.6. Design and Development of the Photoconductivity Setup

We have designed and developed a photocurrent and photoresponse measurement setup in order to study the photoconductivity behaviour of graphene based 1D ZnO NSs. A photograph of the photoconductivity setup is shown in the **Fig. 2.16(a)**. It consists of a light source, electrical contacts through micro probes and a source meter with a computer interfacing. The important components of the setup are labelled in the **Fig. 2.16(a)**. The micro probe station (ECOPIA EPS-500) connected to a source measurement unit (Keithely 2400) is used for the study of I-V characteristics and a 300 W Xenon lamp is used as a light source to excite the sample. Note that the excitation wavelength is selected using a manual monochromator (Oriel Instruments, USA). The I-V setup was interfaced with a computer to collect the data using Lab Tracer 2.0 software. **Figure. 2.16(b)** shows the arrangement of the micro probes and tight focussing of the incident light on to a small area on the sample through a mirror.

A schematic of the photoconductivity measurement and the device structure of the graphene-ZnO NW hybrid UV photodetector in the **Fig. 2.16(c)**. Ag contact was deposited by thermal evaporation under high vacuum on top of the ZnO NWs array surface by keeping a shadow mask with a channel width and length $\sim 0.1 \times 0.1 \text{ mm}^2$. The thickness of the Ag layer is ~ 100 nm. The electrical characteristics of the samples were measured using a Keithley source meter through interfacing with the computer. The light falls exactly on the location between the two metal contacts in the form of a rectangular spot. Slit width can be monitored by the microslits. The wavelength of the incident light can be changed by the manual monochromator. The photocurrent as a function of time can be monitored by the Lab Tracer 2.0 software which is functioned with the Keithely 2400 source meter. Note that the same source meter was used to supply the necessary bias voltage. Photoresponse measurements were carried under the UV light with Illumination power - 0.405 mw/cm^2 in ON and OFF conditions (Excitation wavelength- 365nm). Note that all the measurements were carried out at room temperature and atmospheric condition.

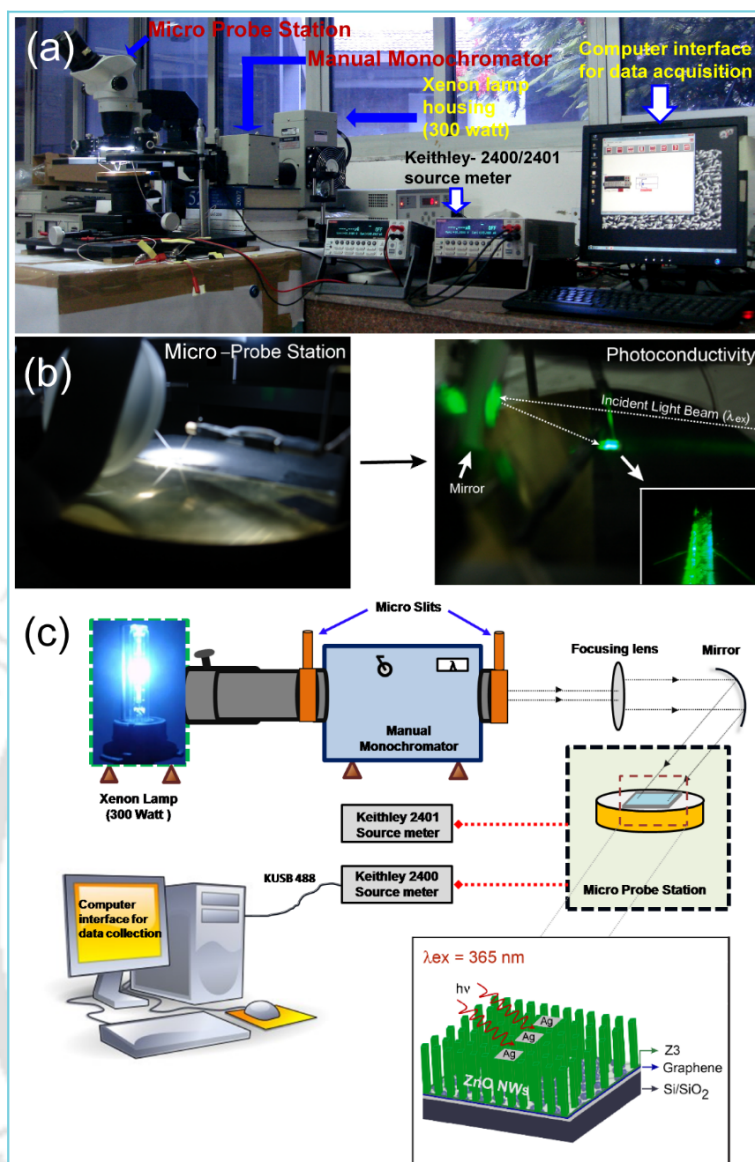


Figure 2.16: (a) Photograph of the photoconductivity setup equipped with micro probe station (ECOPIA EPS-500, South Korea) and a source meter (Keithley 2400). (b) Image of the micro probes on the graphene-ZnO sample and excitation source with tight focusing through a mirror. (b) Schematic of the in-house developed photoconductivity setup used for the fabrication of Graphene-ZnO NR/NW UV photodetector.

2.6. Visible Light Photocatalysis

Visible light Photocatalytic activity of graphene based plasmonic hybrid nanostructures was carried out by a commercial Photocatalytic reactor (Lelesil innovative Systems, Mumbai), which consists of a Xenon lamp source (power rating- 250 W) covering the wavelength range from 400-800 nm. The photograph of the Photocatalysis reactor is shown in the **Fig. 2.17** Photocatalytic activity was estimated from the degradation of methylene blue (MB) as the reference pollutant. MB solution with initial concentration of 10 mg/L was prepared in 100

mL distilled water. The thin films of pristine and graphene plasmonic hybrids on quartz and SiO₂ substrates were prepared and dipped in to the MB dye solution and kept in dark for 2 hours to equilibrate adsorption and desorption of dyes on the surface of the film. This film-dye solution was kept under visible light irradiation for 120 min.). At an interval of 15 min, 5 mL of the irradiated dye solution was taken out and kept for absorption measurement. Photodegradation of MB is monitored by observing the changes in the maximum absorbance of MB at 664 nm.



Figure 2.17: Photograph of visible Photocatalysis setup, which consists of a Xenon Lamp, Power-250 Watt with a wavelength range from 400-800 nm. Note that the arrows indicate the water circulation during the irradiation of sample in-order to reduce the heating effect on the photocatalysts.

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Chapter 3

Controlled Growth of Large Area Single Layer Graphene and its Characterization

In this chapter, we present the growth strategies of graphene (GR) on a Cu foil using CVD technique. We have discussed the various growth parameters, such as flow rates of precursor gases (CH_4 , H_2 and Ar), growth temperature, pressure and effect of pretreatment conditions of the Cu foil on the grain size, shape and evolution of GR layers. Next, clean transfer of GR on the alien substrates followed by H_2 gas annealing is carried out. The size and shape of GR layers, number of layers and disorder due to defects were estimated from the optical microscopy, electron microscopy and micro-Raman spectroscopy/imaging techniques. Intrinsic defects of graphene (in-plane and edge defects) on SLG is characterized using HRTEM and resonance Raman spectroscopy.

3.1. CVD Growth of Graphene

We have synthesized monolayer and few layer GR by using a catalytic CVD system on a Cu foil of thickness 25 μm (Alfa-Aesar). **Figure 3.1(a)** schematically represents the complete details of the preparation of Cu catalyst and CVD growth of graphene. At first, the Cu foil was inserted into a quartz chamber and flushed with Ar gas for 5 min. Then, the chamber was pumped to base vacuum 4×10^{-4} mbar and the temperature was increased to 1000 $^\circ\text{C}$ (growth temperature of GR) at a rate of 25 $^\circ\text{C min}^{-1}$ using a horizontal muffle furnace (Indfur, India). The Cu substrate was pre-annealed at the same temperature, in reduced environment by flowing 200 SCCM H_2 gas for 30 min in order to avoid oxidation of the Cu surface. The final reaction was carried out by controlled flow of CH_4 ~18 SCCM and H_2 ~200 SCCM for 30 min at a temperature of 1000 $^\circ\text{C}$ and a pressure of 4.0 mbar. Since GR was deposited on both sides of the Cu foil, the bottom layer was removed by either reactive oxygen plasma etching or diamond polishing.

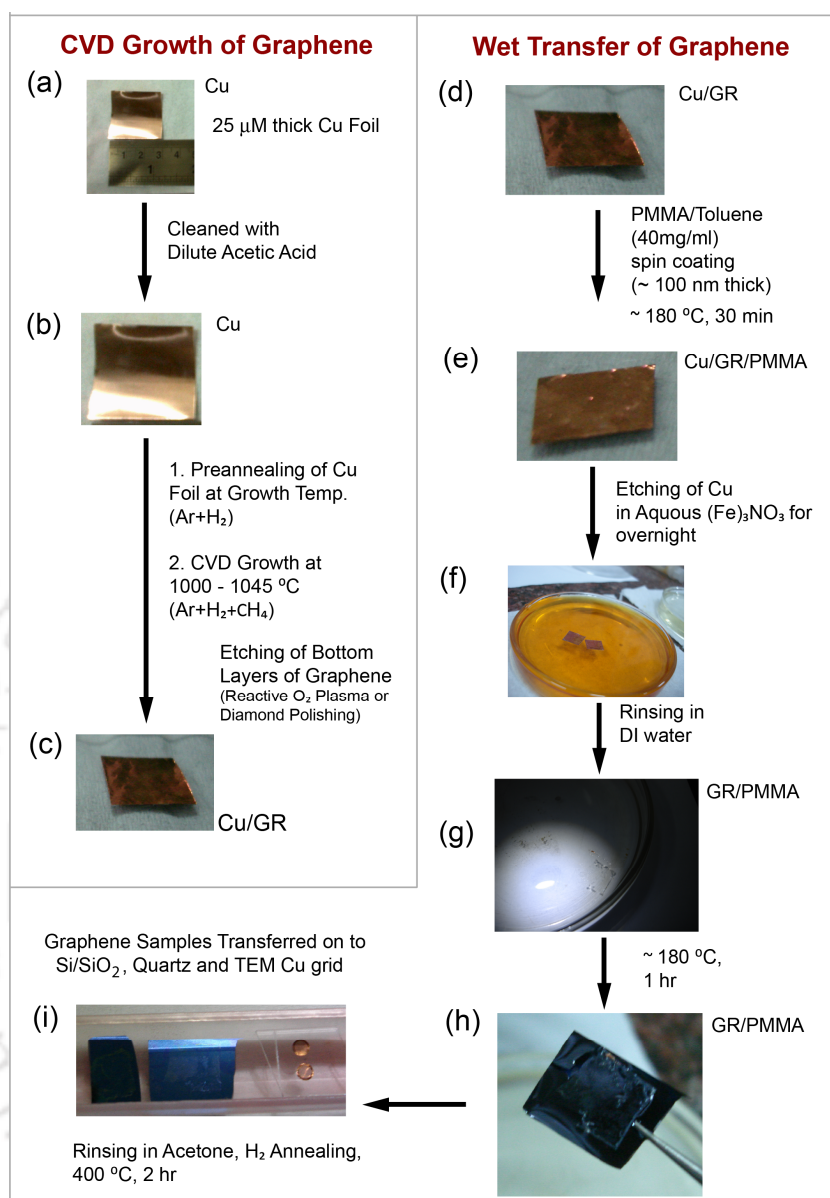


Figure 3.1: (a) Schematic representation of CVD growth of graphene with pre-treatment of Cu substrate. (b) Wet transfer graphene on to different substrates.

3.1.1 Graphene Transfer on to Alien Substrates

The GR layer on top of the Cu foil was transferred on to SiO_2 , quartz substrate and Cu TEM grid by a conventional wet transfer technique.¹ The step by step transfer process of GR is schematically as shown in **Fig. 3.1(b)**. In this process, a thin layer of poly(methyl methacrylate) (PMMA)/toluene (40mg/ml) was spin coated on the Cu/GR layer and the underlying Cu was etched in an aqueous $\text{Fe}(\text{NO}_3)_3$ etchant solution. GR/PMMA floating on the etchant solution was

rinsed in deionized water for few times, until the PMMA and metal impurities were removed. Then, it was scooped and transferred on to required substrates manually. Further, it was kept in oven drying at 180 °C for 1h. GR/PMMA was dissolved in acetone for multiple times to remove the PMMA from the GR layers.

3.1.2. Structural Characterization of Graphene by Micro-Raman Spectroscopy and Optical Microscopy

The crystalline nature and number of layers in CVD synthesized GR were probed primarily by micro-Raman spectroscopy. **Figure 3.2(a)** represents the Raman spectra of as-transferred GR showing three important Raman features, such as D, G and 2D (G') bands. The corresponding scanning location is shown by an OM image in the **Fig. 3.2(b)**. The strong Raman feature observed at 1590 cm^{-1} is the E_{2g} mode (G band), assigned for the in-plane stretching of C-C bonds, which dictates the graphitic sp^2 crystalline nature of the carbon. The Raman mode at 2700 cm^{-1} (a fingerprint of GR, known as the G' or 2D band) originates from the second order double resonance process related to a phonon near the K point in GR. The line shape of the 2D band is very sensitive to the number of layers. The Raman feature at 1352 cm^{-1} , known as the D band, arises from breathing of the hexagonal carbon ring due to the presence of defects. This mode originates from the transverse optical (TO) phonon due to the intervalley double resonance process at the Brillouin zone corner K, such as vacancies or grain boundaries, and substitutional

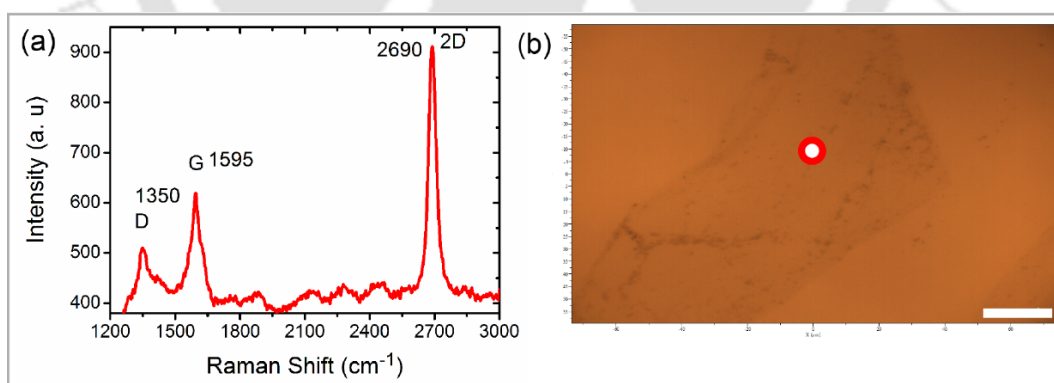


Figure 3.2: (a) A typical Raman spectrum of a CVD grown GR (SLG) scanned with 514.5 nm laser excitation. (b) OM image of GR grown by CVD at a growth temperature 1000 °C. Note that the Raman spectrum was taken after wet transfer of GR onto a SiO_2 substrate.

heteroatoms.²⁻³ A small shoulder at the higher frequency side of the G band ($\sim 1630\text{ cm}^{-1}$) arises from the intravalley double resonance process at the K point and is called the D' band. The D' band mainly originates from structural disorder or edge defect in GR.

3.1.3. H₂ Annealing of Graphene

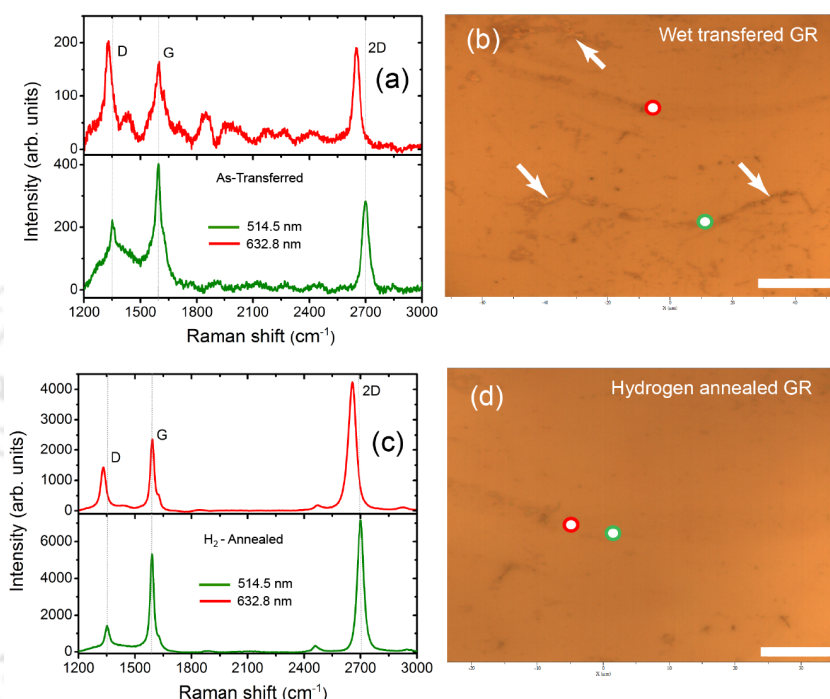


Figure 3.3: Raman fingerprints of GR on SiO₂ substrate and corresponding scanning positions of the OM images: (a-b) before annealing and (b-c) after H₂ annealing. Arrows indicate the residual Cu and PMMA particles. Note that the Raman spectra were recorded at two excitation wavelengths 514.5 and 632.8 nm for the same sample under identical conditions. Scale bars shown in the OM images are 10 μm .

Achieving high quality GR without wrinkles, folds, and surface corrugation is one of the challenging tasks while transferring it from Cu foil to a different substrates. Though wet transfer is a standard protocol, there are still leftover impurities such as PMMA and catalyst NPs along with the oxide traces that are present on the GR substrate. In order to remove these impurities from the GR on SiO₂ and TEM grid, the samples were annealed in H₂ atmosphere. Initially, the GR samples were taken in a quartz boat and kept in the tubular chamber. The chamber was pumped up to a base vacuum of 10^{-5} mbar followed by ramping of the temperature up to 400 °C. The annealing was performed under H₂ gas environment for 2 h. The annealing parameters were optimized to achieve a clean GR without the residual impurities on the GR surface.⁴ The degree

of improvement in the crystallinity and spatial homogeneity of GR layers were confirmed from Raman spectra and Raman mapping in each case before and after annealing. **Figure 3.3(a, b)** represents the Raman spectra of GR before and after H₂ annealing scanned with two excitation wavelengths, namely 514.5 and 632.8 nm. The corresponding scanning locations and removal of the residual PMMA and catalyst particles after H₂ annealing is shown in **Fig. 3.3(c) and (d)**.

3.1.4. Determination of Layer Numbers and Defect Density of Graphene

We estimated the number of layers, crystalline quality and structural defects that are formed during CVD growth of graphene by micro-Raman spectroscopy. The integrated intensity ratio of 2D and G band (I_{2D}/I_G) decides the number of layers while that of D and G (I_D/I_G) conveys the defect density in as-grown graphene.^{1, 5-6} For a SLG, I_{2D}/I_G should be > 2 and FWHM of 2D band

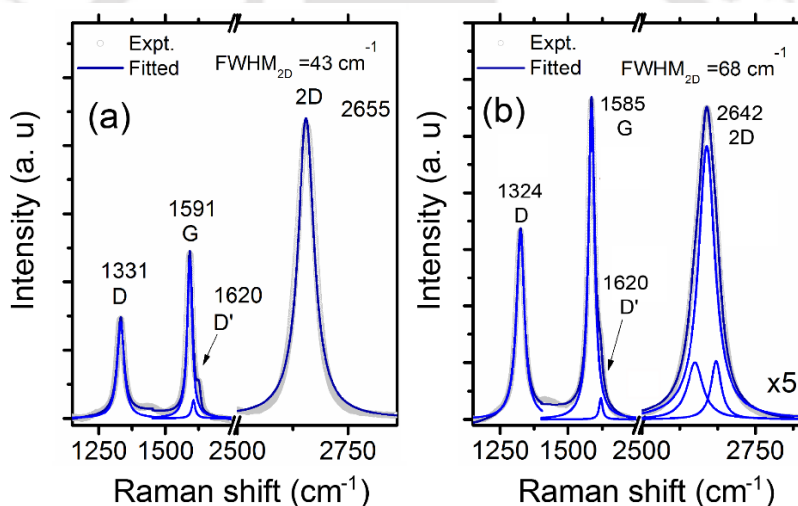


Figure 3.4: Raman spectra recorded with an excitation wavelength of 632.8 nm for (a) SLG and (b) BLG; the experimental data (symbols) are fitted with Lorentzian line shapes (solid line). Characteristic Raman modes are marked with the peak position in cm⁻¹ units.

should must be < 40 cm⁻¹ with a single Lorentzian peak.⁷⁻⁸ **Figure 3.4** represents the Lorentzian line shape of Raman features in SLG and BLG. Note that the Raman spectra were recorded with 632.8 nm laser excitation, which yields high intensity of Raman bands, It is evident from the resonant Raman spectra of **Figure 3.4(a) and (b)**, the intensity of the sharp D band is nearly half the intensity of the G band ($I_D/I_G = 0.6$) and the D' band is relatively weak. This implies the presence of vacancy type defects on the basal plane of graphene including reconstructive defects at the edges that are formed during the growth process.⁹⁻¹⁰ Due to the smaller grain size ($< 1\mu\text{m}^2$), D and D' bands are very strong. In addition, we observed equal intensities of the D and G

bands with FWHM $\sim 31 \text{ cm}^{-1}$ at some portions on the graphene layer. Usually, D and G bands with a large FWHM ($>80 \text{ cm}^{-1}$) arise for a large amount of sp^3 carbon. Such features were not observed in our CVD grown graphene, though it has been observed in the case of chemically prepared graphene sheets and ion bombarded graphene samples.¹¹⁻¹² FWHM of both D and G bands is $\sim 30\text{--}40 \text{ cm}^{-1}$ and it implies the presence of point defects and extended defects on the basal plane of the graphene without losing its sp^2 crystalline nature.¹⁰ This is consistent with the corresponding sharp 2D band. On the other hand, 2D band in SLG shows a FWHM of 43 cm^{-1} , while that in BLG shows a FWHM of 68 cm^{-1} . The relatively higher FWHM in SLG may be due to the presence of various in-plane defects. In order to calculate the defect density (n_D) and (L_D) for a measured I_D/I_G ratio, we have used the empirical relations proposed by Cancado. et al.¹² These empirical relations were based on the I_D/I_G values obtained in Raman spectra of Ar⁺ ion bombarded graphene having point defects with inter-defect distance, $L_D > 10 \text{ nm}$ and it has an error bar of 30%.

$$L_D^2 (\text{nm}^2) = (1.8 \pm 0.5) \times 10^{-9} \lambda_L^4 \left(\frac{I_D}{I_G}\right)^{-1} \quad \dots\dots (3.1)$$

$$n_D (\mu\text{m}^{-2}) = \frac{(1.8 \pm 0.5)}{\lambda_L^4} \times 10^{14} \left(\frac{I_D}{I_G}\right) \quad \dots\dots (3.2)$$

where λ_L is the excitation wavelength (in the visible region) in nm., and ' n_D ' is the defect density.

Using the above empirical relations we have estimated L_D and n_D in our pristine graphene samples and found to be 21.9 nm and $673 \mu\text{m}^{-2}$, respectively. Note that the excitation wavelength used for the L_D and n_D calculation is 632.8 nm .

3.2. Optimization of Growth Parameters for CVD Graphene

A systematic investigation on the CVD growth process of GR was carried out by monitoring the thermodynamic parameters such as gas flow rates (Ar, H₂ and CH₄), growth temperature and pressure etc. Based on our experimental observations, we have framed four different growth schemes as described in the **Table. 3.1**. **Table. 3.1** illustrates the CVD growth kinetics of the GR and step by step understanding of the growth parameters that are optimized to achieve the large

Table 3.1: Summary of the growth parameters for CVD growth of GR and the nature of the GR layers obtained in each case

Schemes	Base Press. (m bar)	Growth Press. (m bar)	Growth Temp. (°C)	Pre-annealing of Cu foil at Growth Temp. (min)	H ₂ Flow during the Pre-annealing of Cu foil (SCCM)	Ar:H ₂ :CH ₄ Flow Ratio (SCCM)	Growth Time (min)	Area (μm ²)	No. of Graphene Layers
Scheme1	4×10 ⁻⁴	4.0	1000	30 min	200	0:200:18	30	~ 1-25	Defective SLG
Scheme2	4×10 ⁻⁴	2.2	1045	1h	100	300:50:10	20	~ 50	Defective BLG and FLG
Scheme 3	4×10 ⁻⁴	1000	1045	3h	500	0:500:5	20	1600	FLG
Scheme 4.	4×10 ⁻⁴	1000	1045	3h	500	0:500:2	15	>10 ⁵	SLG

area defect free SLG. In all the growth schemes, base pressure of the quartz chamber was kept at 10⁻⁴ mbar and growth pressure was varied in the range of low pressure (~ 2.2 mbar) to atmospheric pressure. Growth temperature was varied in the range of 1000 and 1045 °C. Prior to the CVD growth, smoothness of the Cu top surface without having any folds, corrugation, marks, and scratches is very important for the nucleation of carbon adatoms. Initially Cu foil is cleaned with dilute acetic acid for few minutes followed by rinsing in acetone. This helps to remove the oxide traces on the surface of the Cu foil.¹³ Preannealing of Cu foil before CVD growth of GR play an important role to achieve the large area SLG. In each scheme, we have performed the preheating of Cu foil at the growth temperature. This will increase the grain size of the Cu and decrease the oxidation of Cu surface in reduced environment. Monitoring the preannealing time and H₂ gas flow basically decides the number of nucleation sites of the carbon adatoms on Cu catalyst during the CH₄ flow.¹⁴

3.2.1. Growth Scheme 1

In this scheme, GR growth was carried out at 1000 °C with lower flow rates of H₂ while CH₄ flow was kept at 18 SCCM. We found the formation of GR grains having average sizes below 1 μm². **Figure 3.5(a)** represents the FESEM image of the as-transferred GR onto SiO₂ substrate grown by scheme 1 (see **Table 3.1**). **Figure 3.5(b)** is a magnified view of region of I of **Fig. 3.5(a)** that shows a coverage of smaller GR grains. In addition, we found the formation of various shapes of the multi-layer graphene (MLG) grains such as circular, star, flower shapes as shown in the **Fig. 3.5(c-f)** at identical growth conditions. Note that the duration of preannealing was 30

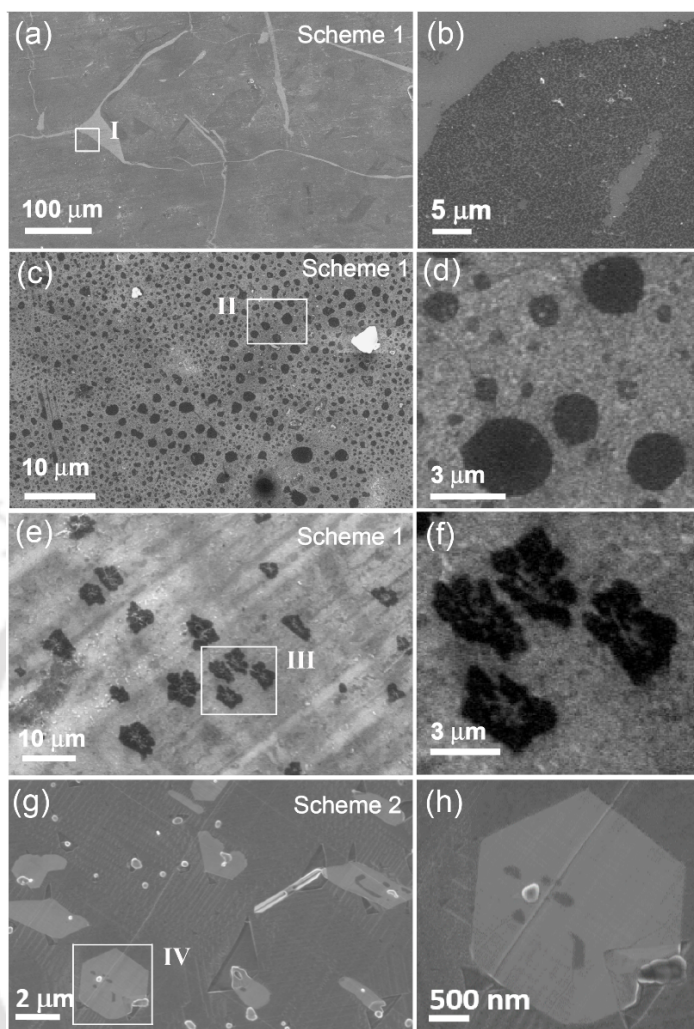


Figure 3.5: FESEM images of various graphene grains showing shape evolution: (a) CVD GR transferred onto a SiO₂ substrate. (b) Magnified view of a region I marked in Fig (a), which implies smaller grain size ($< 1 \mu\text{m}^2$). (c-d) Formation of circular and flower type GR grains in scheme 1. (d-e) Magnified view of a region of II and III marked in the Fig. (c) and (d), respectively, which signifies a formation of few microns of FLG. (g) Formation of hexagonal GR grains in scheme 2. (h) Magnified view of region of II marked in the Fig. (g).

min in H₂ (200 SCCM) atmosphere. Based on Raman characteristic features of the GR sample grown in this scheme is a defective graphene (DGR) which has plenty of point and extended defects on basal plane of the SLG and BLG. The overall quality and area of coverage of GR in this scheme is not impressive.

3.2.2. Growth Scheme 2

In this case, we increased the preannealing time to 1h and reduced the H₂ flow rate to 100 SCCM. During the graphene growth, the gas proportion mixture Ar:H₂:CH₄ was kept at

300:50:10. **Figure 3.5(g)** shows the nucleation of hexagonal GR on the Cu foil. Interestingly, we found that, each GR grain on Cu foil is separated by an average distance of $\sim 10 \mu\text{m}$. It indicates the formation of larger size Cu grains that reduces nucleation of excess GR grains due to the longer duration of preannealing. However, longer time heating leads to the surface roughness of the Cu foil (see **Fig. 5(g)**) that may form more structural defects on GR layer.

3.2.3. Growth Scheme 3

In our next experiment, we performed CVD growth with longer duration of preannealing of Cu foil at 1045°C in higher concentrations of H_2 flow (500 SCCM). Our experimental results show that, it helps to increase Cu grain size (few tens of microns) and reduce the excess nucleation centers of carbon adatoms on the Cu, which helps to as minimize the oxidation of Cu and large

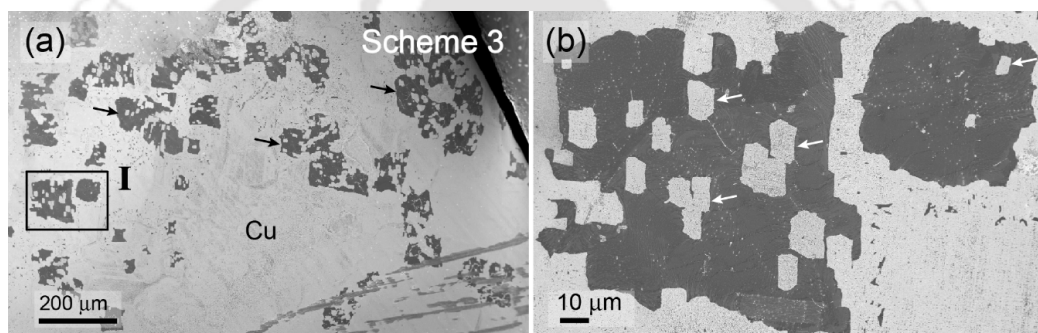


Figure 3.6: FESEM images of large area CVD grown GR on Cu foil: (a) Formation of larger GR grains ($\sim 1600 \mu\text{m}^2$) at longer duration of pre annealing of Cu foil at 1045°C in H_2 gas environment. (b) Magnified view of region I marked in the Fig. (a), which represents the FLG with the grain size more than $1000 \mu\text{m}^2$. The black and white arrows indicate the nucleation sites of the large area FLG domains and Cu grains, respectively.

area coverage of the SLG at higher concentrations of H_2 flow. **Figure 3.6(a)** represents the FESEM image of the GR growth under scheme 3, which shows the grain size $\sim 1600 \mu\text{m}^2$ area with few layer coverage. The arrows indicate the nucleation sites of the large area GR grains. **Figure 3.6(b)** is a magnified view of region I of **Fig. 3.6(a)**, which shows two individual FLG grains of area $\sim 70 \times 70 \mu\text{m}^2$ and $\sim 30 \times 30 \mu\text{m}^2$. Arrows indicate the Cu islands inscribed within the larger GR grain. In this growth scheme, CH_4 flow rate was supplied only 5 SCCM.

3.2.4. Growth Scheme 4

Here, the protocol was similar to scheme 3, except the CH_4 flow rate was reduced to 2 SCCM, and during the ramping/cooling stage, we maintained the Ar: H_2 mixture as 20:300 SCCM.

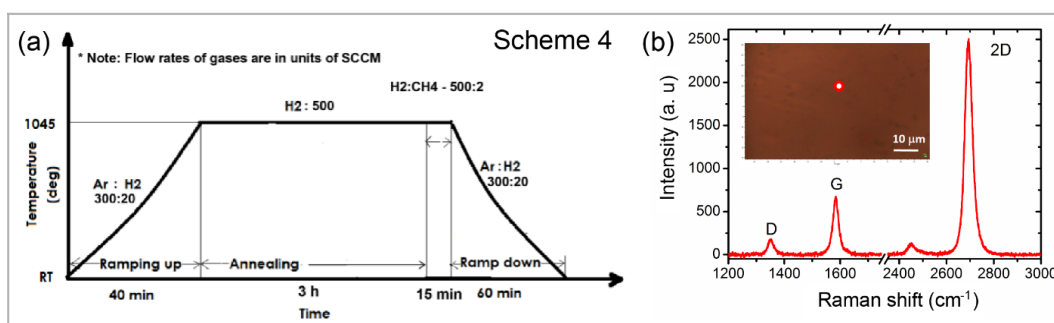


Figure 3.7: (a) Time line profile of the CVD growth parameters in which millimetre area defect free SLG was achieved. (b) Typical Raman signatures of the SLG and corresponding scanning location was shown in the OM image as inset.

The step by step CVD process is shown as the time line profile for the growth in Fig. 3.7(a). In this case we obtained very large area GR with mm² area coverage. **Figure 3.7(b)** shows a typical Raman spectra of millimeter area SLG and corresponding OM image of the sample. The color contrast of OM image is significant for the millimeter area SLG. Raman spectra consists of a strong 2D band and a symmetric G band, while the weak D band conveys the negligible disorder in the as-transferred GR onto SiO₂ substrate.

3.3. Uniformity of Graphene Layers after Transfer on to SiO₂ and Cu TEM Grid

Position dependent Raman measurements were performed to estimate the uniformity of GR layer over the SiO₂ substrate. **Figure 3.8(a)** depicts a set of Raman features of as-transferred GR with λ_{ex} of 514.5 nm corresponding to the scanning positions marked by the serial numbers shown in the optical microscope (OM) image of **Fig. 3.8(b)**. **Figure 3.8(c)** represents the same GR sample transferred on to a Cu TEM grid and corresponding SAED pattern showing the single crystalline hexagonal lattice spots of sp^2 hybridized carbon atoms. Raman data acquired at several spots on GR show similar Raman features. These collective Raman spectra revealed the coverage of large area SLG and BLG in the as-transferred GR sample, as confirmed from the Raman line shape analysis of the 2D band. Note that no apparent shift in G band was observed for spectra taken at different spots, indicating uniformity of the as-transferred GR layer.⁷ However, a marginal shift in the position of the 2D band for different spots may be due to local nonuniformity/wrinkles in the layer while transferring from the Cu substrate to the SiO₂ substrate. Post Growth annealing of GR was performed in order to remove the charge impurities

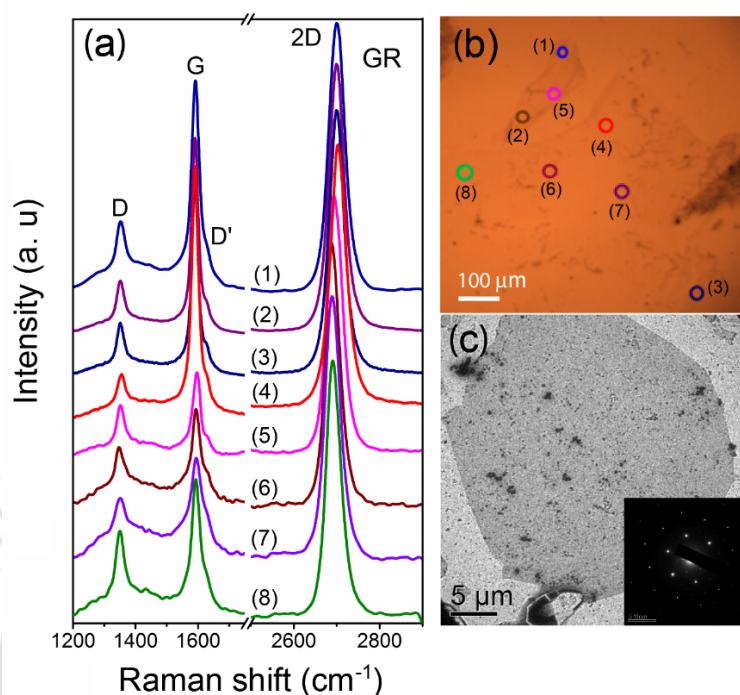


Figure 3.8: (a) Characteristic Raman features of GR transferred onto SiO₂ substrate at different locations of the samples and (b) corresponding OM image showing the scanned area for each spectra marked with a serial number. These spectra were recorded with 514.5 nm excitation. (c) Low resolution TEM image of a GR layer transferred onto a TEM grid; the inset shows the corresponding diffraction pattern of the hexagonal single crystal *sp*² carbon atoms.

coming from the PMMA and Cu catalyst NPs. The crystalline quality of as transferred GR was improved by the GR annealing as described earlier.

3.4. Excitation Wavelength Dependent Raman Spectra of Graphene

Raman spectral features of GR and DGR were recorded using different visible laser excitation wavelengths (λ_{ex}) such as 632.8, 514.5 and 488 nm. The λ_{ex} dependent Raman characteristics in GR and DGR are shown in the **Fig. 3.9(a) and (b)**, respectively. It clearly distinguishes the structural quality and evolution of intrinsic defects on the GR and DGR from the line shape features of D, G, D', 2D and D+D' bands. The Raman finger prints of GR showing a sharp G and 2D bands with $I_{2D}/I_G > 2$ is significant for the perfect *sp*² crystallinity and SLG coverage without

any significant point or extended defects.⁷⁻⁸ In DGR, D, D' and D+D' bands are quite strong with a FWHM $< 30 \text{ cm}^{-1}$. We found the FWHM of 2D band is $> 40 \text{ cm}^{-1}$ for all the λ_{ex} that may be due

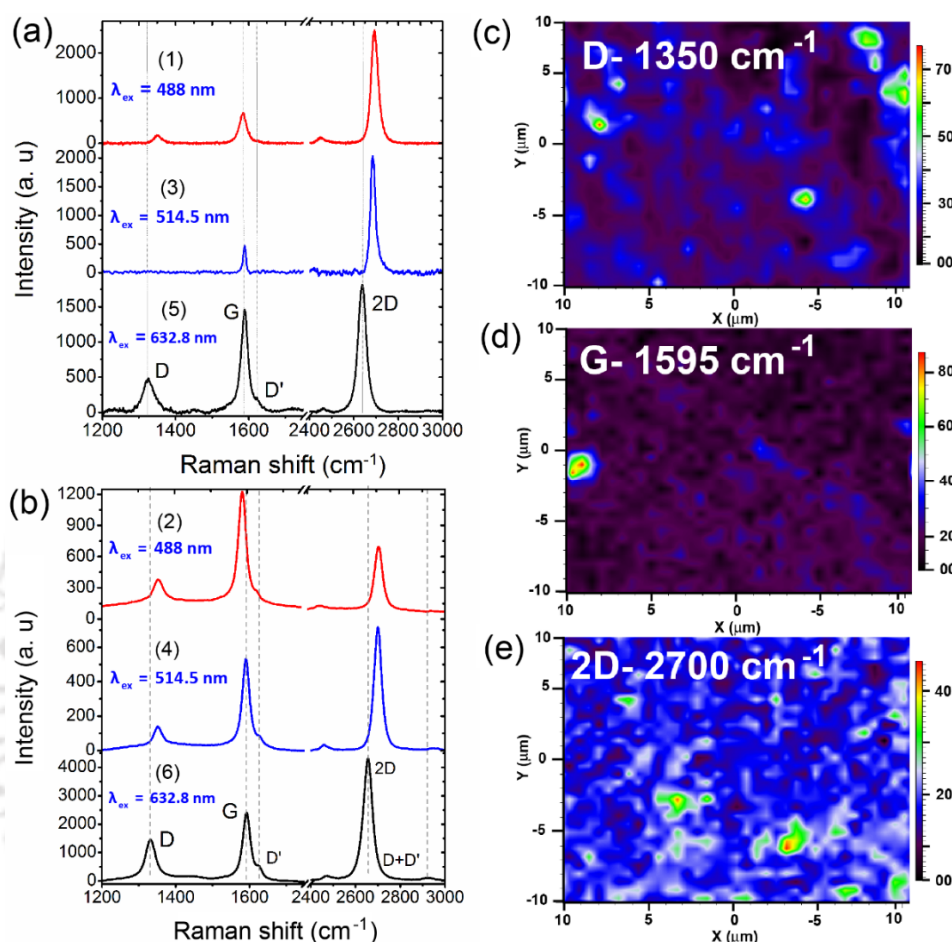


Figure 3.9: (a) Characteristic Raman features of GR transferred onto SiO_2 substrate at different locations of the samples and (b) corresponding OM image showing the scanned area for each spectra marked with a serial number. These spectra were recorded with 514.5 nm excitation. (c) Low resolution TEM image of a GR layer transferred onto a TEM grid; the inset shows the corresponding diffraction pattern of the hexagonal single crystal sp^2 carbon atoms.

to the presence of atomic defects present on the graphene lattice.¹² Interestingly, we observed the intensity of 2D band is half that of the G band in SLG though it has a symmetric Lorentzian at $\lambda_{\text{ex}} = 488 \text{ nm}$ (see **Fig. 3.9(b)**). The considerable asymmetry and broadening in the line shape of G-band signifies the lattice distortions due to disorder or introduction of foreign atoms in to the sp^2 carbon lattice (doping).^{6, 12} Lorentzian line shape parameters such as FWHM, I_D/I_G and I_{2D}/I_G

from peak fitting of these bands are very important to estimate the structural evolution when the GR layer is functionalized with the suitable nanomaterials, which we are going to discuss in the next chapter. D, D', 2D, D+D' and 2D' are dispersive in nature and the physical origin of these double resonance Raman active modes of GR are well understood from the previous reports.⁸ On the other hand, graphitic G-band at 1590 cm^{-1} is a non dispersive characteristic Raman mode which arises from the sp^2 hybridised carbon from the in-plane stretching of C–C covalent bonds of the GR. This is clearly depicted from our λ_{ex} dependent Raman studies on GR.

3.5. Raman Imaging

Raman mapping was performed on GR sample for the well-known D, G and 2D bands for the surface coverage and uniformity of GR layer. **Figures 3.9(c–e)** represent the Raman mapping images scanned in an area of $10 \times 10\text{ }\mu\text{m}^2$, which shows a full coverage of SLG as evident from a sharp and prominent 2D peak at $\sim 2700\text{ cm}^{-1}$. The graphitic G band at $\sim 1595\text{ cm}^{-1}$ signifies the sp^2 hybridization of carbon atoms and assigned for the E_{2g} (high) mode of in-plane C–C stretching vibration.² The ratio of intensities of 2D and G bands I_{2D}/I_G is ~ 1.00 , which indicates the presence of both SLG and FLG. The high intensity of the defect band D at $\sim 1350\text{ cm}^{-1}$ implies the presence of point and line defects in GR. Some of these defects might have been introduced during the wet transfer process.

3.6. HRTEM Studies

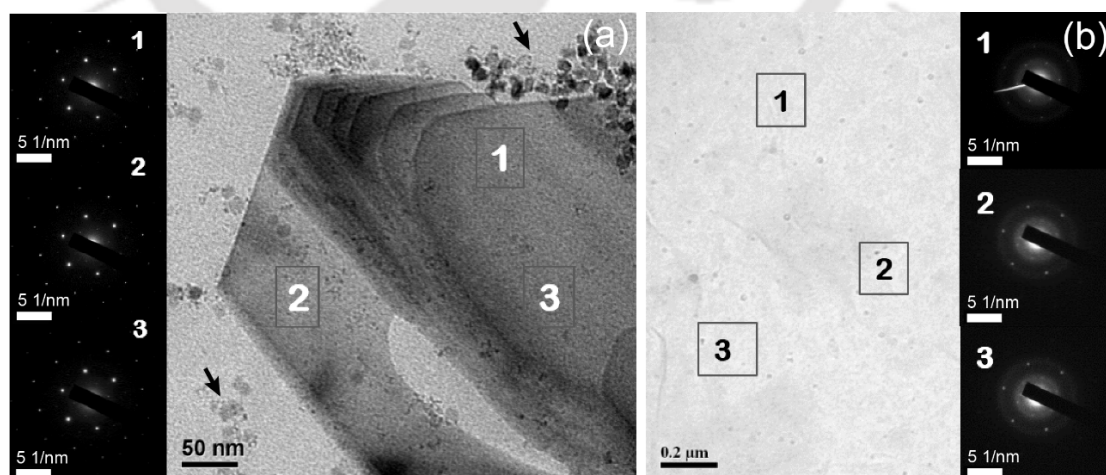


Figure 3.10: (a) TEM image of the hexagonal shaped MLG and corresponding SAED patterns are significant for the sp^2 hybridised carbon lattice. (b) TEM image of large area defect free GR and

corresponding SAED patterns are significant for the single layer coverage. The corresponding scanned locations of SAED patterns are marked with a serial numbers.

Extensive investigation of crystalline quality and various structural defects of GR are classified from HRTEM and SAED techniques. **Figure 3.10(a)** represents the TEM image of a hexagonal shaped MLG grains and corresponding SAED patterns. SAED was taken at the location shown by the serial numbers. The SAED analysis depicts the hexagonal lattice of sp^2 hybridized carbon atoms. Arrows indicate the residual PMMA and Cu catalyst particles. **Figure 3.10(b)** represents a TEM image of a large area defect free SLG and the SAED patterns are significant for the sp^2 crystallinity of SLG. Note that the corresponding locations of the SAED patterns are noted by the serial numbers in the image. These TEM results are consistent with the micro-Raman analysis discussed in the previous section.

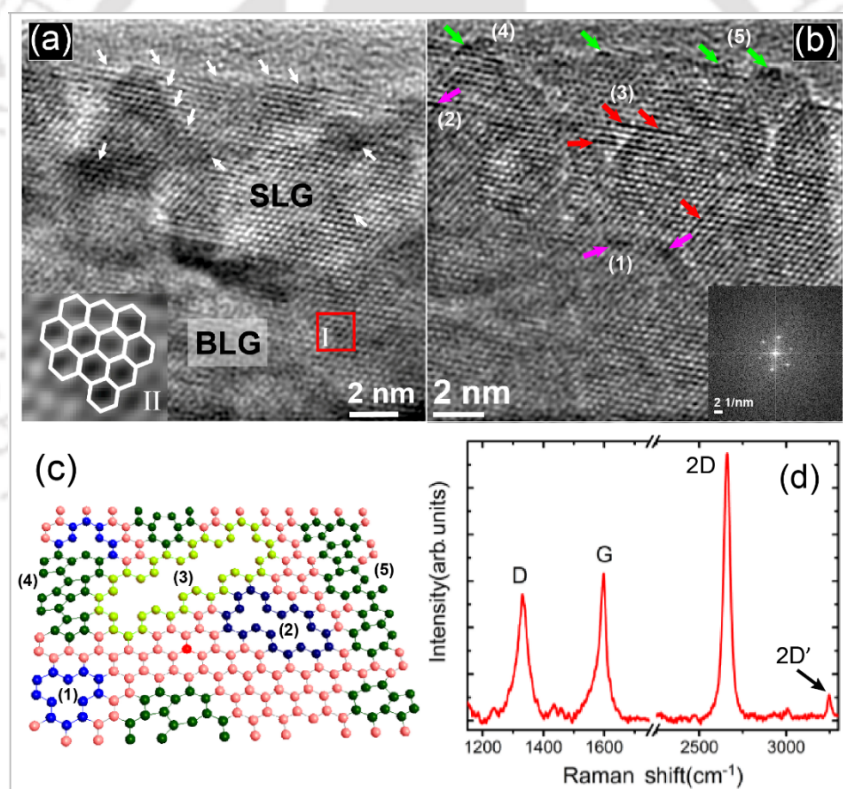


Figure 3.11: (a) HRTEM image GR showing SLG and BLG. The white arrows indicate wrinkles and edge on SLG. The contrast difference in the image is due to the wrinkles of the GR layer. Inset II is a magnified image of region of I. (b) HRTEM image of GR with the corresponding SAED pattern in the inset; various colored arrows indicate the presence of different kinds of defects (green, edge defects; red, line defects; pink, vacancies). (c) Schematic of the molecular model of a GR sheet with various defects, such as (1) single vacancy, (2) bi vacancies, (3) line defects, (4) zigzag, and (5) arm chair edge reconstructions highlighted by colored carbon atoms on the basal plane, which was modeled by the ATK

simulation tool (Quantumwise, 11.8.2 version). (c) Raman features of defective SLG sample, showing nearly equal intensities of sharp G and D bands and additional band at 2D' (3250cm^{-1}). This implies the presence of point/extended defects on the SLG basal plane and imperfect edges.

Figure 3.11(a) shows the HRTEM image of the as grown GR layer showing SLG and BLG. The arrow marks indicate the wrinkles (dark contrast regions) and edge of the GR layer. Inset II shows a magnified view of region of I in **Fig. 3.11(a)**, which depicts the honeycomb hexagonal lattice of carbon atoms on the GR plane. **Figure 3.11(b)** illustrates various kinds of defects in the same GR sample indicated by different colored arrows: green-edge imperfections; red-line defects; pink-vacancies and corresponding SAED patterns. A schematic of typical point and extended defects on the GR layer, such as single, bi, multiple vacancies, line defects, and edge reconstruction, as simulated by ATK 11.8.2, (Quantumwise), is shown in **Fig. 3.11(c)**. Such defects are inevitably present in our CVD grown GR samples. Note that the DGR sample was grown in the case of scheme 1. **Figure 3.11(d)** represents a set of Raman spectra for a DGR where the intensities of the D and G bands were found to be nearly equal, implying significant presence of in-plane defects such as mono, bi, and multiple vacancies.^{6,9} Some additional Raman features are found to be D+D' (2930 cm^{-1}), 2D'(3250 cm^{-1}) and these are significant for the extended defects such as line and edge reconstruction.⁶

3.7. Summary

In this chapter we successfully demonstrated the CVD growth of graphene on Cu catalyst and its clean transfer on to various substrates. We extensively investigated the growth parameters of CVD such as preannealing of Cu, H_2 , CH_4 flow rates that decide the large area coverage of SLG. Uniformity, disorder, defects of graphene layers were systematically investigated from micro-Raman, HRTEM techniques. Some of the important findings from this chapter are.

1. Millimeter area monolayer GR was synthesized by thermal CVD technique
2. Longer duration ($>1\text{ hr}$) of H_2 pre-annealing (500 SCCM H_2 Flow) and pre-treatment of Cu foil yields large area GR
3. Spatial uniformity and various In-plane, edge defects were probed from micro-Raman and HRTEM imaging.
4. Control of defects in the as-grown graphene was achieved by controlling the growth parameters.

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Chapter 4

Defect Mediated Efficient Physical Functionalization of Graphene with Transition Metals

In this chapter, we present the details of physical functionalization of graphene with TM NPs and the role of structural defects on the functionalization various TMs such as Au, Ag, Cu and CoPc organic molecules on GR with/without defects were deposited in it and the SERS and SPR effects from the GR-TM plasmonic hybrids were studied. Wavelength dependent resonance Raman characteristics were probed from the GR-TM plasmonic hybrids. A quantitative analysis of defects and defect mediated TM NPs interaction with graphene was investigated by resonance Raman spectroscopy, SPR absorption, Raman imaging and HRTEM from the spatial distribution of TM NPs through the defects on a GR layer. We have estimated the contribution of SERS and LSPR in each case before and after RTA treatment of all the GR–TM hybrids.

4.1. Fabrication of Graphene-Transition Metal Plasmonic Hybrids

4.1.1. Physical Functionalization of Graphene with Transition Metal Films

At first, various TMs such as Au, Ag and Cu ultra-thin films were deposited on the GR layer by radio frequency (RF) magnetron sputtering process under Ar gas atmosphere with a RF power <5W. TM films were deposited in a controlled way for 30-60s at a deposition rate of 0.8 Å/s. We optimised the thickness of TM deposition over GR by depositing for different deposition times. **Table 4.1** represents the list of GR-Au samples that are prepared at different deposition times. We quantified the extent of TM deposition on graphene, which do not deteriorate the graphitic structure. All the TM films were deposited on SiO₂/GR substrate and GR transferred on to TEM Cu grids. High purity TMs (99.999%) targets (2inch diameter) were used for the sputter deposition. Note that the cobalt phthalocyanine (CoPC) organic molecules were deposited on graphene by thermal evaporation technique.

4.1.2. RTA of Graphene-Transition Metal Films

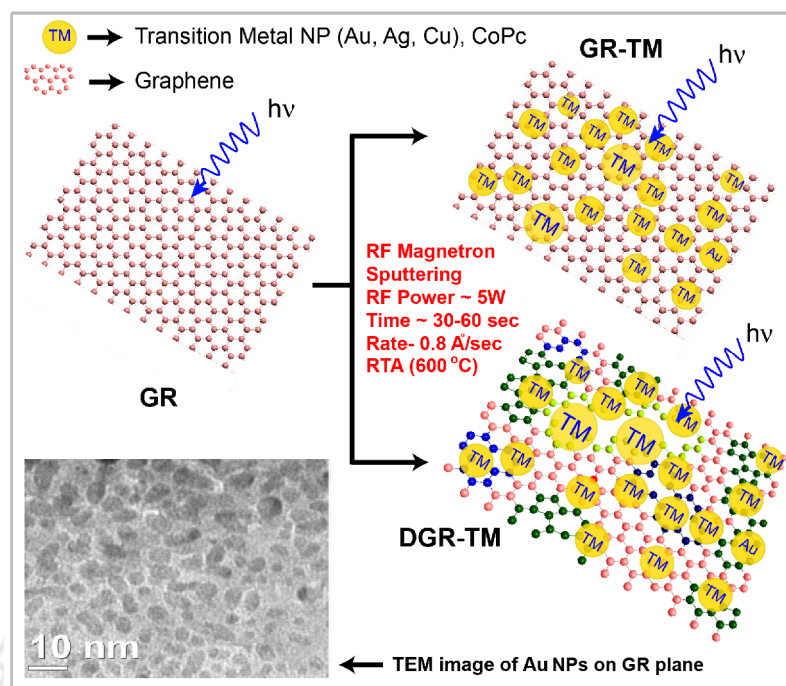


Figure 4.1: Schematic of the fabrication of graphene-TM plasmonic hybrids. TM thin films are deposited by RF magnetron sputtering technique followed by RTA treatment.

The GR-TM and DGR-TM substrates were subjected to RTA treatment in order to see the interaction of TM NPs on the graphene at 600 °C for the duration of 3 minutes in Ar gas atmosphere (200 SCCM) for various GR substrates with/without defects, which are coated on SiO₂, Quartz and TEM grids. The TM NPs were found to be nearly uniform size in the range 10-20 nm. A schematic process of physical functionalization of GR and DGR with TM NPs is shown by a **Fig. 4.1**. We investigated the interaction of TM-NPs with defective graphene extensively to probe the defect enhanced efficient physical functionalization in DGR-Au plasmonic hybrids and that are compared with the DGR-Ag, DGR-Cu and DGR-CoPc organic functional hybrids.

4.2. Raman Spectroscopy of Graphene-Transition Metal Plasmonic Hybrids

4.2.1. Optimization of Graphene Transition Metal Layer on Graphene

At first, for controlled physical functionalization of graphene with TM clusters using RF magnetron sputtering and to minimize degree of disorder during sputtering process, we have performed Au deposition on graphene at different time intervals and optimised the thickness of Au layer that does not deteriorate the *sp*² crystallinity of graphene. Au film was deposited

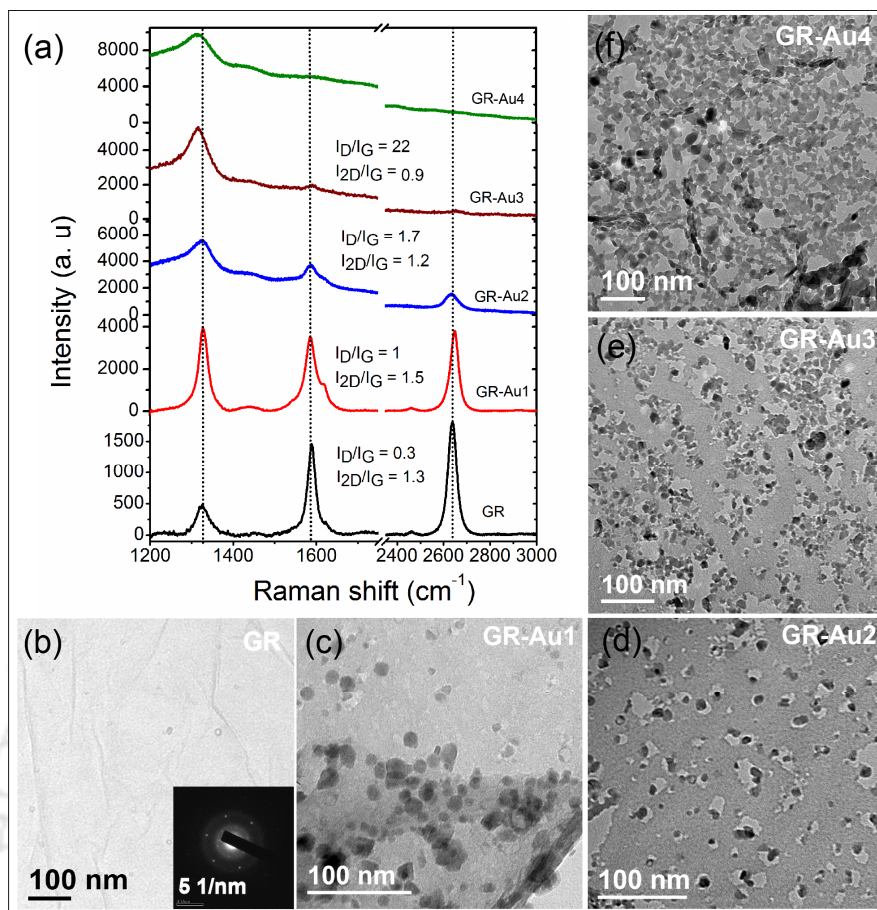


Figure 4.2: (a) Raman line shape evolution and (b-f) TEM surface morphology of the GR-Au plasmonic hybrids prepared for different deposition times (30-180 sec).

on the graphene substrates for four different deposition times 30, 60, 120 and 180sec. The complete details of the samples are shown in the **Table 4.1**. **Figure 4.2** represents the Raman line shape features in GR-Au plasmonic hybrids for different deposition times and the surface morphology as studied by HRTEM imaging of suspended graphene and Au islands. It is interesting to note that the Au clusters are suspended by some distance and spread across the whole GR substrate. It is most likely that the interaction of Au clusters is initiated from the vacancy defects that are formed during the RF sputtering process and then defect mediated covalent functionalization of graphene with Au clusters takes place on the graphene plane (see **Fig. 4.2**). We found some damage of the graphene layer at higher deposition times (>120sec), which was clearly revealed from the weak 2D band and a broad line shape of D band in Raman spectra. Note that we calculated the defect density (n_D) and inter defect distance (L_D) in our GR samples using the empirical relations discussed in **Chapter 3**.¹⁻² L_D and n_D was calculated from the Raman line shape analysis as a function of I_D/I_G and λ_{ex} in each case as shown in the **Table 4.1**. It is found that the enhanced n_D was observed in case of

GR-Au4 while in GR-Au5, the graphitic structure of GR was completely deteriorated. HRTEM image analysis is consistent with the Raman line shape. Based on the experimental observations, we found that 30-60sec is an optimum deposition time to achieve controlled GR-Au plasmonic hybrids using our sputtering system without losing its sp^2 crystallinity.

Table 4.1: Raman line shape parameters such as I_D/I_G and I_{2D}/I_G estimated from the Lorentzian fitting and L_D , n_D are calculated as a function of I_D/I_G and λ_{ex} using the empirical relations (1) and (2) discussed in the **Chapter 3**.

Sl. No	Sample	Deposition Time (sec)	I_D/I_G	I_{2D}/I_G	L_D (nm)	n_D (μm^{-2})
1.	GR	0	0.3	1.3	19	737
2.	GR-Au1	30	1	1.5	17	1125
3.	GR-Au2	60	1.7	1.2	13	1913
4.	GR-Au3	120	22	0.9	3.6	24750
5.	GR-Au4	180	-	-	-	-

4.2.2. Micro-Raman Studies

In order to understand the role of defects in the functionalization of GR, we have investigated the evolution of Raman features in GR and DGR samples after physical functionalization with comparatively. Note that the characteristic Raman features of GR and DGR were discussed in the **Chapter 3**. **Figure 4.3** represents an evolution of Raman fingerprints in pristine and Au functionalized GR (**Fig. 4.3(a)**) and DGR (**Fig. 4.3(b)**) and the respective scanning locations are shown in the OM image. Note that both the samples were prepared under identical deposition conditions. The sharp G and 2D band ($I_{2D}/I_G > 2$) with negligible D band is significant for the perfect sp^2 crystallinity with monolayer coverage of graphene in GR. The surface modification of Au NPs on GR give rises to an appearance of D band and a considerable redshift in 2D band due to the in-plane lattice strain in the graphene layer, which is arises from the coverage of Au NPs. Note that we have not observed any significant shift and change in the FWHM of G-band ($\Delta\omega_G$) after Au deposition, which reveals the noncovalent interaction of Au NPs with GR. The sharp D and D' bands in DGR are significant for the various intrinsic defects (vacancies, line and extended defects etc.) on the graphene layer. The site selective defect mediated interaction of Au NPs on DGR layer

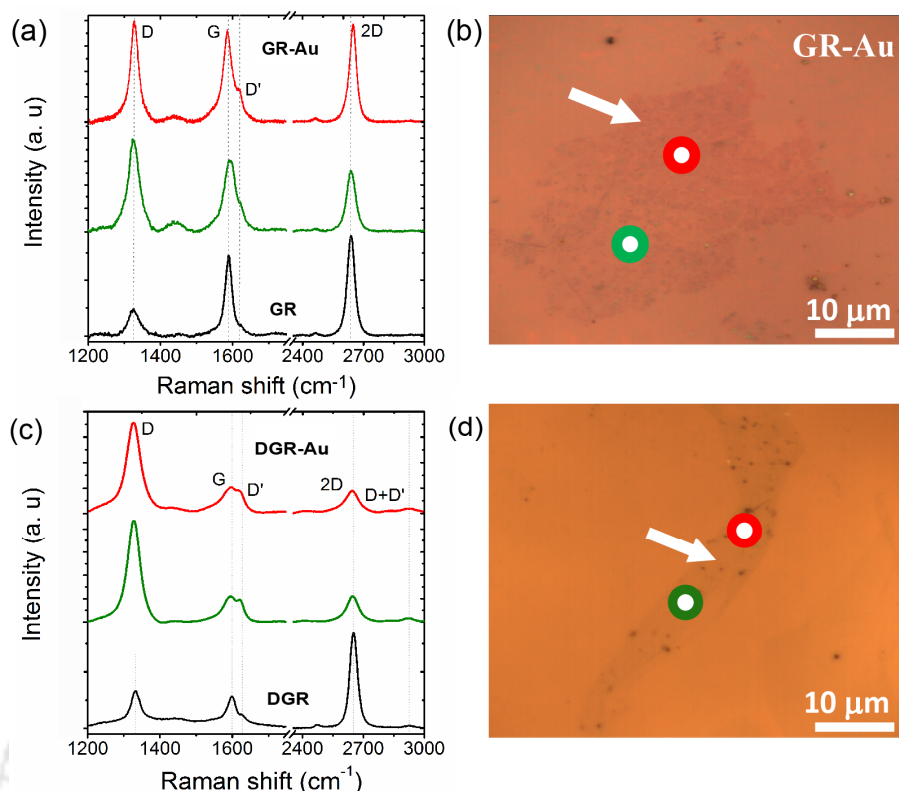


Figure 4.3: Comparison of Raman features for (a) GR, GR-Au, (c) DGR, DGR-Au and corresponding scanning locations are shown in the OM image (b), (d), respectively. White arrow indicates the GR-Au and DGR-Au layer.

was clearly revealed from the strongly enhanced intensity of the D, D' and D+D' as compared to that of the G, 2D bands (see **Fig. 4.3(c)**). We will discuss more details of the same in a later section along with its characterization results. Note that both G and 2D bands show a red shift, significant for the p-doping of GR.³ A new Raman band at 1430 cm⁻¹ represents interaction of Au NPs at the edge sites of graphene layer.⁴ Raman features of DGR were equally enhanced after Au functionalization while in DGR defect related Raman modes are enhanced significantly, which is due to the strong bonding of Au clusters at defect sites that creates a lattice distortion on the graphene plane.

It is well known that except the G band, all second order double resonance Raman modes D, D', 2D, D+D', 2D' including weak combinational modes between 1700 to 2300 cm⁻¹ of graphene are strongly dispersive in nature with respect to λ_{ex} .⁵⁻⁶ We have carried out the Raman studies on DGR and DGR-Au with λ_{ex} =632.8 nm, as strong resonance Raman features were observed in DGR sample at this wavelength. **Fig. 4.4(a)** depicts the comparison of Raman features of DGR and DGR-Au, and inset shows an enlarged view of the enhanced second order double resonance weak Raman modes after Au deposition on DGR. It may be

noted that no substantial change in the FWHM ($\Delta\omega_D$) and position of D and D' bands was observed after Au deposition. It is clear that in DGR-Au, the D band intensity is enhanced by a factor of ~ 33 , while the D' band is enhanced only by a factor of ~ 13 as compared to that of GR. In contrast, the intensity of G, 2D, D+D', 2D' bands are increased by a factor of ~ 5 in DGR-Au. Interestingly, the 2nd order weak modes are equally enhanced in DGR-Au. In addition, it is found that the FWHM of the 2D band ($\Delta\omega_{2D}$) in DGR-Au is significantly higher (70 cm^{-1}) than that in DGR (43 cm^{-1}). The higher FWHM in DGR-Au may be partly caused by the diffusion of Au atoms into the graphene layer due to the presence of defects.

In order to understand the different level of enhancement of different Raman bands and specific role of Au NPs in the Raman enhancement, we performed functionalization of graphene with another noble metal Cu and an organic semiconductor, CoPc thin film ($\sim 5\text{ nm}$). **Fig. 4.4(b)** illustrates the comparative Raman features of DGR and Cu coated DGR (DGR-Cu) samples. In case of DGR-Cu, D band intensity is enhanced by a factor of ~ 2 , while that of G and 2D bands are reduced by a factor of 2 and 4, respectively. Further, $\Delta\omega_{2D}$ is almost identical in both DGR (43 cm^{-1}) and DGR-Cu (44 cm^{-1}), which is in contrast to the higher $\Delta\omega_{2D}$ (70 cm^{-1}) in DGR-Au. In case of CoPc coating on DGR, D, G and D' bands are marginally enhanced only by a factor of 1.5, while the 2D band is reduced to 0.6 of the original value. Thus, the DGR-Au system shows very high enhancement in both D and D' bands as compared to the cases of DGR-Cu and DGR-CoPc.

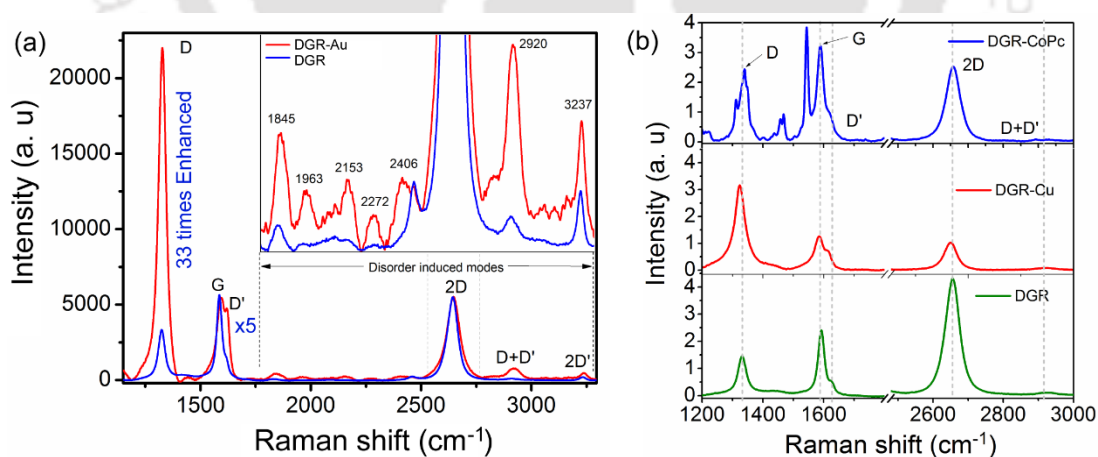


Figure 4.4: (a) Comparison of the Raman features of DGR before and after physical functionalization with Au NPs (blue and red lines): Evolution of Raman modes D, G and 2D bands. Inset shows the comparison of the second order double resonance weak Raman modes (D', 2D, D + D', and 2D' bands) in zoomed view, in the range $1700\text{--}2300\text{ cm}^{-1}$ for the DGR and DGR-Au samples. (b) Comparison of Raman features in DGR, DGR-Cu and DGR-CoPc hybrids measured with 632.8 nm excitations.

The Raman enhancement may have two contributions, one caused by the surface plasmon resonance (SPR) of Au NPs in the vicinity of defects in graphene and other due to the enhanced defect density in DGR-Au as compared to that of bare DGR. Au induced stronger enhancement in D and D' bands as compared to the enhancement in G and 2D bands, suggests preferential clustering of Au NPs at the defect sites and SPR enhancement effect in the Raman spectra. Since the Au NPs are well known for its high SPR effects as compared to the Cu NPs, our results are fully consistent with the hypothesis that Au NPs preferentially migrate to the defect sites in DGR. SPR absorption from the DGR, DGR-Au, DGR-Ag and DGR-Cu hybrids are discussed in the next section. Note that the SPR absorption induced reduction in Raman intensity is insignificant here, since the surface coverage of the Au NPs on the graphene is much smaller than the maximum possible coverage. Interestingly, SPR absorption induced reduction in Raman intensity was observed in RTA treated samples. In case of CoPc on graphene, SPR enhancement is less as expected from its dielectric behaviour. Despite the absorption loss in the CoPc layer, SPR enhancement was observed in this case. One may expect aggregation and bonding of the respective atoms/molecules at the defect sites of graphene. The strongly enhanced D and D' bands in the DGR-Au spectrum thus confirms the strong interaction of Au NPs at the in-plane defects and edges.

Au NPs induced charge transfer from Au to graphene was reported based on the downshift in the G and 2D bands.⁷ In our experiment, no reduction in the intensities of G and 2D bands were found on Au coated DGR. However, SPR induced Raman intensity enhancement was less in G and 2D bands as compared to the D band. Further, we noticed a small up shift ($\sim 3 \text{ cm}^{-1}$) in the 2D band and relatively large up shift in the G band after Au functionalization of graphene. This is indicative of the hole doping of the graphene layer caused by the Au NPs attached at the defect sites.⁷ Besides the SPR enhancement in D, D', and G bands due to functionalization with Au NPs, a significant enhancement in second order weak modes in the range of $1700\text{--}2300 \text{ cm}^{-1}$ was also observed, as shown in the **Fig. 4.4(a)**. In particular, the mode at 1963 cm^{-1} becomes stronger after Au functionalization. The stronger second order modes may be partly due to the SPR enhancement and partly due to adatom induced defects/disorder as well as the interlayer interactions.⁵ The exact origin of these second order weak modes is not understood in the literature, though it has been attributed to combination modes in some cases.⁶ It is likely that some of these modes may be caused by the defects/disorder induced by the incorporation of the Au NPs in DGR. In

presence of defects, the k-selection rule is relaxed and thus some of the forbidden modes may become Raman allowed modes in the defective GR.

4.2.3. Raman Mapping

Figure 4.5 illustrates the areal intensity maps of characteristic Raman modes D, G and ratio of intensity I_D/I_G in DGR-Au and DGR-Ag plasmonic hybrids in the scanning area $5 \times 5 \mu\text{m}^2$ and $10 \times 10 \mu\text{m}^2$, respectively. Note that the intensity scale bars are separately shown for better visibility of each band. **Figure 4.5(a-b)** and **(c-d)** shows the relative areal intensity ratio maps of the D and G

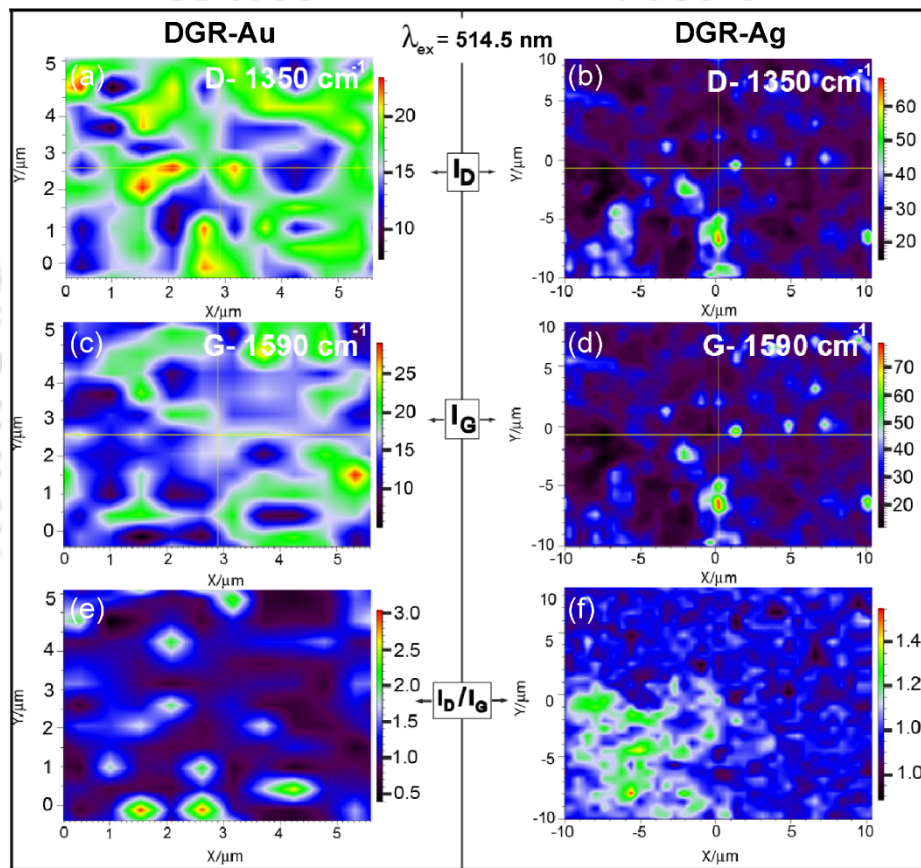


Figure 4.5: Spatial Raman mapping images for the D, G bands and their ratio of intensities (I_D/I_G) for (a) DGR-Au (b) DGR-Ag samples. Note that the scanning area of the Raman mappings for DGR-Au is $5 \times 5 \mu\text{m}^2$ and for DGR-Ag is $10 \times 10 \mu\text{m}^2$, respectively.

bands in DGR-Au and DGR-Ag, respectively which are an evidence for the sp^2 crystallinity with large coverage of SLG and BLG and covered with TM NPs at various point and extended defects in the graphene layer. **Figure 4.5(e-f)** depicts the areal intensity variations of the D, G bands from the I_D/I_G map, which signifies the TM NPs coverage on DGR substrate.

4.3. HRTEM Analysis

Figure 4.6 shows the TEM images various graphene transition metal plasmonic hybrid nanostructures. DGR-Au (**Fig. 4.6(a)**), DGR-Ag (**Fig. 4.6(b)**) and DGR-Cu (**Fig. 4.6(c)**) hybrids were prepared on a TEM Cu grid. It indicates that the Au NPs are present at the defect sites of graphene, more prominently at the edge defects. Raman analysis shows that the as synthesized graphene contains large number of defects on the basal plane and imperfect edges, as evident from the D' band in the pristine graphene. After Au deposition, it was found that the Au islands were formed not only at the edges (see **Fig. 4.6(b)**) but also at the defect sites on the basal plane of graphene. In all the samples the size of TM NPs varies in the range of 5

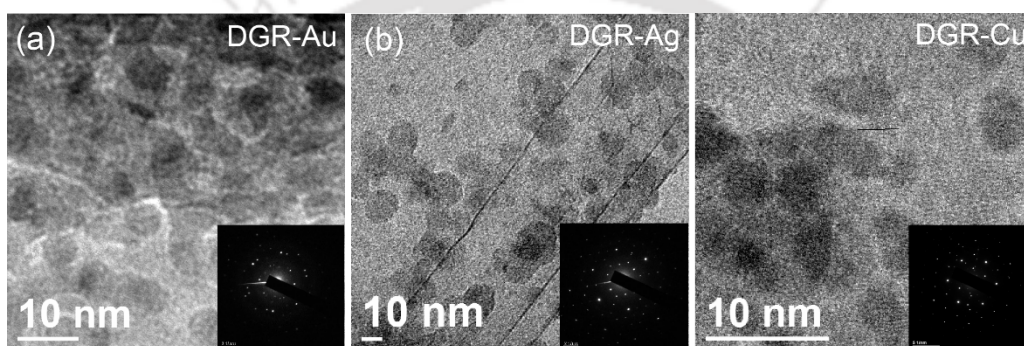


Figure 4.6: TEM images of graphene TM hybrid nanostructures: (a) DGR-Au, (b) DGR-Ag and (c) DGR-Cu. The corresponding SAED pattern are shown as inset in each case.

to 10 nm with oval shape. We found a considerable increase in vacancy defects after TM functionalization of DGR TM NPs. Interestingly, we observed a major enhancement in the intensity of D and D' bands after Au deposition, as compared to that of G and 2D bands as discussed in the previous section.

The HRTEM images of DGRAu at the graphene edge and in-plane defect sites with corresponding SAED patterns are shown in **Fig. 4.7(a)** and **(b)**, respectively. **Figure 4.7(c)** and **(d)** show the inverse fast Fourier transform (IFFT) images of regions I and II marked in **Fig. 4.7(a)** and **(b)**, which depict the interface of Au cluster at the graphene imperfect edge and in-plane defect sites, respectively. Lattice fringes of both Au and graphene are clearly discernable in the IFFT images (**Fig. 4.7(c)** and **(d)**). Blue and red coloured arrows indicate the lattice fringes of SLG and BLG in DGR-Au sample, respectively. The bright and dark contrast portions in **Fig. 4.7(c)** arise due to the wrinkles present on the basal plane of graphene.

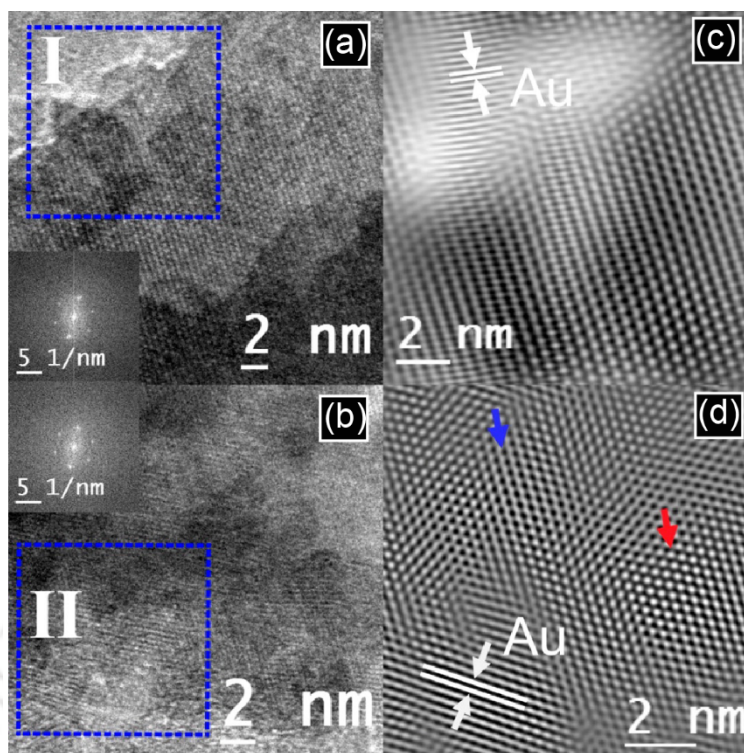


Figure 4.7: HRTEM lattice images of DGR-Au hybrid: (a) Au NPs at the graphene edge and (b) Au NPs at the in-plane defects in graphene basal plane. The corresponding FFT patterns are shown as inset in each case. (c-d) IFFT images of regions I and II shown in (a) and (b) depicts the lattice fringes of both graphene and Au NPs side by side. Blue and red arrows in (d) indicate the single and bi layer graphene lattice fringes.

Distribution of Au NPs on the graphene layers is further probed by HRTEM imaging, as shown in **Fig. 4.8(a)**. The sample was obtained with direct deposition of Au on graphene transferred on to a TEM grid. Bright and dark contrast regions represent the lattice patterns of the graphene without and with Au NPs located by blue coloured arrows and white marked ovals, respectively. The white markers indicate the typical distance between centres of two Au NPs, which are ~ 5 nm (a) and ~ 9 nm (b). The analyses done over the several Au NPs shown in the HRTEM image reveals an average distance of ~ 7 nm. Presuming that the Au NPs are present only at the defect sites, average distance between the nearest-neighbour defect sites would be same as above. Interestingly, the inter defect distance calculated from the Raman analysis (discussed later) is found to be in excellent agreement with the above HRTEM analysis. The defect mediated embedding of Au NPs with a size of 10 nm in graphene is depicted in **Fig. 4.8(b)**. The lattice fringes of Au are clearly seen in the image. The effect of Au clustering on graphene layer is shown further by the IFFT image in **Fig. 4.8(c)**, which corresponds to the region I in the **Fig. 4.8(b)**. This image reveals a kind covalent functionalization of graphene with Au by displaying clear lattice fringes of both of

Au and graphene side by side. Blue and red coloured arrows indicate the lattice patterns and atomic distortions due to the Au–C bonding originated from the defect sites on the basal plane of graphene lattice.

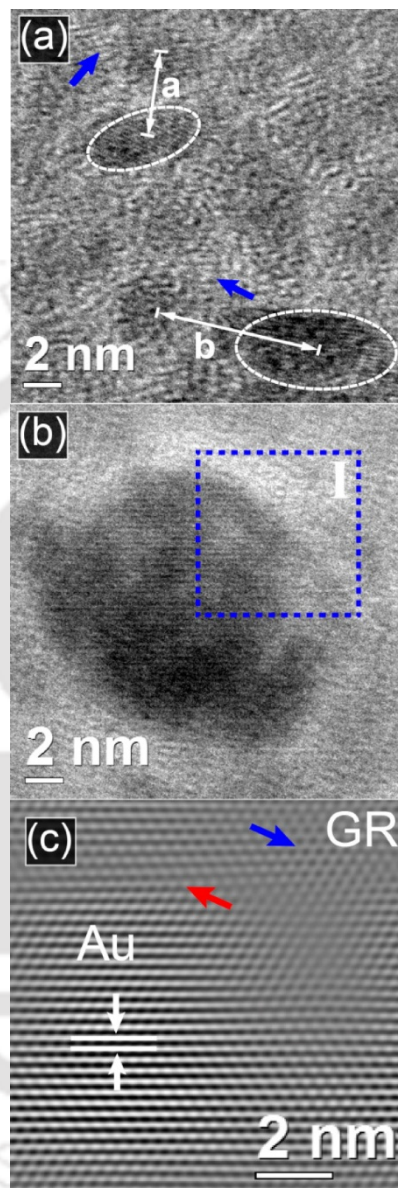


Figure 4.8: HRTEM lattice images of DGR-Au placed on to a TEM grid: (a) Au NPs (size ~ 5 - 10 nm) located at the in-plane defects in graphene. Lattice fringes of both graphene and Au NPs are indicated by blue arrows and white marked oval regions (bright and dark contrast regions), respectively. The white coloured marker lines indicate the distance ($a = 5$ nm, $b = 9$ nm) between two neighbouring Au NPs. (b) Magnified lattice image of GR and Au shown in (a) indicating covalent bonding of Au NPs (~10 nm) with graphene lattice. (c) IFFT image of the marked region I shown in part b, showing the lattice fringes of both the graphene (blue arrow) and Au cluster. The red colored arrow shows the lattice distortion on the graphene basal plane due to Au–C bonding.

4.4. XPS Studies

XPS measurement was carried out to confirm the Au functionalization at defect sites in graphene. **Fig. 4.9(a)** and **(b)** represent the high resolution core level C-1s XPS spectra in DGR and DGR-Au samples, respectively. **Fig. 4.9(c)** represents the core level Au-4f spectra in DGR-Au sample. The spectrum shown in **Fig. 4.9(c)** is deconvoluted into 4 bands. The band at 284.45 eV corresponds to C=C (sp^2) bond arising from in-plane stretching of carbon atoms on graphene surface, C-C band at 284.78 eV is attributed mostly to the sp^3 defects, such as vacancies and point defects and substitutional atoms,⁸ consistent with Raman spectra discussed earlier. The bands at 287.76 and 290.15 eV are due to the partial epoxy (C-O-C) and carboxylic (COOH) functional groups attached to graphene and the peak at 292.96 eV is

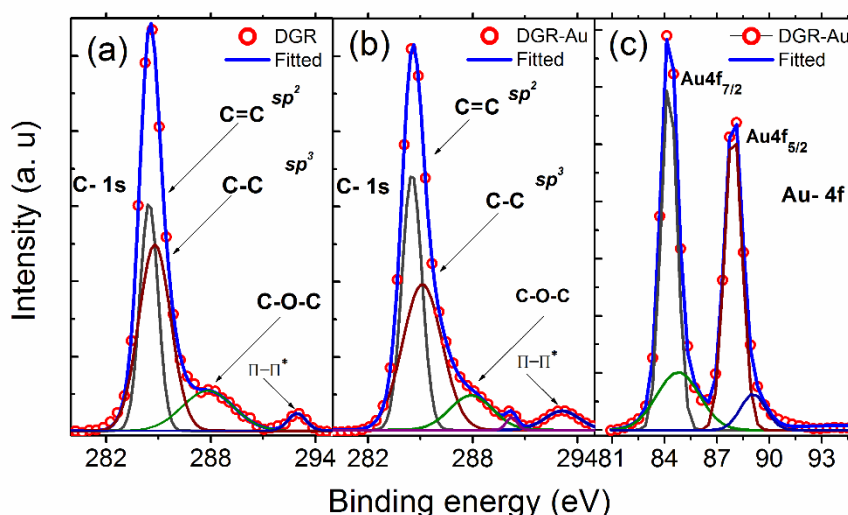


Figure 4.9. Core level XPS spectra: (c) C-1s of GR, (d) C-1s of GRAu, and (e) Au-4f of GRAu, fitted with Gaussian line shape in each case. Contributions from different species are labelled in each case.

attributed to sp^2 -hybridized carbon atoms due to the $\pi-\pi^*$ shake up features.⁹ After surface modification with Au, the XPS spectra show an upshift in the binding energy and broadening of both sp^2 and sp^3 bands. The changes in the peak parameters obtained from the fitting are summarized in **Table 4.2**. The shift in binding energy is due to the change in the Fermi level of graphene after Au functionalization.¹⁰ This is consistent with the Raman analysis that showed a shift in the G and 2D bands in DGR-Au. XPS analysis also revealed an increase in the FWHM of sp^2 and sp^3 bands by 0.15 and 0.31 eV, respectively, which may be due to the longer Au-C bonds caused by the covalent functionalization initiated at defect sites on graphene.¹⁰ Interestingly, the ratio of integrated intensity of sp^3 to sp^2 band calculated from

Table 4.2: Fitting parameters of the C-1s core level XPS spectra of DGR and DGR-Au. Peak position and FWHM are in eV unit. I_{DGR} and $I_{\text{DGR-Au}}$ represent integrated intensities of the corresponding bands in DGR and DGR-Au, respectively.

DGR				DGR-Au		
Band	Peak	FWHM	I_{DGR}	Peak	FWHM	I_{DGRAu}
C=C (sp^2)	284.46	1.19	28067	284.52	1.34	36380
C-C (sp^3)	284.78	2.09	42046	285.12	2.64	39008
C-O-C	287.76	3.25	14233	287.90	2.88	9940
π - π^*	292.96	1.18	2298	293.11	2.32	4497

Gaussian line shape fitting was found to be 40% lower in DGR-Au as compared to that in DGR, strongly indicating covalent functionalization of graphene at the defect sites with Au and enhancement (reduction) in sp^2 (sp^3) band, as evident from the data presented in **Table 4.2**. Note that the line width of C-O-C band is more than double of the C=C (sp^2) band that indicates an attachment of native oxygenated functionalities on the graphene layer over the sp^3 sites during the room temperature storage. The Au-4f bands show additional two Gaussian peaks at binding energies 84.78 and 89.06 eV (**Fig. 4.9(c)**) that may be due to the nominal oxidation of Au NPs surface. These results clearly establish the physical functionalization of DGR with Au due to the presence of in-plane defects and are fully consistent with the Raman and HRTEM analyses. The up shift in Raman peak position and large broadening of 2D band in **DGR-Au** are due to the change in electronic structure of the graphene after Au functionalization.

4.5. Position Dependent Raman Profile

We further looked into the spatial uniformity and Au clustering through defect sites in DGR-Au by quantifying the defect density from the Raman intensity profile of D and G bands. If we assume that the SPR effect caused equal intensity enhancement in both D and G bands such that the intensity ratio remain unaffected, such intensity ratio (I_D/I_G) can be used to the estimate the average inter defect distance (L_D) and areal defect density (n_D).¹ **Figure 4.10(a)** represents a set of Raman spectra scanned at the different locations of DGR-Au, as shown in the OM image of **Fig. 4.10(b)**. Each spectrum was monitored by the position of scanned area where the areal density of Au NPs is expected to be proportional to the areal density of defects. These spectra were taken on DGR-Au substrate under identical conditions. In order to calculate the n_D and L_D for a measured I_D/I_G ratio, we have used the empirical relations presented by Cancado. et al.¹ given by

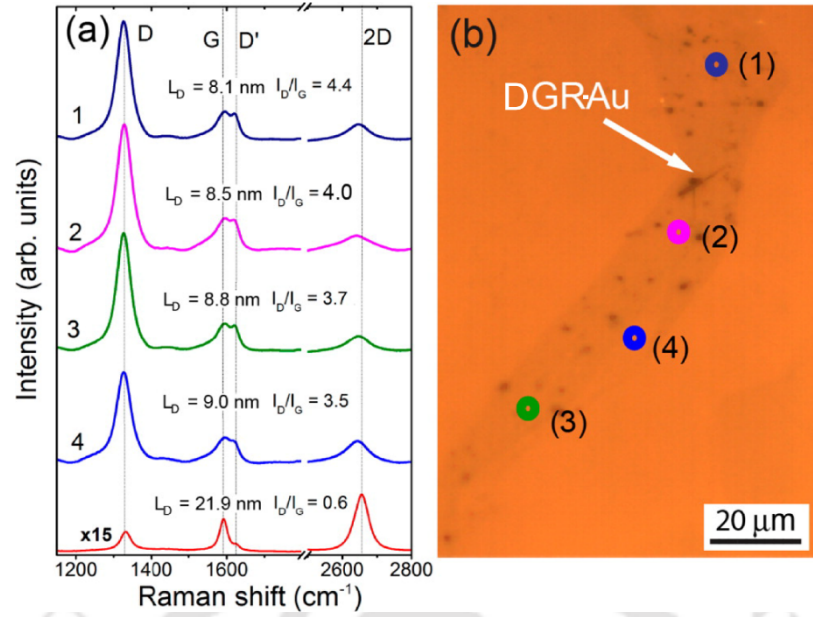


Figure 4.10: (a) Position dependent Raman profiles of DGR-Au and DGR measured with $\lambda_{\text{ex}} = 632.8$ nm. Inter defect-distance (L_D) values at each position were calculated from I_D/I_G ratio using eq. (3.1). Note that the spectrum for the pristine GR shown at the bottom is scaled up by a factor of 15 for comparison. (b) Corresponding OM image of scanning positions.

$$L_D^2 \text{ (nm}^2\text{)} = (1.8 \pm 0.5) \times 10^{-9} \lambda_L^4 \left(\frac{I_D}{I_G} \right)^{-1} \quad \text{..... (3.1)}$$

$$n_D \text{ (}\mu\text{m}^{-2}\text{)} = \frac{(1.8 \pm 0.5)}{\lambda_L^4} \times 10^{14} \left(\frac{I_D}{I_G} \right) \quad \text{..... (3.2)}$$

where λ_L is the excitation wavelength in nm.

Using these empirical relations, the calculated L_D varies in the range of 8.1-9.0 nm and n_D varies in the range 3985-4950 μm^{-2} for DGR-Au. On the other hand, pristine DGR shows an L_D of 21.9 nm and corresponding n_D of 673 μm^{-2} , as discussed in **Chapter 3**. This implies a 6-7 fold increase in n_D after Au deposition on DGR. Interestingly, manual counting of the point defects in the HRTEM image of DGR and DGR-Au also nearly 6 fold increase in the defect density after Au deposition. Thus, despite the large error bars involved in the empirical formula of equation (2), the Raman results are in close agreement with the HRTEM image analysis. Further, we have measured the average distance between centres of neighbouring Au NPs at several positions in the HRTEM image. Interestingly, it is found that the average distance between two Au NPs is ~ 7 nm (see **Fig. 4.8(a)**), which is very close to the value of 8-9 nm calculated from the Raman analysis. Note that Raman analysis of the defect density is limited to the defects that are Raman active and sensitive to the D band. It has been found

that perfect zigzag edges, charged impurities, intercalants, and uniaxial and biaxial strain in graphene do not contribute to D band.¹⁶ Thus, Raman analysis based on D band intensity may underestimate the defect density. However, in the above analysis we have neglected any additional enhancement of D band due to the local SPR effect of the Au NPs as compared to the SPR effect on the other bands. Thus, these two competing effects taken together make the result of Raman analysis consistent with HRTEM analysis. Further analysis of the spectra shown for four different positions (**Fig. 4.10(a)**) reveals that there is no significant shift in peak position and change in FWHM of D, G, D' and 2D bands for different locations of the DGR-Au sample scanned. Since the scanned area covers several square micrometers, any local nonuniformity in the nanometer scale may not be reflected in the Raman data. Thus, the DGR-Au sample can be assumed to have good spatial homogeneity. A small down shift in the 2D peak position may be arising from local charged impurity present in the DGR-Au hybrid due to functionalization with Au atoms.⁸

A comparison of the FWHM of different Raman bands in DGR and DGR-Au samples indicate that FWHM of 2D and G bands are nearly doubled in DGR-Au as compared to that of DGR. On the other hand, FWHM of D and D' bands do not change significantly despite a large change in intensity. This indicates that D and D' bands are resonantly enhanced due to SPR effect at the defect sites of functionalized DGR-Au without losing sp^2 crystalline nature of graphene. Note that the asymmetry and broadening of the G and 2D bands are due to the change in the electronic structure of graphene owing to Au interaction.

4.6. Effect of Number of Graphene Layers

The effect of number of layers in graphene on the Au functionalization was further studied by line shape analysis of the Raman spectra. **Figure 4.11(a)** represents the Raman features of DGR-Au for SLG, BLG and FLG. From the deconvolution of G band using Lorentzian line shapes, as shown in the **Fig. 4.11(b–c)**, no shift in G [1596 cm^{-1}] and D' [1620 cm^{-1}] bands were observed. Interestingly, $\Delta\omega_{2D}$ in Au coated SLG and pristine BLG shows nearly identical values FWHM $\sim 70\text{ cm}^{-1}$. Thus, the Au coated SLG behaves like a pristine BLG where interaction between the Au and SLG layers may be as significant as that between the two layers of graphene in a BLG (see **Fig 3.4(b)**). This is an important observation and it signifies the strong interaction between the Au and defective graphene layers.

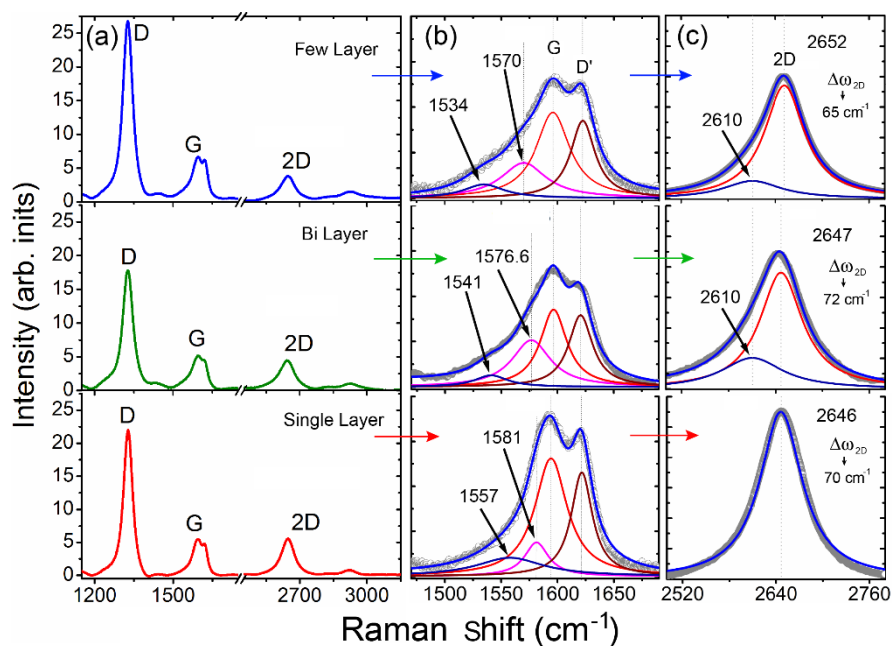


Figure 4.11: Comparison of the Raman spectra for SLG, BLG and FLG after Au deposition: (a) D, G and 2D bands. (b) Lorentzian line shape fitting of G, D' and additional low frequency modes marked in cm^{-1} unit. (c) Fitting of the 2D band, peak position and FWHM are marked in cm^{-1} unit each case.

Beside the common modes, additional Raman modes at 1581, 1576.6 and 1570 cm^{-1} were observed after Au deposition on SLG, BLG and FLG, respectively, which may be due to the covalent functionalization of Au at the defect sites.¹⁰ A systematic down shift in the additional bands was observed as the number of graphene layers increases. The lower frequency peaks at ~ 1557 , 1541 and 1534 cm^{-1} may be resulting from the strain caused by the formation of Au–C bonds creating lattice distortions on the surrounding in-plane C–C stretching bonds of sp^2 carbon atoms, as discussed with reference to **Fig. 4.8(c)**.¹¹ A weak feature at ~ 1440 cm^{-1} next to the D band in **Fig. 4.10(a)** arises probably from the sp^3 C contribution in the functionalized DGR–Au. In case of BLG–Au, the intensity of D band is marginally lower, which may be due to the interlayer interaction in graphene.

Note that despite the chemically inert nature of the defect free graphene and Au atoms, defects in graphene causes strong interaction with Au atoms leading to physical functionalization of GR. Such Au functionalized graphene may be highly desirable for binding with other functional molecules with graphene for biosensing and bioimaging applications. The functionalized graphene may be useful as nanocarrier and find applications for drug delivery and photocatalytic applications. Note that the strength of the interaction of Au and graphene is expected to be proportional to the initial defect density and nature of defects in graphene. However, there would be a limitation on graphene–foreign material

interaction with respect to areal density of defects without losing the sp^2 crystalline nature of graphene that we have found in the optimization of Au deposition on GR. Further, control of the defect density during the growth and by post-growth processing will provide the additional handle for the practical use of the concept demonstrated here.

4.7. Effect of RTA Treatment

Effect of RTA treatment on Raman features of DGR-Au plasmonic hybrids are demonstrated in **Fig. 4.12(a-b)** measured at two excitation wavelengths (632.8 and 514.5 nm). With the Au layer on graphene before and after RTA treatment, the high ratio of I_D/I_G and corresponding low L_D is significant for the Au clustering at the intrinsic defect sites formed on the graphene surface.¹²⁻¹³ Due to RTA treatment there is a local diffusion of Au atoms on graphene plane which makes the line shape broad for all characteristic Raman bands (see **Fig. 4.12(b)**). This is more evident from the HRTEM analysis which we have discussed in the previous section. FESEM images of the pristine and RTA treated DGR-Au samples are illustrated in the **Fig. 4.12(c) and (d)**, respectively. Inset shows the FESEM image of the Au NPs fabricated on the SiO_2 substrate. During the RTA treatment of the substrate at 600°C in Ar atmosphere, Au atoms migrate and segregate at the defect sites to form Au clusters and dewetting (liquid and solid) may be higher at the pristine graphene sites. Indeed, we observe distinctly different behavior of Au clustering on SiO_2 substrate and SiO_2 /graphene substrates coated with Au layer during the RTA process (see **Fig. 4.12(d)**). Spherical Au nanoparticles are formed in the former case, while nonspherical or dumbbell shaped bigger Au NPs are formed in the later case. The dramatic increase in intensity of D band as compared to that of G-band after Au deposition indicate a SERS enhancement of the Raman intensity caused by preferential clustering of the Au atoms specifically at the defect sites in graphene, while in RTA treated samples the intensity of Raman features are reduced by a factor nearly ~ 10 . This provides a very important insight on the enhanced localized SPR absorption due to the formation of bigger Au NPs over the graphene plane after RTA treatment. Absorption spectra of DGR-Au before and after RTA treatment will be discussed in the next section. Recently, Wang et al. provided direct evidence of metal doping/ clustering at the in-plane defect sites in graphene by in-situ aberration-corrected TEM.¹³ Stability of the metal clusters was argued on the basis of high binding energy of the metal-vacancy complex in graphene. Note that some of the Au atoms may diffuse through the graphene¹⁴ and form chemical bonds with carbon atoms of

graphene as longer Au–C bonds¹³ and this may be responsible for the dumbbell shaped Au NPs (see **Fig. 4.12(d)**).

Shape deformation and larger dimension of the Au NPs clearly indicate that large number of Au atoms migrate and cluster preferentially at the defect sites, driven by the dewetting behavior of Au on the graphene layer¹⁵ and for energy minimization. FESEM image analysis shows that areal density of Au NPs in presence and absence of graphene layer, areal density of Au NPs on the SiO₂ substrate are ~ 25 and $117 \mu\text{m}^{-2}$, respectively. In presence of graphene layer, areal density of Au NPs is reduced by a factor of ~ 5 . This reduced density of Au NPs on graphene layer is dictated by the Au thickness and dewetting behavior of graphene and the density of defects in the graphene layer. Interestingly, Raman analysis shows that average areal density of defects in pristine graphene and DGR-Au hybrid layer is in the range 490–860 and 3985–4950 μm^{-2} , respectively. It implies a nearly six-fold increase in defect density after Au deposition by sputtering.

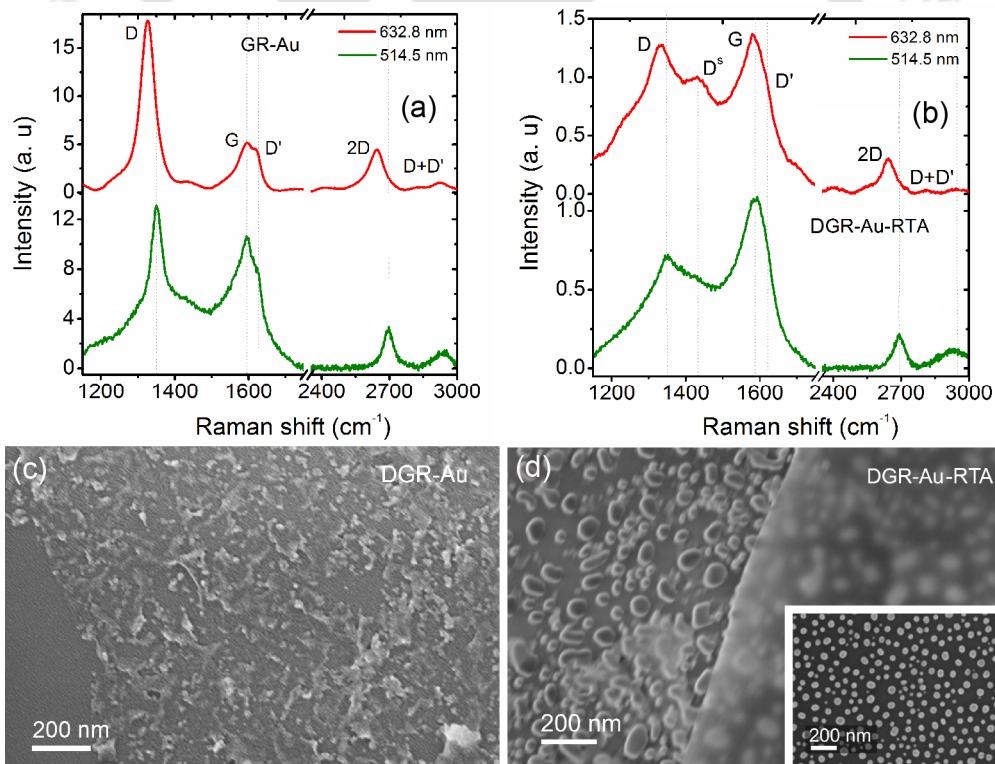


Figure 4.12: Excitation (λ_{ex}) wavelength dependent Raman features in DGR-Au (a) before and (b) after RTA treatment measured at $\lambda_{\text{ex}} = 514.5$ nm and 632.8 nm. (c) FESEM image of pristine DGR-Au and (d) RTA treated DGR-Au on SiO₂ substrate. Inset shows the spherical Au NPs on SiO₂ substrate.

On the other hand, Au NP density is only about 5% of the graphene defect density, which is limited by the thickness of the Au layer deposited.

4.8. Optical Absorption Studies

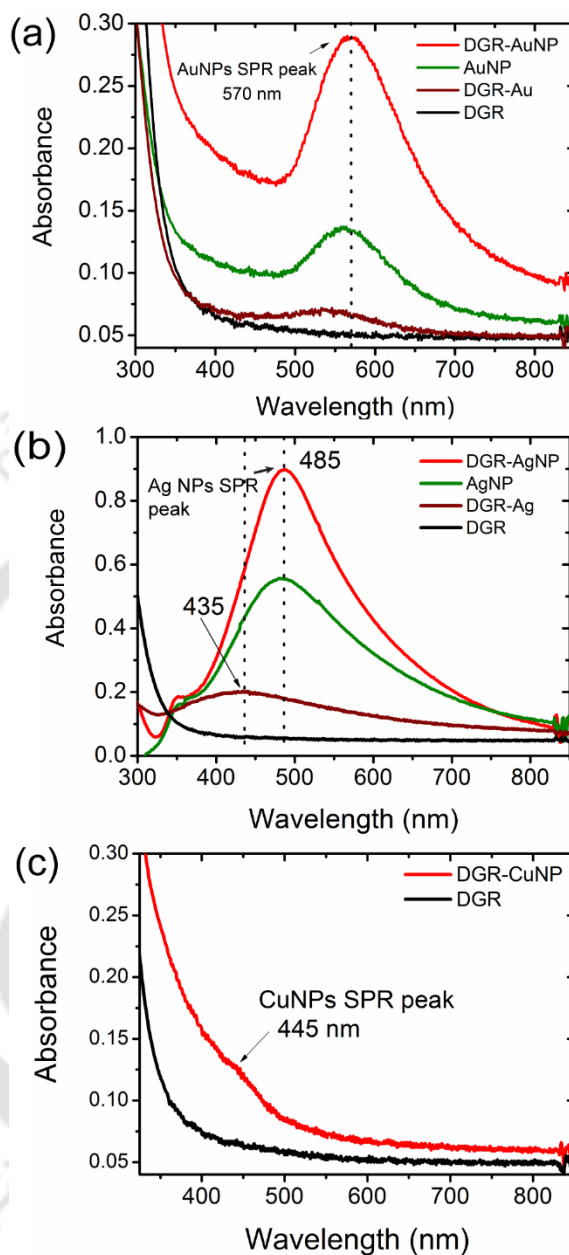


Figure 4.13: SPR absorption spectra of Graphene-TM plasmonic hybrids: (a) DGR-Au, (b) DGR-Ag and (c) DGR-Cu before and after RTA process. In each case spectra of DGR, TM NPs are also shown for comparison. Note that the centres of LSPR absorption bands are denoted in ‘nm’ scale each case.

In order to support the resonance Raman effect, we have performed the absorption measurements of DGR, DGR-Au, DGR-Ag and DGR-Cu hybrids fabricated on the quartz substrates. **Figure 4.13(a-c)** shows the absorption spectra of DGR-Au, DGR-Ag and DGR-Cu in comparison with pristine graphene on quartz substrate. Au, Ag and Cu NPs SPR peaks were found at 570, 485 and 445 nm respectively. The key points identified from this data are:

the strong SPR absorption peak in DGR-Au and DGR-Ag than that of DGR-Cu and the peak intensity is enhanced after RTA treatment. Further, SPR absorption peak of DGR-Au and DGR-Ag is stronger by a factor of ~ 5 after RTA process and it shows a redshift, which may be due to the strong covalent functionalization of Au with defective graphene. Note that after RTA treatment we have observed the reduction in the SERS signal as discussed in the previous section. The size and shape of the Au NPs decide the amount of SPR enhancement. Due to small size of the TM NPs formed here limited by the thickness of the TM layer, SPR enhancement was about only one order of magnitude. Note that the SPR absorption induced reduction in Raman intensity is insignificant in the RTA untreated samples, since the surface coverage of the Au NPs on the graphene is much smaller than the maximum possible coverage.⁷ One may expect aggregation and bonding of the respective atoms/molecules covalently at the defect sites of graphene, which reduces the SERS signal and increases the SPR absorption after RTA. The broadening of D, G, D' and 2D bands (see **Fig. 4.12(b)**) in the DGR-Au-RTA spectrum thus confirms the strong interaction of Au NPs at the in-plane defects and edges.

4.9. Summary

1. We have fabricated various graphene-TM plasmonic hybrids, such as Au, Ag, Cu and CoPC organic molecule, on to the CVD graphene with/without defects in it and studied the SERS and SPR effects from the graphene-TM plasmonic hybrids before and after RTA treatment.
2. Defect enhanced efficient physical functionalization of graphene with Au NPs was demonstrated, for the first time.
3. A quantitative analysis of defects and defect mediated TM NPs interaction of graphene was studied by resonance Raman spectroscopy, SPR absorption, Raman imaging and HRTEM from the spatial distribution of TM NPs through the defects on a graphene layer.

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Visible Light Photocatalysis and SERS Detection using Graphene-Transition Metal Plasmonic Hybrids

In this chapter, we demonstrate the application of graphene and Au plasmonic hybrid nanostructures (NSs) for plasmon enhanced visible light photocatalysis and SERS sensing of organic dye molecules. We develop the graphene based hybrid photocatalysts, which show enhanced visible light photo degradation performance of methylene blue (MB) dye molecules. Extensive role of structural defects and oxygen functional groups in CVD graphene (GR) and chemically derived graphene (CDG) for the enhanced visible light photocatalytic degradation of MB was established. Further, two organic dye molecules, rhodamine 6G (R6G) and fluorescein (FL) with high sensitivity in the visible light were used for the detection of SERS from the graphene and GR–Au plasmonic hybrids and corresponding enhancement factors were calculated from the standard Raman bands ranging between 600–1800 cm^{-1} for both the dye molecules on bare SiO_2 and quartz substrates. We have achieved an impressive SERS enhancement factor of $\sim 10^2$ – 10^3 from GR–Au plasmonic hybrids with respect to the bare SiO_2 substrate.

5.1. Protocol for the Visible Light Photocatalysis

A systematic investigation on visible photocatalytic activity from the pristine and Au functionalized GR and GO plasmonic hybrids was carried out by degradation experiments of methylene blue (MB) as a reference pollutant. A schematic representation of photodegradation process with Au functionalized GR and GO plasmonic hybrid is shown in **Fig. 5.1**. MB solution with initial concentration of 10 mg/L was prepared in 100 mL distilled water. The thin films (Area- 1 cm^2) of pristine and GR-Au plasmonic hybrids on quartz and SiO_2 substrates were prepared and dipped in to the MB dye solution and kept in dark for 2h to equilibrate the adsorption and desorption of dyes on the surface of the film.

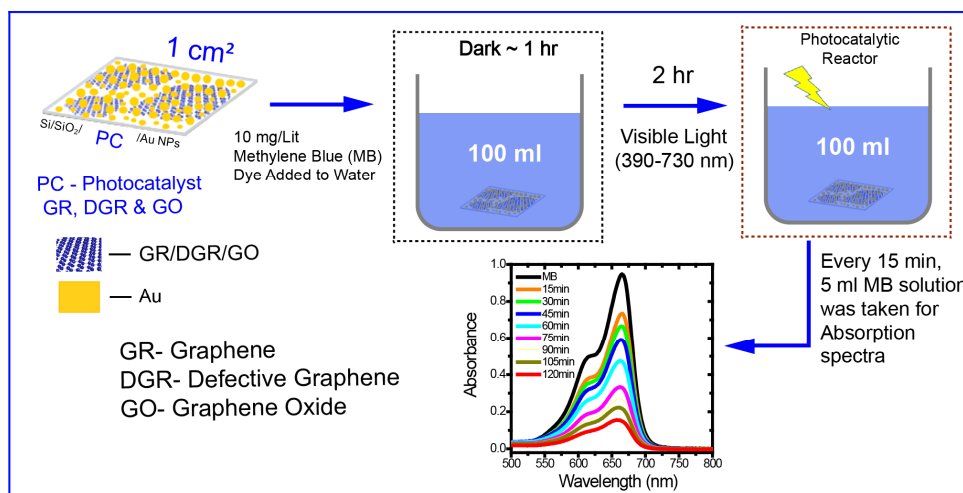


Figure 5.1: Schematic representation of the preparation of GR-Au plasmonic hybrid photocatalysts and the visible light Photocatalysis degradation experiment.

A description of the samples substrates is tabulated in the **Table 5.1**. The film-dye solution was kept under visible light irradiation for 120 min. (xenon lamp, power-250 Watt, wavelength range from 390-750 nm). After an interval of 15 min, 5 mL of the irradiated dye solution was taken out and kept for absorption measurement. Photodegradation of MB is monitored by observing the changes in the maximum absorbance of MB at 663 nm.

5.2. HRTEM Studies

First, we have investigated the structural morphology of the GR-Au, DGR-Au and GO-Au plasmonic hybrid photocatalysts using HRTEM to judge the homogeneity, and the covalent interaction of Au NPs at the structural defects and oxygen functional groups prior to the Photocatalysis experiment. The surface modification of graphene and GO with Au NPs was demonstrated for the samples prepared on a TEM Cu grid. **Figure 5.2** represents the morphological features of different graphene and Au plasmonic hybrids and dewetting behaviour of Au NPs near the defect sites. **Figure 5.2(a)** shows the TEM image of GR after physical functionalization with Au NPs and corresponding HRTEM image shows a single Au NP and graphene lattice. The SAED pattern of GR-Au NPs hybrid is shown in the upper left inset of **Fig. 5.2(a)**. **Figure 5.2(b)** represents the TEM image of suspended graphene and covalently attached Au NPs at vacancy type defects in DGR and the inset shows a magnified view of the same. In DGR sample, the shape deformation and larger dimension of the Au NPs clearly indicate that large number of Au atoms migrate and

Table 5.1: Details of the various pristine and Au functionalized graphenes (CVD graphene and graphene oxide) used for the present study and sample codes.

Sl. No	Details of the Sample	Sample Code
1.	Pristine CVD Graphene	GR
2.	Defective CVD graphene	DGR
3.	Graphene Oxide	GO
4.	Au coated on Pristine CVD Graphene, RTA	GR-Au
5.	Au coated on Defective CVD Graphene, RTA	DGR-Au
6.	Au coated on Graphene Oxide, RTA	GO-Au

cluster preferentially at the defect sites, driven by the dewetting behavior of Au on the graphene layer and for energy minimization. **Figure 5.2(c)** shows the TEM image of the GO-Au plasmonic hybrid, which shows a perfect spherical Au NPs formed on the surface of the GO basal plane. The inset of the **Fig. 5.2(c)** shows the HRTEM image of the lattice patterns of Au NPs functionalized on GO. The surface dewetting of Au NPs on the GO plane is less significant, which may be due to the presence of the multilayer graphene sheets

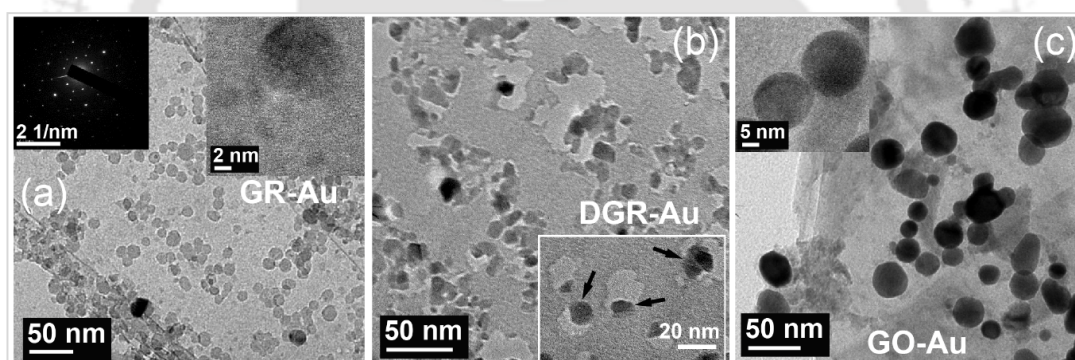


Figure 5.2: (a) TEM image of GR after Au functionalization the corresponding HRTEM image of single Au NP, and graphene lattice and SAED pattern are shown as insets. (b) The site selective covalent bonding of Au NPs at defect sites of DGR; the inset shows the HRTEM image of Au NPs at in-plane vacancy sites of graphene. (c) TEM image of functionalized GO with Au NPs. Uniform spherical Au NPs with average diameter ~ 20 nm have been formed. The inset shows the HRTEM image of Au NPs and GO interface.

associated with various oxygenated functional groups and weak covalent interaction of Au with GO. TEM image analysis clearly distinguishes the site selective physical functionalization of Au NPs on graphene plane, while in case of GO-Au it is at oxygen functional groups sites. Note that the average size of Au NPs in all the samples varying in the range of 10-20 nm.

5.3. Optical Absorption Studies

Next, the optical absorption measurements has been carried out on the pristine and Au functionalized GR, DGR and GO samples in order to understand the effect of surface functionalities and intrinsic defects on graphene before and after physical functionalization. Note that the structural evolution, SERS and SPR effects from the GR-Au

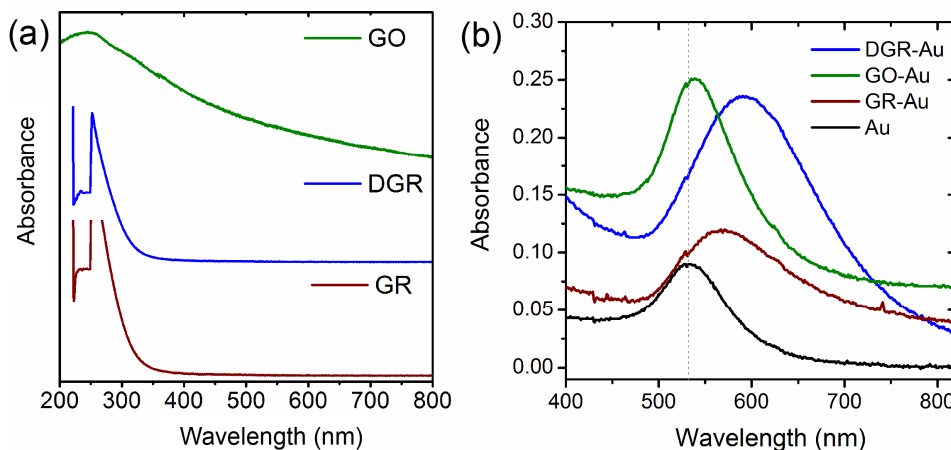


Figure 5.3: (a) Optical absorption spectra of pristine GR, DGR and GO on the quartz substrate. (b) Optical absorption spectra of GR and GO after physical functionalization with Au NPs. A strong surface plasmon resonance absorption peak was found in all GR-Au plasmonic hybrid samples.

plasmonic hybrids were discussed in **Chapter 4** extensively. **Figure 5.3** represents the optical absorption spectra from the pristine and GR-Au plasmonic hybrids prepared on the quartz substrates. In **Fig. 5.3(a)**, a comparison of the absorption features from GR, DGR and GO clearly reveals that the GR and DGR are completely transparent over entire wavelength in the UV-visible-NIR region as compared to that of the GO sample. Note that, the optical absorption from DGR sample is similar to that of GR, though the former contains various kinds of structural defects on the basal plane and at the edges (see the HRTEM image, **Fig. 3.11** in **Chapter 3**). In contrast, the GO shows a broad UV-visible absorption band centred at 250 nm due to the stacking of various in-plane oxygenated functional groups corresponding to defect induced intermediate energy states (sub-bands), i.e transition from $n-\pi^*$ states.¹⁻² **Figure 5.3(b)** represents the absorption spectra from the Au functionalized GR, DGR and GO on the quartz substrate with a comparison with the as prepared Au NPs. For pristine Au NPs, A strong SPR band was centred at 532 nm was observed in the visible region while in case of GR-Au, DGR-Au and GO-Au, it was at 570, 590 and 540 nm, respectively. In comparison to the AuNPs, there is a huge red shift in the plasmon band of GR-Au and DGR-

Au, whereas GO-Au shows a slight redshift. This is due to the overall increment in the refractive index due to surrounding dielectric medium of Au NPs in GR-Au, DGR-Au and GO-Au samples.³ However, in our samples, the red shift and broadening of Au plasmon band is also expected from the defect mediated interaction of Au NPs on the graphene basal plane.⁴ The diffusion of Au clusters/atoms in graphene⁵ and formation of longer Au–C bonds⁶ are believed to cause the broadening of SPR absorption band in the present case. Interestingly, the line width and peak position of the Au plasmon peak is insignificant in case of GO-Au that may be due to the weak covalent interaction and functionalization of Au NPs at the oxygenated functional groups.⁷

5.4. Visible Light Photodegradation Performance Studies

The photocatalytic degradation of organic dye molecules or hazardous pollutants is one of the great challenges to control the environmental pollution and also a conventional approach to characterize the efficient photocatalysts. Photocatalytic degradation performance of pristine and Au functionalized graphene plasmonic hybrid catalysts was estimated from the efficiency of visible light degradation of aqueous MB organic dye solution after exposure to visible light irradiation (390 to 750 nm) for different time duration. **Figure 5.4** shows the absorption spectra of MB after different irradiation times by using pristine graphene and Au functionalized graphene photocatalysts. Note that the absorption spectrum was acquired at regular time laps of 15 min each for 120 min during the photolysis process. The percentage of photodegradation of MB from different photocatalysts were evaluated with respect to the photodegradation of MB solution without any catalyst (blank MB) substrate in it under identical conditions, by measuring the absorption intensity in each case. A systematic analysis of the visible light photodegradation performance of each sample is plotted in the **Fig. 5.4** for the MB absorption band of MB centred at 663 nm, as shown for pristine Au (**Fig. 5.4(a)**), GR (**Fig. 5.4(b)**), GR-Au (**Fig. 5.4(c)**), DGR (**Fig. 5.4(d)**), DGR-Au (**Fig. 5.4(e)**), GO (**Fig. 5.4(f)**) and GO-Au (**Fig. 5.4(g)**). **Figure 5.4(h)** represents a bar graph of the photodegradation performance profiles for all the pristine and GR-Au plasmonic hybrid catalysts. It is clear that, DGR-Au, GO and GO-Au show the superior photodegradation performances, such as 67%, 70% and 85 %, respectively after irradiating the sample for 120 min. The photocatalytic activity of pristine Au NPs and blank MB is also examined for the

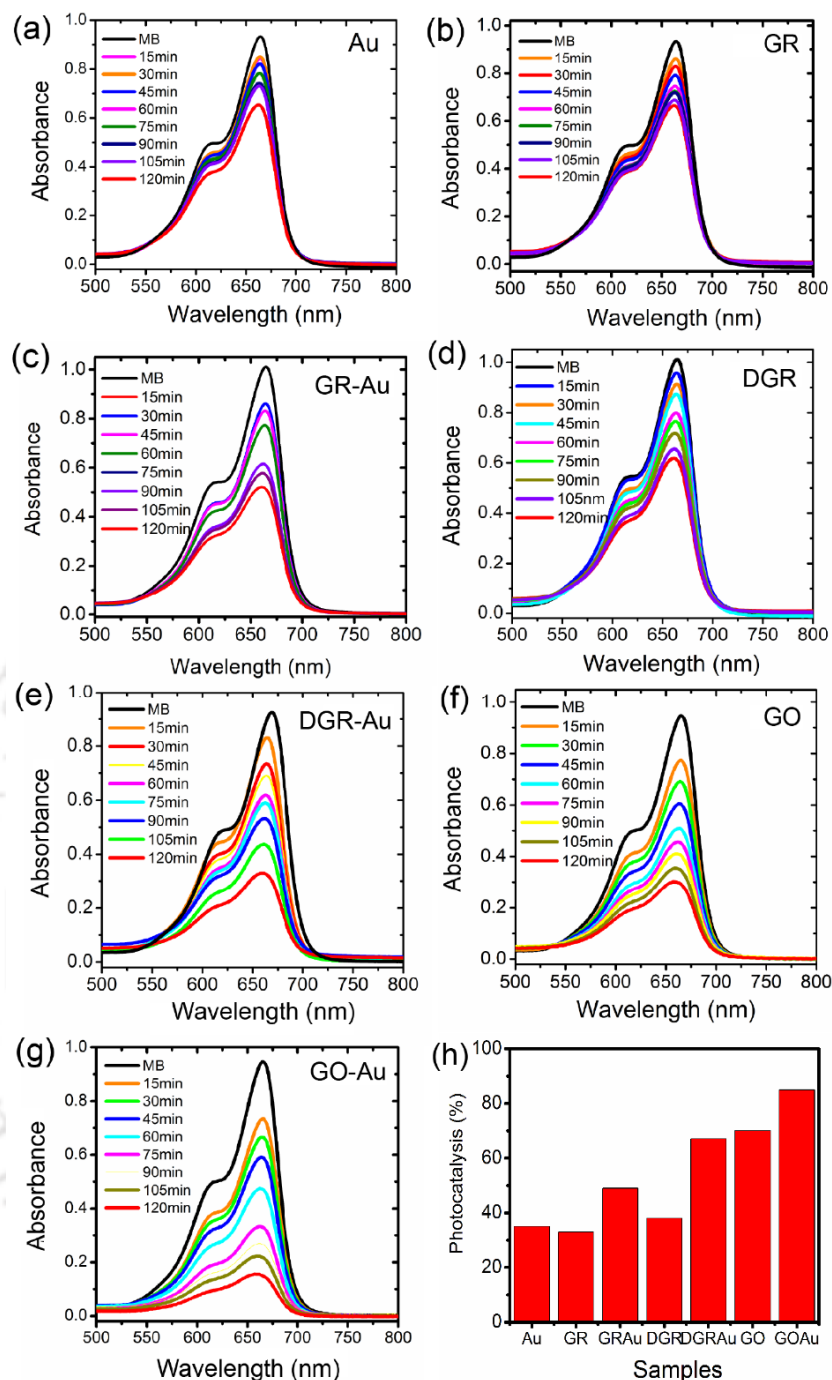


Figure 5.4 : Visible light photocatalysis degradation performance of pristine GR, DGR and GO with/without Au functionalization in a standard MB aqueous dye solution: (a) Au, (b) GR, (c) GR-Au, (d) DGR, (e) DGR-Au, (f) GO and (g) GO-Au catalyst substrates. (h) A bar diagram showing the comparative performances of various hybrid catalysts. Note that the absorption spectra of each irradiated sample was taken at an interval of 15 min.

comparison and it shows only 35% degradation. The photocatalytic activity is enhanced nearly by 2.5 times in case of DGR-Au and GO-Au plasmonic hybrid catalysts. This is a

significant achievement using pristine graphene and graphene transition metal plasmonic hybrid photocatalysts, for the first time.

Figure 5.5(a) plots the percentage of degradation C_t / C_0 versus the irradiation time under different conditions. Here, C_0 and C_t denote the concentration of MB solution after irradiation for a time period of '0' and 't' min, respectively, when the adsorption–desorption equilibrium was achieved. The degradation of the MB was considered as a pseudo-first-order reaction, expressed by the rate equation $\ln(C_0 / C_t) = kt$, where k is a first order rate constant.⁸⁻¹⁰ The value of k is calculated from the Log plot of C_t / C_0 with respect to the irradiation time (t) using a linear fit, as shown in the **Fig. 5.5(b)**. Note that the symbols represent the experimental data and solid colored straight lines corresponds to the fitted data for the first order rate equation. **Figure. 5.5(c)** represents a comparison of the k values for different catalysts and it clearly shows a dramatic change in the k after Au functionalization in DGR and GO. The rate constant was enhanced by a factor of 4.5 and 3, in case of DGR-Au and GO-Au, respectively. On the other hand, no significant enhancement was observed in case of pristine GR and GR-Au photocatalysts. The results reveal that the DGR-Au and GO-Au photocatalyst substrates displayed higher photocatalytic efficiency than the pristine samples having the same size, indicating enhanced photocatalytic activity due to the presence of plasmonic metals functionalized at intrinsic defect sites in DGR and oxygen functional groups in GO, respectively. For effective dye adsorption on catalyst surface, it is essential to achieve a good interfacial contact between dye and catalyst.

The low photocatalytic efficiency in Au, GR and GR-Au may be due to less adsorption of MB dye molecules on the catalyst surface, and less absorption of visible light. On the other hand, in case of DGR-Au, GO-Au and GO it shows higher efficiencies due to the increased adsorption of MB on the catalyst substrates due to the presence of defects in DGR (see **Fig. 5.2(b)**), while in case of GO, there are plenty of in-plane epoxy and hydroxyl functional groups.² When MB molecules get adsorbed on the GO or DGR surface the dye gets sufficient active sites to interact, and the π - π interactions between MB and GO/DGR strongly holds them together. We believe that Au NPs play the dual role on graphene plane, i.e. wide range of visible absorption and enhanced charge transfer to graphene during the visible light irradiation in the photolysis process. When light is absorbed by the Au-GO and Au-DGR,

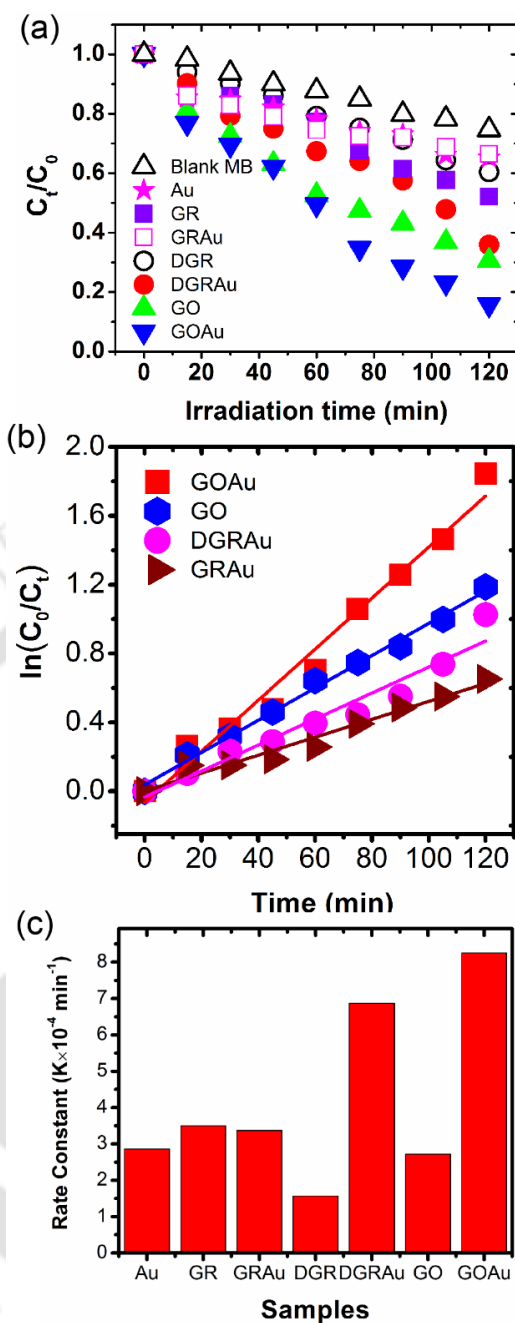


Figure 5.5: (a) Visible light photocatalytic activity (C_t/C_0) of graphene and Au functionalized graphene as a function of irradiation time. Note that C_t and C_0 represent the concentration of MB after irradiation time 't' and before irradiation, respectively. (b) Semi log plot of a photodegradation efficiency of MB plotted as a function of irradiation time and corresponding first order rate constant (K) was calculated from the linear fitting. Note that the symbols represent the experimental data and solid lines corresponds to the fitted data. (c) Comparison of the rate constant before and after Au physical functionalization of graphene catalyst substrates for visible light photocatalysis.

electrons and holes are separated on the nanosheet. Whereas MB gets sensitized under visible light to MB* and subsequently releases free electrons to GO, the photo generated carriers on the nanosheet are captured by functional groups and adsorbed O₂ or –OH part and forms reactive hydroxyl radicals. The hydroxyl radicals finally interact with the MB molecule and subsequently degrades it. The lower photocatalytic efficiency in pristine and GR-Au plasmonic hybrids is expected from less adsorption of the MB molecules on the inert surface of the defect free graphene. However, photocatalysis efficiency of GR-Au is marginally higher than the DGR that may be due to the presence of plasmonic NPs. In short, Au NPs on graphene enhances the visible photocatalysis efficiency in the GR-TM plasmonic hybrids. **Figure 5.6** shows a schematic of the possible mechanism of visible light photocatalysis from the GR-TM plasmonic hybrids and extensive role of structural defects and oxygenated functional groups have been elucidated based on our experimental observations.

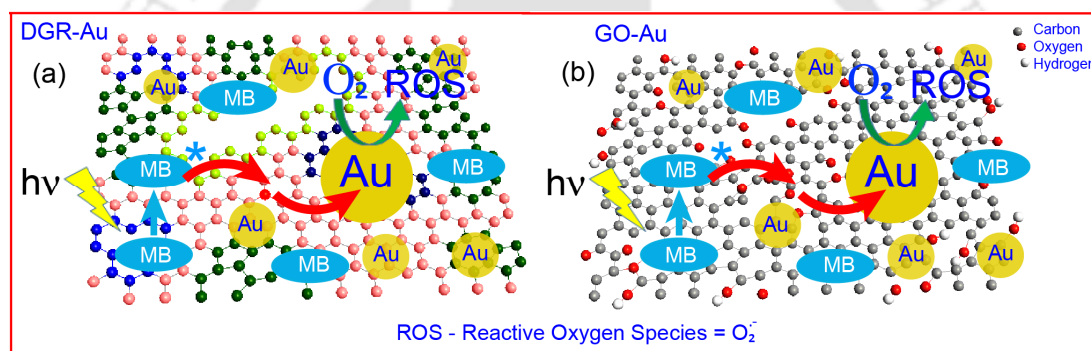


Figure 5.6: Proposed mechanism of visible light photocatalysis in DGR-Au and GO-Au plasmonic hybrid photocatalysts.

5.5. Fabrication of Graphene and Graphene-Au Plasmonic Hybrid SERS Sensors

In this section, we will discuss the efficacy of GR and GR-Au as a substrate for surface enhanced Raman scattering (SERS) that is a powerful tool for enhancing Raman signal of adsorbed molecules. Some common molecules are used for Raman probes, such as Rhodamine 6G (R6G) and Fluorescein (FL) are deposited equally on GR and GR-Au on SiO₂ and quartz substrates using solution soaking. By comparing the Raman signals of molecules on GR-Au and SiO₂ substrate, we observed that the intensity of the Raman signals on GR-Au is much stronger than that of the GR and SiO₂ substrate. For solution soaking, we can observe Raman signals from the molecules on GR-Au substrates even though the concentration is as low as

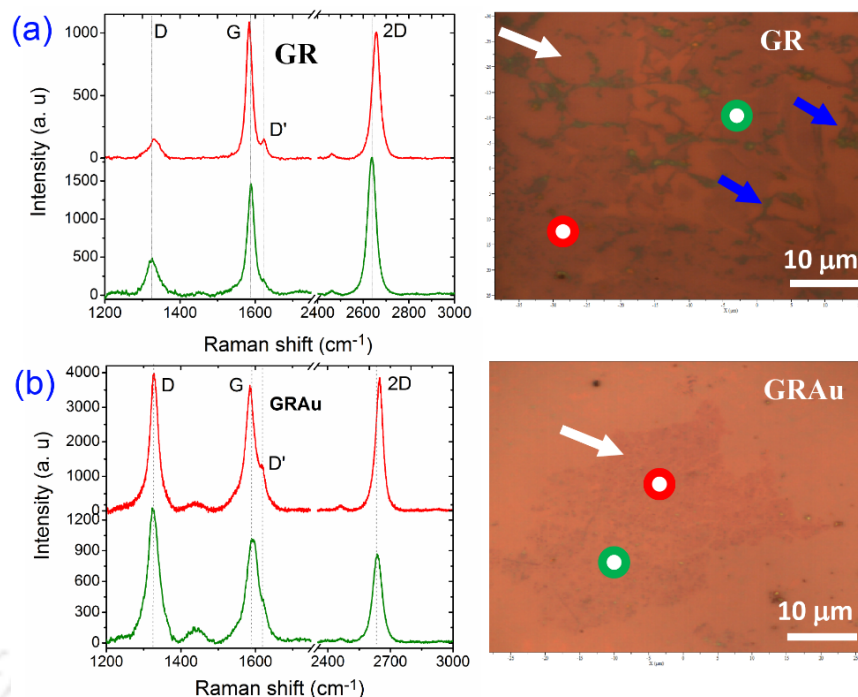


Figure 5.7: Raman spectra of large area single layer (a) GR and (b) GR-Au for different locations and corresponding locations are shown in the OM image (right). White arrow indicate the GR and GR-Au layer, respectively.

10^{-2} - 10^{-3} μM , while there is only a fluorescence background from the SiO_2 substrate that is consistent with the SPR absorption measurements. The enhanced intensity of GR-Au plasmonic hybrid SERS substrate is believed to be primarily a chemical enhancement (CM) due to the easier charge transfer between graphene and Au NPs. We have achieved the Raman enhancement factors of the order of 10^2 - 10^3 which were calculated by taking the signals on the SiO_2 substrate as reference, and these are found to be dependent on the vibrational symmetry of the molecules. This is an interesting observation from the GR-Au hybrid SERS substrates, which were fabricated for the Raman enhancement on the surface of graphene and plasmonic interface.

At first, the organic dye molecules (R6G and FL) were deposited on to SiO_2 and quartz substrates by dipping in an aqueous dye solution of 10 ml with a dye concentration 10^{-2} and 10^{-3} μM . GR and GR-Au SERS substrates were soaked in the dye solution for 1 h and dried in the vacuum oven at $\sim 100^\circ\text{C}$ for 10 min. Note that all the samples were prepared on SiO_2 and quartz substrates. The SERS effect of GR and GR-Au was estimated from the enhancement of the Raman features of dye molecules in the range of 600 - 1800 cm^{-1} .

5.6. SERS Studies on Graphene and Graphene-Au Hybrids

Prior to the SERS measurements from the dye molecules, pristine and Au functionalized graphene samples were characterized from the micro-Raman spectroscopy. **Figure 5.7(a)** and **(b)** represent the Raman spectra of pristine graphene and corresponding OM image of the scanned locations, respectively. White and blue arrows indicate the graphene layer transferred on to a SiO₂ substrate and residual PMMA particles, respectively. The characteristic line shape of the Raman features such as D, G and 2D bands reveal the large area coverage of SLG. **Figure 5.7(c)** and **(d)** represents the Raman spectra of the GR-Au sample and corresponding OM images, respectively. The intensity of the D band is increased significantly after Au deposition. The red shift and increase in the FWHM of both G and 2D bands is an indication of the Au functionalization with graphene without losing its sp^2 crystallinity. Raman spectra were collected from GR, GR-Au, Au coated SiO₂ substrates under the same conditions (integration time, laser power, focus, etc.). We have performed the micro-Raman measurements at 632.8 nm laser excitation wavelength, which shows resonant Raman features in GR and GR-Au hybrids (see **Chapter 4**).

Figure 5.8(a) and **(b)** represent the SERS spectra of FL and R6G collected on the pristine GR, GR-Au, Au coated SiO₂ substrates, respectively. Note that the SERS spectra were acquired for 10^{-2} and 10^{-3} μ M concentrations and denoted by 1 and 2 in each sample, respectively. Raman spectra show the symmetry vibrational modes of the dye molecules, which are existing in the range of 600-1800 cm^{-1} . The Raman signals at 1187, 1336, 1421, 1505, 1560, 1603 and 1641 cm^{-1} are very strong in case of FL on GR-Au SERS substrate, and the weak Raman bands at 614, 643 and 772 cm^{-1} are still distinguishable on monolayer GR-Au substrate, while on Au and graphene substrates these bands are weak. In case of R6G we found the strong Raman signals at 614, 777, 1314, 1363, 1512 and 1650 cm^{-1} . For both the dye molecules, we found graphene and Au induced fluorescence background on SiO₂ substrate. We observed the GR and GR-Au fluorescence quenching from the both the dye molecules.¹¹ We estimated the Raman enhancement in each case from the SERS spectra after subtraction of the fluorescence back-ground of graphene and Au, The intensity of each spectrum was normalized with respect to the 1188 and 614 cm^{-1} bands in GR-Au-FL1 and GR-Au-R6G1 samples, respectively. It clearly depicts that the enhanced Raman signal from the GR-Au substrates for the both the dye molecules.

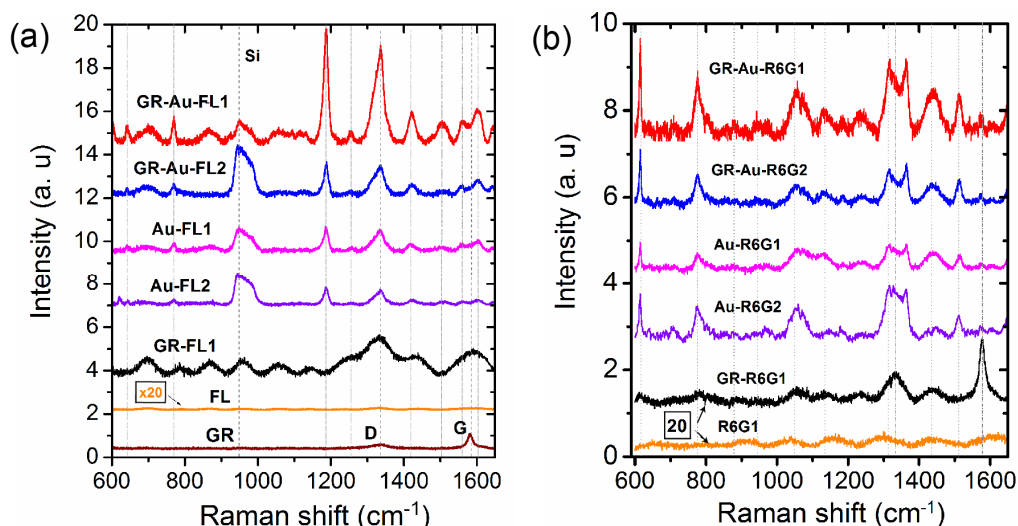


Figure 5.8: A comparison of Raman enhancements from GR, GR-Au and Au SERS substrates after subtraction of fluorescent background for (a) Fluorescein (FL) and (b) Rodamine 6G (R6G) dye molecules. Note that each spectra is normalized with respect to the intensity of peak at 1188 and 614 cm⁻¹ in GR-Au-FL1 and GR-Au-R6G1, respectively. The Raman spectra of pristine graphene is also shown in (a) for the comparison.

Figure 5.9(a) shows a schematic illustration of the dye molecules on graphene and GR-Au plasmonic hybrids. Further, we have studied the effect of adsorption of the molecules on the SPR absorption spectra of the GR-Au plasmonic hybrids in comparison with pristine samples. **Figure 5.9(b)** and **(c)** represent the SPR absorption spectra of GR and GR-Au before and after soaking of dye molecules with a comparison with the pristine graphene sample on quartz substrate. Note that the absorption spectrum of pristine Au is also shown for the comparison. The SPR absorption peak for FL on Au and GR-Au substrates are found at 560 and 582 nm, while that of R6G are found at 528, 536 nm, respectively. The relative intensity of SPR absorption from FL dye molecules coated on GR-Au substrates is higher than that of the Au substrate by a factor of 2, while in case of R6G both GR-Au and Au shows almost identical intensity of absorption (see **Fig. 5.9(b)** and **(c)**). We found that, there is a redshift (582 nm) and a blue shift (543 nm) of SPR band in FL and R6G, respectively. The SPR absorption enhancement and shift in SPR peak in the GR-Au case may be due to the enhanced charge transfer from underlying graphene to Au and dye molecules due to the strong interaction of graphene with Au NPs.⁴ **Figure 5.9(d)** shows the absorption spectra of FL and R6G dye taken for the 10⁻² μM concentration in aqueous media. The absorption centres of FL and R6G are at 464 and 523 nm, respectively.

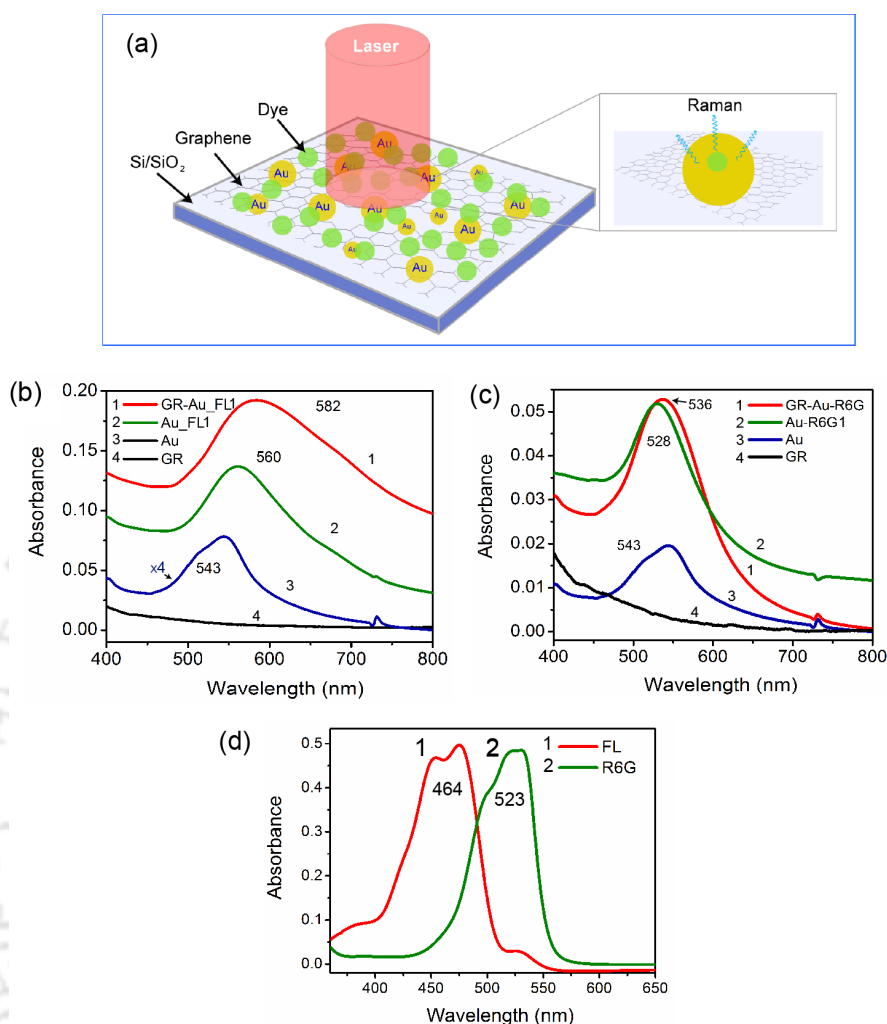


Figure 5.9: (a) Schematic illustration of the dye molecules adsorbed on GR, GR-Au hybrids and a SiO₂ substrate, and the micro-Raman measurements at excitation 632.8 nm. Optical absorption spectra from (b) FL, (c) R6G dye molecules (10^{-2} μ M) coated on Au and GR-Au deposited quartz substrates. For comparison, spectra of GR and Au are also shown in each case. (d) Optical absorption spectra of FL and R6G in aqueous media.

We have estimated the enhancement factors of the common Raman bands observed in the dye molecules as shown in **Table 5.2**. It reveals that the dye molecules do not show the significant Raman enhancements on pristine graphene as compared to the GR-Au and Au SERS substrates. GR-Au SERS substrates show superior Raman enhancement of the order of 10^3 . Note that, we have performed the SERS measurement for all the substrates at two

different dye concentrations and found the similar behaviour. Based on the experimental observations, the mechanism of SERS enhancement is discussed below.

Table 5.2: Position of Raman bands and corresponding enhancement factors for different substrates with FL and R6G calculated with respect to the Raman intensity of molecule on SiO₂ substrate.

	Fluorescein (FL)				Rhodamine 6G (R6G)			
	Peak (cm ⁻¹)	GR-FL1 (10 ³)	GR-Au-FL1 (10 ³)	Au-FL1 (10 ³)	Peak (cm ⁻¹)	GR-R6G1 (10 ³)	GR-Au-R6G1 (10 ³)	Au-R6G1 (10 ³)
1.	643	0.54	1	0.34	614	0.08	1.1	0.2
2.	771	0.2	0.2	0.1	777	0.1	0.7	0.32
3.	1188	0.22	0.86	0.18	1050	0.06	0.18	0.08
4.	1334	0.36	0.9	0.2	1312	0.06	0.18	0.06
5.	1421	0.42	0.7	0.16	1362	0.14	0.64	0.2
6.	1505	0.18	1.36	0.24	1434	0.04	0.12	0.04
7.	1561	0.28	0.34	0.1	1512	0.02	0.3	0.1
8.	1598	0.3	0.42	0.14				
9.	1644	0.28	0.66	0.32				

5.7. Mechanism of SERS Enhancement

There are numerous experimental and theoretical works on SERS studies, which reveal about the enhancement mechanism.¹¹⁻¹⁴ Normally, the two widely accepted mechanisms are electromagnetic mechanism (EM) and chemical mechanism (CM). In case of the EM mechanism, the enhancement of the local electromagnetic field increases the cross section of the Raman scattering. The contribution to the electromagnetic enhancement is primarily due to the surface plasmons excited by the incident light. The enhancement is roughly proportional to $|E|^4$ and can go up to 10^8 or more, where E is the intensity of the electromagnetic field.^{13, 15} Compared to EM, CM is based on a charge transfer between the molecule and the substrate and enhancements are usually 10 - 10^2 . In many cases, the two mechanisms coexist. In present case, we have observed the Raman enhancement in our GR-Au hybrids in the order of 10^3 (see **Table 5.2**). We believe that the Raman enhancement in our samples is primarily based on CM mechanism due to the strong π - π interaction of dye

molecules with inert nature of graphene surface containing strong sp^2 hybridized carbon atoms and covalently functionalized with Au NPs. However, due to the SPR absorption from the Au NPs on graphene surface, it may contribute some of the EM enhancements also. Ideally rough metal surfaces like Au, Ag and Cu etc. show the huge Raman enhancements.¹¹ GR-Au and Au hybrid substrates are thought to be marginally rough in nature not as flat as graphene which may contribute the EM enhancement. Since Au particles are embedded in graphene, it will have large curvature and absorb a large extent of incident light to produce surface plasmons.

We deposited the dye molecules by purely solution soaking in which the distance between the molecule is expected to be below 0.2 nm and the Fermi level of the metal substrate to symmetrically match with the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the molecule, so that charge transfer can occur from the graphene-Au to the molecule.¹³ First, we consider the graphene as a one atom thick and smooth surface without any fluctuations¹³, Second, it has high optical transparency (97.7%). Besides, the surface plasmon on graphene is in the frequency range of terahertz rather than the visible range. On the basis of these considerations, only graphene is not expected to support directly the EM enhancement. On the other hand Au NPs possess huge SPR absorption in the visible region, as we discussed in previous section (see **Fig. 5.8(e) and (f)**). In conclusion, the possible enhancement in GR-Au plasmonic hybrids is mainly due to CM mechanism, while the contribution of EM enhancement cannot be ruled out. However, the magnitude the Raman enhancements reported in the literature is 2-17 times using pristine graphene as a SERS substrate, while for the GO-Au and Ag plasmonic hybrids of the order of 10^1 - 10^2 based on the CM mechanism.^{13, 16-17} In the present case, the enhanced charge transfer between the dye molecule and the GR-Au plasmonic substrate is high, the Raman enhancement of the order of 10^3 is achieved here.

5.8. Summary

We implemented graphene and GR-Au plasmonic hybrids for the efficient visible photocatalysis and SERS applications. A systematic investigation on enhanced photocatalysis and SERS was explored. The important findings from our results are summarized below.

1. We achieved a strong 85% photodegradation of MB dye molecules using GR-Au and GO-Au hybrid photocatalysts.
2. Graphene and GR-Au plasmonic hybrids were implemented for the SERS applications and achieved an impressive Raman enhancements in the order of 10^3 .



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Graphene Assisted Controlled Growth of ZnO Nanostructures on Graphene

In the present chapter, we demonstrate graphene assisted controlled fabrication of ZnO nanowires (NRs), nanowires (NWs) and nanoribbons (NRBs) on few layer and single layer graphene at relatively low temperature using Au catalyst and ZnO seed layer without catalyst. The pseudo-epitaxial growth mechanism of ZnO nanostructures (NSs) on the graphene plane was proposed based on the results on different pretreated substrates. A systematic study is performed on the effect of various Au catalyst and self-catalyst buffer layers on graphene and pretreatment conditions on the formation of vertically aligned ZnO NRs/NWs. A new growth strategy has been proposed for the vertically aligned hexagonal faceted GR-ZnO NRs/NWs hybrids having enhanced optical and optoelectronic properties. GR–Au catalyst layer and self-catalyst layer are shown to result in the formation of highly aligned ZnO NRs and NWs based on the vapor-liquid-solid (VLS) and vapor-solid (VS) growth mechanism.

Microstructure characterization is made on the as-grown GR-ZnO hybrids to assess the crystalline structure, nature of interaction of graphene and ZnO seed layer, role of defects, etc. Further, rapid thermal annealing (RTA) and furnace annealing (in vacuum and Ar gas atmosphere) were performed on the as grown GR-ZnO hybrids to improve the crystalline quality and to probe the evolution of various intrinsic and extrinsic defects on ZnO NSs.

6.1. PVD Growth Schemes of ZnO Nanostructures on Graphene

Various kinds of ZnO nanostructures, such as NRs, NWs and NRBs were grown on the GR substrate by using a PVD technique for different pretreated substrates. Here we present the Au catalytic and self-catalytic growth schemes of vertical ZnO NSs on GR substrates. **Figure. 6.1** represents the schematic of the substrate layers on Si/SiO₂ and subsequent growth parameters used for the controlled fabrication of ZnO NSs. The novelty of growing well-aligned ZnO NSs on graphene in both the cases is the growth at relatively low temperature and the substrate pretreatment conditions.

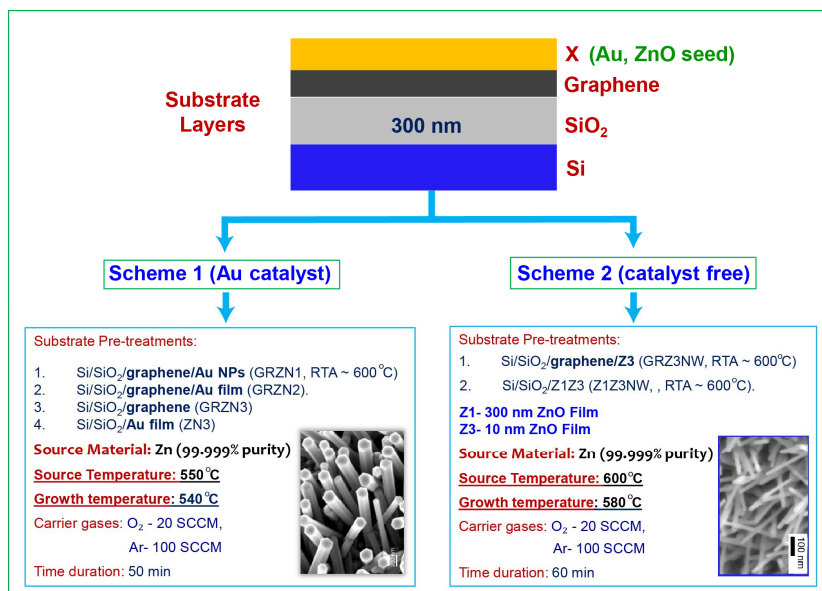


Figure 6.1: Schematic of the growth schemes and the growth condition used for the growth of highly aligned ZnO NRs/NWs by Au catalyst and catalyst free approaches.

6.1.1. Scheme 1 (Catalyst Mediated)

In this scheme, ZnO NSs were grown on the GR-Au film hybrid catalyst substrates. The preparation and structural quality of GR-Au hybrids were discussed thoroughly in **Chapter 4**. The vertically aligned ZnO NRs and NWs were fabricated on rapid thermally annealed GR-Au catalyst substrates. For the growth of ZnO nanostructures, commercial activated Zinc powder (purity ~ 99%, Aldrich) was taken as a source material in an alumina boat and placed at the center of a horizontal quartz tube and kept inside a horizontal muffle furnace. The Au coated graphene substrates with or without RTA treatment were placed downstream ~ 5 cm away from the source. Initially, the quartz chamber was pumped to a pressure ~ 10^{-3} mbar. The source temperature was maintained at ~550°C and substrate temperature was at ~540°C, and throughout the temperature ramp 300 SCCM of Ar gas was flushed until it reached the set point with a heating rate 18°C/min in order to prevent the oxidation of the graphene. When the furnace reached the source temperature (550°C), 20 SCCM of O₂ gas was introduced and gas pressure inside the chamber was maintained at 1.4 mbar for the growth time of 50 mins. After the completion of reaction, the furnace was cooled down to room temperature. ZnO deposition was carried out on four different sets of substrates under identical growth conditions, as described in the **Table 6.1**.

Table 6.1: Details of the substrate pre-treatment conditions and morphology of the resulting ZnO nanostructures that are grown in **Scheme 1**.

Sample code	Substrate with pre-treatment	ZnO nanostructures
GRZN1	SiO ₂ /graphene/AuNP, RTA	NRs, aligned, hexagonal
GRZN2	SiO ₂ /graphene/Au film	NWs, aligned
GRZN3	SiO ₂ /graphene	NRBs, random
ZN3	SiO ₂ /Au NP, RTA	NWs, random

In order to improve the crystalline quality of as-grown GR–ZnO hybrid NSs, we performed post-growth annealing at 500 and 700°C in Ar atmosphere (50 SCCM flow) for 1 hour and studied the resulting structural and photoluminescence (PL) properties (discussed in next chapter (**Chapter 7**)).

6.1.2. Scheme 2 (Catalyst Free)

In this scheme we demonstrate the graphene mediated self-catalytic growth of ZnO NSs on GR substrates at relatively low growth temperature (580°C) in presence and absence of ZnO seed layers, as shown in the schematic of **Fig. 6.1**. Prior to the PVD growth of ZnO NSs, high quality ZnO thin films with three different thicknesses: ~300 nm (code–Z1), ~100 nm (code–Z2) and ~10 nm (code–Z3) were deposited by RF magnetron sputtering on different graphene substrates for the growth of ZnO NSs. Note that, high purity commercial ZnO sputtering target (99.999%, Kurt J. Lesker Company) has been used as source for the ZnO film growth. Initially the chamber was evacuated to a base pressure of 6.7×10^{-6} mbar and during the sputtering it was maintained at 1×10^{-2} mbar. The RF power was kept at 100 W. The substrates were heated to 200°C for better crystallinity and uniformity of the ZnO grains. Further, these ZnO thin films were subjected to RTA treatment at 600°C in Ar gas ambient (200 SCCM) atmosphere for 3 minutes using a commercial RTA system (MILA3000, Ulvac, Japan) in order to further improve the crystalline quality as well as for the removal of excess oxygen related defects on the ZnO films on various substrates. Improvements in the crystallinity of ZnO grains and their phases were confirmed from XRD, micro-Raman and HRTEM analyses. ZnO NSs were grown on the above prepared GR–ZnO seeded substrates under growth conditions similar to the parameters used in the **Scheme 1**, except for the

growth temperature (580 °C) and time (60 min) (see **Fig. 6.1**). The details of the sample descriptions of GR-ZnO seeded substrates and corresponding morphology of the ZnO NSs are tabulated in the **Table. 6.2**.

Table 6.2: Details of the substrate and hybrid samples grown in Scheme 2

Sl. No.	Base Substrate	Substrate Code	Substrate description	Sample	Morphology of the ZnO NWs
1	SiO ₂ , Quartz	GR	Graphene layer only	GRNW	Randomly orientated sparse NWs
2	SiO ₂ , Quartz	GRZ3	10 nm ZnO on graphene, RTA	GRZ3NW	Vertical NWs
3	SiO ₂ , Quartz	Z1Z3	10 nm ZnO on 300 nm ZnO layer, RTA	Z1Z3NW	Dense & randomly orientated ZnO NWs
4	SiO ₂	Z2Z3	10 nm ZnO on 100 nm ZnO layer, RTA	Z2Z3NW	Dense & randomly orientated ZnO NWs
5	SiO ₂	Z3	10 nm ZnO layer only, RTA	Z3NW	Randomly orientated ZnO NWs

6.2. Structural Studies on Substrate Layers

6.2.1. Micro-Raman Studies

Prior to the growth of ZnO NWs, the quality of as-synthesized GR samples was first characterized by Raman imaging/spectroscopy and electron microscopy, which we have discussed in **Chapter 3**. Further the structural quality and interaction of Au NPs in GR-Au catalyst substrates were discussed in **Chapter 4** from the line shape analysis of the characteristic Raman features and HRTEM before and after RTA treatment. The quality of GRZ3 seeded substrates was evaluated from the characteristic Raman line shape analysis before and after sputtering. **Figure 6.2(a)** and **(b)** represent the typical Raman spectra of graphene and GRZ3 thin film hybrid before and after deposition of 10nm thick ZnO film. Raman signatures of SLG (see the black curve in the **Fig. 6.2(a)**) are peaked at 1350 cm⁻¹ (D band), 1593 cm⁻¹ (G band), 1620 cm⁻¹ (D' band) and 2689 cm⁻¹ (a sharp 2D band). The ratio of integrated intensities of 2D and G band i.e. $I_{2D}/I_G = 2$ signifies the dominance of SLG. In GRZ3, the ratio of relative integrated intensity of I_D/I_G is enhanced by a factor of 2.4 and I_{2D}/I_G is reduced by a factor of 2.5 with respect to the pristine graphene, which signifies the

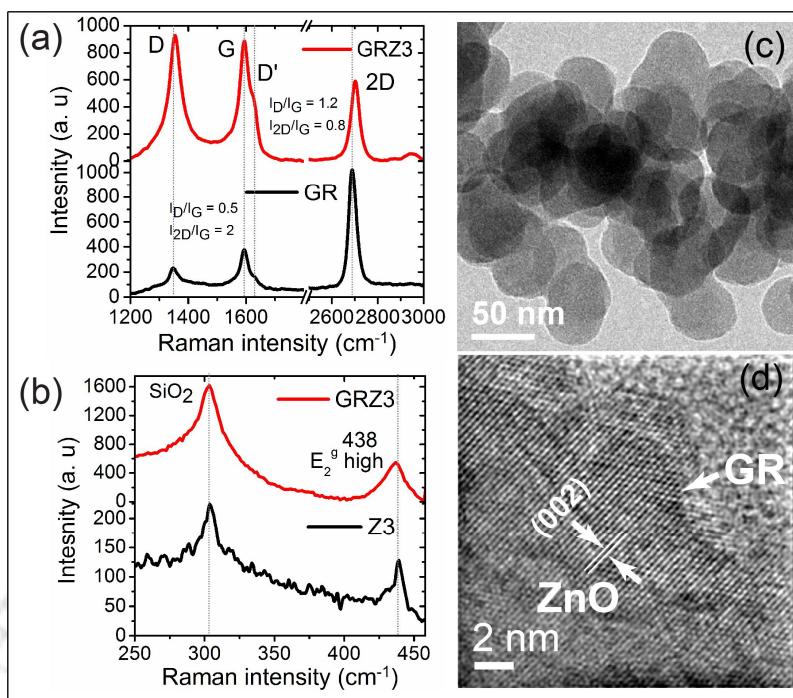


Figure 6.2: (a) Comparison of Raman spectra of graphene before and after ZnO film deposition. (b) E₂^g high mode (438 cm⁻¹) of hexagonal wurtzite phase of ZnO with and without graphene. (c) HRTEM image of the ZnO grains (30-40 nm). (d) HRTEM image of the graphene-ZnO interface showing lattice pattern of (002) plane from ZnO and sp² crystalline lattice of graphene.

disorder and compressible strain in graphene induced by the ZnO layer. Note that the line shape of 2D band without any asymmetry is identical to the few layer graphene that denotes the uniform coverage of ultra-thin ZnO seed layer over the SLG in GRZ3 which behaves like a few layer graphene. An important observation for the epitaxial relation and covalent interaction between graphene and ZnO was evidenced from the redshift (13 cm⁻¹) of 2D band in GRZ3. Confirmation of wurtzite phase for the ZnO seed layer was clear from the appearance of the E₂^g high mode at ~ 438 cm⁻¹. The FWHM of the E₂^g high mode was increased in the GRZ3 as compared to that of Z3 substrate due to the strong interaction of the ZnO seed layer with the graphene.

6.2.2. HRTEM Studies

The morphological features of ZnO seed layer was estimated from the HRTEM imaging. **Figure 6.2(c)** represents a TEM image of the ZnO grains, which shows clearly uniform size (30-40 nm) distribution. These ZnO grains on graphene play an important role for the vertical

alignment of ZnO NWs in the PVD growth. In order to support the Raman results, we have performed the HRTEM imaging for the GRZ3 hybrid thin film. **Figure 6.2(d)** illustrates the image of graphene and ZnO (002) plane interface. SLG lattice pattern can be clearly seen at the outer edge of the thin film that is shown by the white coloured arrow. The (002) plane of ZnO on graphene layer was clearly seen at the inner part of the HRTEM image.

6.2.3. XRD Studies

Further, orientation and crystalline structure of the ZnO seed layers were assessed from the XRD studies. **Figure 6.3(a)** represents the XRD pattern of Z1Z3 substrate after RTA treatment. The XRD pattern shows strong peaks at $2\theta = 31.96^\circ, 34.66^\circ$ and 36.44° corresponding to (100), (002) and (101) planes of Wurtzite ZnO in Z1Z3. **Figure 6.3(b)** shows the XRD pattern of the ultra-thin Z3 film. Z3 seed layer consists of a large area single crystalline wurtzite phase ZnO grains with the crystalline orientation along (002) plane on Si/SiO₂ substrate. The calculated grain size ~ 50 nm of the ZnO from the XRD patterns of Z3, which is consistent with the HRTEM analysis. Covalent interaction of ZnO grains with graphene was evidenced from the HRTEM and micro-Raman results. Note that (100), (101) and (102) crystalline phases of Z3 are significant for the nucleation of ZnO NWs during the PVD growth (discussed later). These ZnO grains act as the seeds for the growth of vertical ZnO nanostructures during the vapor deposition process.

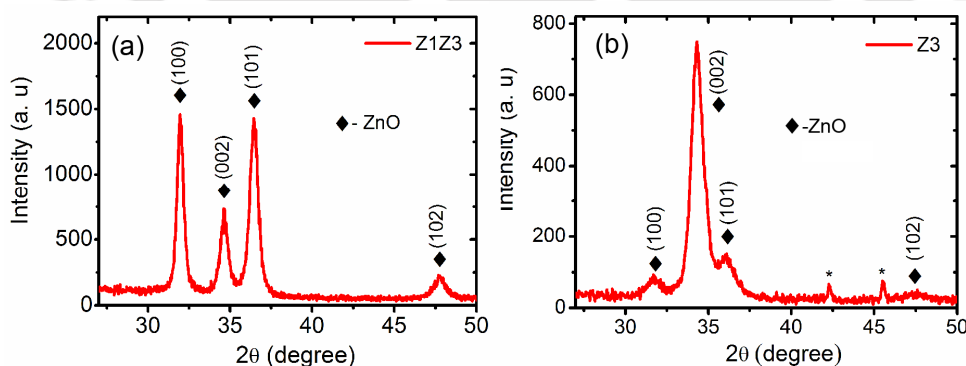


Figure 6.3: XRD pattern of (a) Z1Z3 and (b) Z3 layer on SiO₂ after RTA treatment. The prominent peaks correspond to the (100), (002) and (101) planes of Wurtzite ZnO. Note that the Z3 (10 nm) seed layer shows a strong (002) peak significant for the formation of single crystalline ZnO grains.

6.3. Structural Studies on Graphene-ZnO Hybrid Nanostructures

6.3.1. FESEM Studies of Morphology

A systematic study on the individual role of graphene, Au catalyst, ZnO seed layers and the effect of GR–Au film, GR–Au NPs, GR–ZnO hybrids were carried out to elucidate the growth mechanism of various ZnO nanostructures. In the following subsections, we present each of these cases systematically.

6.3.1.1. Effect of Graphene Layer and Graphene–Au Film

Figure 6.4 illustrates the individual role of graphene and Au layers in the formation of ZnO NWs and NRBs on the graphene substrate. **Fig. 6.4(a)** shows a low resolution FESEM image of ZnO nanostructures grown on the graphene with/without Au layers formed by masking with a copper grid (used in TEM) while depositing the Au film. The regions I and II with bright and dark contrasts refer to the absence and presence of Au coating on the graphene layer, respectively. The region III refers to a transition region between regions I and II. **Figure 6.4(b)** and its inset show higher magnification images of region I clearly showing randomly oriented and nonuniform ZnO NRBs formed on graphene in absence of the Au layer. In contrast, a dense and nearly aligned array of ZnO NWs is formed in case of GR–Au film layer (region II), as shown in **Fig. 6.4(c)**. Inset of **Fig. 6.4(c)** shows higher magnification image of the ZnO NWs that clearly reveals the absence of any hexagonal faceted NWs. **Fig. 6.4(d)** shows the magnified view of the FESEM image of ZnO NRBs grown on the region III. In region III, the density of the NRBs is lower than that of region I, due to the finite thickness and rough edge of the mask that reduces the nucleation sites for the growth of the ZnO NRBs. Thus, Au catalyst plays a crucial role in the growth and vertical alignment of the ZnO NWs on the graphene substrate. The critical role of Au catalyst in the vertical growth of ZnO NWs on usually employed dielectric surface has been extensively studied. It will be evident from the discussion below that in the present case the underlying graphene layer plays a crucial role in the growth of the aligned ZnO NWs.

6.3.1.2. Effect of Graphene–Au NPs (RTA treated)

Figure 6.5(a) and **(b)** shows the low resolution FESEM images of the RTA treated GR–Au substrate before and after the growth of ZnO NRs, respectively. Regions with dark contrast in the images refer to the coverage of graphene. **Figure 6.5(c)** and **(d)** show the magnified view of the respective regions with GR–Au NPs and the transition region due to the mask edge.

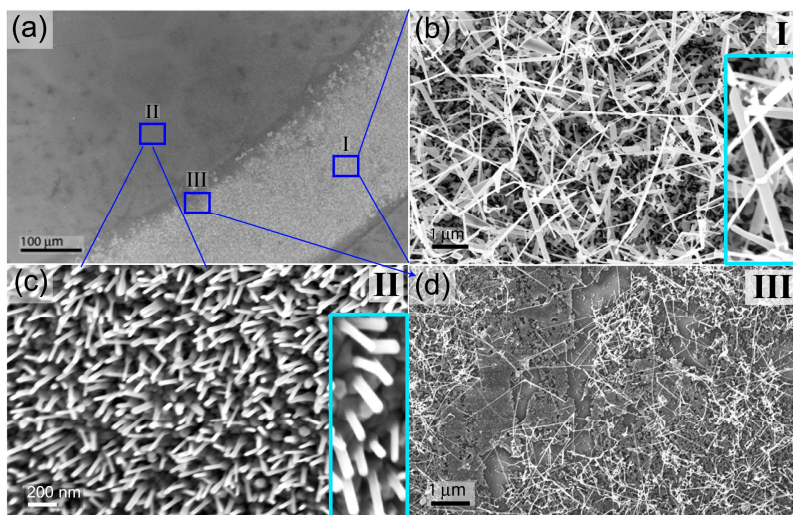


Figure 6.4: (a) FESEM image of ZnO NWs/NRBs grown on the SiO₂/graphene/Au film; regions I with bright contrast refer to graphene layer without Au film and region II with dark contrast refers to the graphene layer with Au film. Region III refers to the transition region between region I and II. (b–c) Magnified view of the regions I and II depicting the growth of randomly oriented ZnO NRBs and aligned ZnO NWs, respectively. Inset in (b) and (c) shows higher magnification images of the NRBs and NWs, respectively. (d) Magnified view of region III showing nonuniform growth of ZnO NRBs in absence of Au layer.

The vertical alignment and hexagonal facets of ZnO NRs are clearly seen by the morphological features. Interestingly, in presence of GR-Au NPs layer, dense ZnO NRs with clear hexagonal facets are formed even at 540°C. The growth of aligned ZnO NRs and NWs on graphene at this temperature is significant and it establishes the important role of graphene in the low temperature vapor phase growth of ZnO NRs hybrids with clear hexagonal facets.

Figure 6.5(e) and **(f)** show a magnified view of the images shown in **Fig. 6.5(c)** and **(d)**, respectively. **Figure 6.5(f)** along with its inset depicts that randomly oriented ZnO NWs/NRBs are formed even in the presence of Au catalyst NPs (RTA treated) on the Si/SiO₂ substrate without the graphene layer. Further, these NRs/NWs do not possess hexagonal facets, as shown in the inset of **Fig. 6.5(f)**. Morphological analysis revealed that the ZnO NRs shown in **Fig. 6.5(e)** have clear hexagonal facets and are vertically aligned with an average diameter $\sim 150 \pm 50$ nm and length of ~ 2 μ m yielding a high aspect ratio of 12 ± 2 . Dark spots on the top face of the ZnO NRs refer to the presence of Au catalyst particles and this implies a VLS growth mechanism taking place for the ZnO NWs growth.

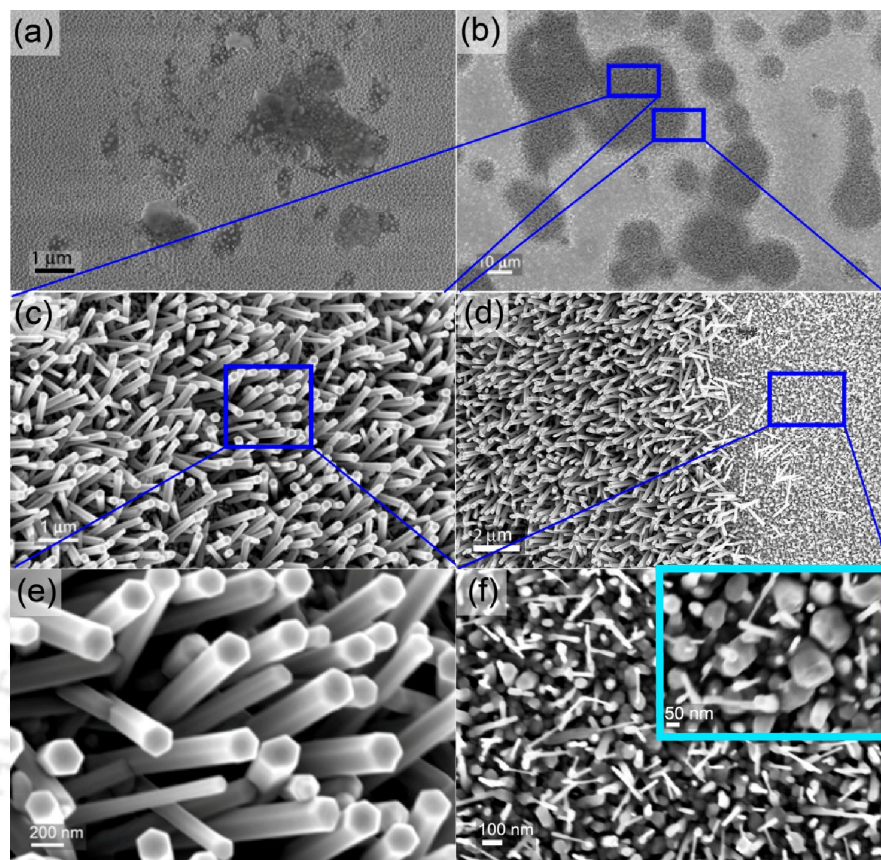


Figure 6.5: FESEM images of graphene/Au NPs (RTA treated) substrates (a) before and (b) after the growth of ZnO NRs. The region with dark (bright) contrast refers to presence (absence) of graphene layer. (c) Magnified view of the portions of (b) with graphene layer marked with boxes, depicting the growth of aligned ZnO NRs (GRZN1) with hexagonal facets on the graphene layer; (d) magnified view of a portion of (b) with and without graphene layer shown side by side. No clear NRs are formed in absence of graphene layer. (e–f) A magnified view of ZnO nanostructures shown in (c) and (d), respectively. Nonuniform NWs without any hexagonal facets can be seen in the inset of (f).

It may be noted that due to the relatively lower temperature (540°C) growth adopted here, neither Au catalyst nor graphene layer alone on a Si/SiO₂ substrate yield aligned ZnO NRs/NWs, as shown in **Fig. 6.4(b)** and **6.5(f)**, respectively. This demonstrates the superiority of GR-Au hybrid catalyst over conventionally used Au catalyst for the fabrication of vertically aligned ZnO nanostructures, such as ZnO NRs and NWs. By controlling the interaction between GR-Au film and GR-Au NPs through appropriate pretreatment conditions, it has been possible to control the morphology and orientations of the ZnO nanostructures. The areal densities of NRs and NWs in the GRZN1 and GRZN2 samples are $\sim 1.4 \times 10^9$ and $\sim 8.4 \times 10^9 \text{ cm}^{-2}$, respectively, which are larger than the earlier reports.¹⁻² The areal density was

estimated by manual counting of the average number of NWs and NRs existing within a certain area of the FESEM images at different locations of the sample. The upper portion of some of the aligned NRs look slightly bent that may be due to fluctuations in the flow of carrier/high flow rate.

6.3.1.3. Direct Growth on SiO_2 and SiO_2/Au NPs without Graphene Layer

In absence of a graphene layer, the direct growth of ZnO nanostructures on SiO_2 substrate yielded ZnO nanotetrapod like structures. However, the growth on SiO_2/Au NPs (RTA treated Au film) substrates yielded randomly oriented dense ZnO NRs/NWs as discussed before (see **Fig. 6.5(f)**). It may be noted that no aligned NRs/NWs are formed on these substrates at the present growth temperature. In essence, the relationship between substrate pre-treatment conditions and the morphology of the ZnO nanostructures can be summarized by a schematic shown in **Fig. 6.6**. This emphasizes the importance of graphene in the self-assembly of Au NPs on it and the GR-Au NPs hybrids as a versatile 2D platform for the fabrication of aligned ZnO NRs with hexagonal facets.

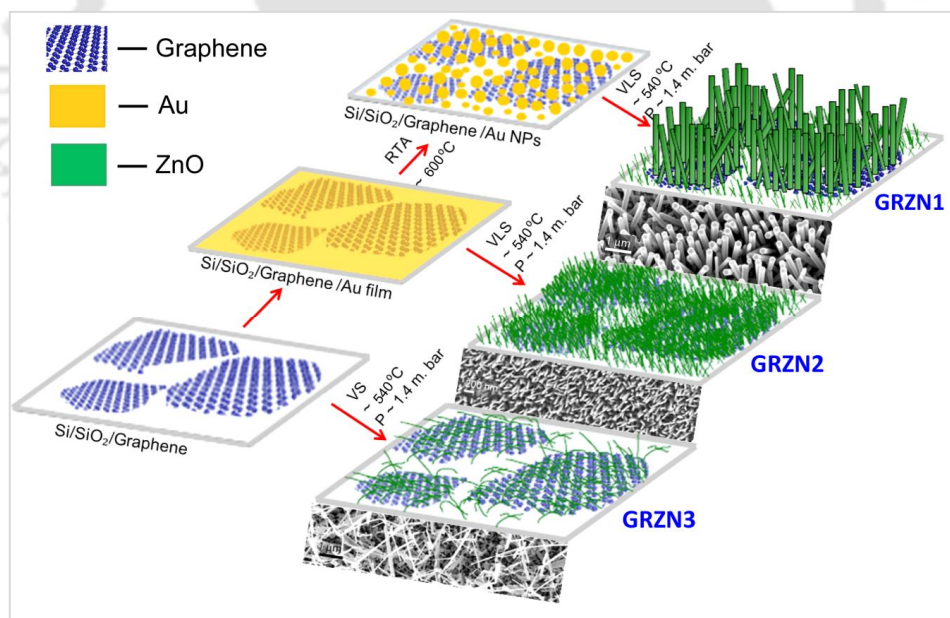


Figure 6.6: Schematic of the growth processes and resulting morphology of GR-ZnO hybrid NRs (GRZN1), NWs (GRZN2) and NRBs (GRZN3) for different substrate configurations grown by thermal vapor deposition of scheme1.

6.3.1.4. Effect of Number of Graphene Layers

The effect of number of graphene layers including graphene edges on the structure and quality of the ZnO hybrid structure are studied systematically. **Figure 6.7(a)** and **(b)** depict the ZnO NWs formation at the edges and basal plane of the multi layer graphene (MLG). **Figure 6.7(c)** and **(d)** are the high magnification FESEM images for the magnified portions of region I and II shown in the **Fig. 6.7(a)** and **(b)**, respectively. **Figures 6.7(c)** and **(d)** are the evidences for the vertical alignment and random orientation of ZnO NWs at the edges and in-plane sites of graphene, respectively. This is due to the inert nature of the sp^2 hybridized carbon atoms and strong π - π interaction on honey comb sheet, which minimize the surface energy for the incoming ZnO vapor to grow vertical NWs on it.

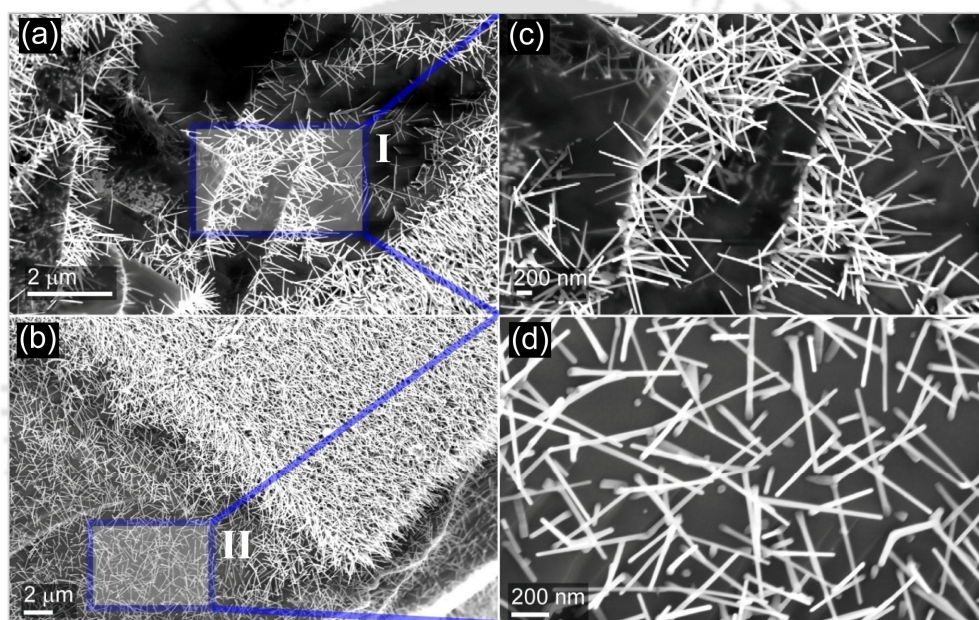


Figure 6.7: (a-b) FESEM images of ZnO NWs grown at the edges and the surface of multi-layer graphene. The dark contrast regions indicate the graphene layers. (c-d) Enlarged view of the region I and II shown in (a) and (b), respectively, significant for the vertically aligned ZnO NW growth at the edges and nanotetrapods on the basal plane of graphene.

Presence of Au catalyst or self-catalyst ZnO can overcome this problem to achieve highly aligned ZnO NWs, which we have achieved in our growth **schemes 1 and 2**, for the first time. In addition, the weak interaction of Au on surface of the MLG leads to the growth of the NWs at the edges of RTA treated GR-Au substrate. The wide variation of aspect ratio was found in the as-grown NWs/NRs with respect to the number of graphene layers. Non-uniformity of the graphene layers is one of the reasons for not growing ZnO NWs on the

basal plane of the MLG and the density of the NWs is comparatively less which proves that the MLG edges behave like nucleation sites for the growth of aligned NWs (see **Fig 6.7(b)**). Interestingly, the tip of the NWs that were grown on MLG edge does not possess hexagonal facets, while the NRs grown on GR-Au NPs substrate have perfectly hexagonal facets. This provides a clue that a close lattice matching between hexagonal ZnO and graphene body centered sites may be responsible for clear hexagonal faceted ZnO NRs on SLG and BLG. Kim et al has reported the vertically aligned ZnO nanowall formation at the step edges and kinks of the graphene layer.³ However, in case of MLG, density of NWs is less than that of the FLG. Interestingly, we have found that the substrates consisting of the SLG and BLG covered with RTA treated Au NPs have vertically aligned ZnO NRs with perfectly hexagonal facets (GRZN1). On the other hand, without the presence of graphene layer, no proper NRs are formed at the present growth temperature even in the presence of Au catalyst. In presence of SLG and BLG, dense NRs are formed. This is an important observation and it establishes the role of graphene in the low temperature vapor phase growth of ZnO NRs and NWs on graphene.

6.3.1.5. Effect of ZnO Seed Layer

In the self-catalytic growth scheme, the RTA of the ZnO thin film leads to formation of bigger grains of ZnO with improved crystallinity and the partial removal of defects in ZnO. These ZnO grains grown on the graphene layer play a crucial role in the vertical growth and alignment of the ZnO NWs. Due to similarity in hexagonal crystalline structure of graphene and ZnO, it leads to the epitaxial like growth of the ZnO NWs on graphene. **Figure 6.8** represents the FESEM image of ZnO nanostructures grown on various graphene substrates coated with ZnO seed layers, as mentioned in **Table 6.2**. **Figure 6.8(a)** and **(b)** illustrates the case of GRZ3 and Z1Z3, respectively. In the inset of the **Fig. 6.8(a)**, the vertical growth of ZnO NWs on ultrathin ZnO buffer layer (Z3) coated GR substrate is clearly visible. On the other hand, dense bundles of randomly oriented ZnO NWs can be seen on Z1Z3 substrate. This clearly indicates that GR layer below the Z3 film, which has some kind of epitaxial relation with the ZnO seed layer, promotes the growth of vertically aligned NWs. Interestingly, the ZnO NWs that were grown on GRZ3 substrate show very strong UV PL as compared to the NWs on Z1Z3 substrate. Note that the visible PL is prominent in all the as-grown ZnO NWs on graphene samples (discussed in the next chapter). The Z1Z3 and

Z2Z3 layers show similar crystalline features after RTA treatment, which is consistent with the XRD results.

6.3.1.6. Effect of Various Buffer Layers

A. GRZ3: In this case, a 10 nm ZnO seed layer is present over the graphene buffer layer for the growth of the ZnO NWs. The NWs grown on GRZ3 are relatively better aligned than those grown on Z1Z3 (**Fig. 6.8(b)**). This implies that the graphene buffer layer assists the ZnO grains in the vertical alignment of the NWs. Interestingly, the lattice mismatch between the hexagonal ZnO crystal and graphene bond centered sites is very low.⁴ This could lead to epitaxial growth of ZnO NWs on graphene. Self catalysed VLS growth of vertically aligned GaAs and InAs NWs on graphene substrates has been reported by Munshi et al.⁴ and Hong et al.⁵, respectively and it was suggested to be assisted by the strong van der Waals interactions. Our results are consistent with the above reports.

B. Z1Z3: In this case a 10 nm ZnO seed layer is present on the 300 nm ZnO layer as the bottom layer, without the graphene layer. A dense and randomly oriented ZnO NWs growth takes place on Z1Z3 (see **Fig. 6.8(b)**). This can be attributed to the large number of overlapping grains on the ZnO thin film. The buffer layer Z3 seems to have negligible effect on the NW alignment. Once again, it implies that absence of graphene layer leads to random orientation of the ZnO NWs.

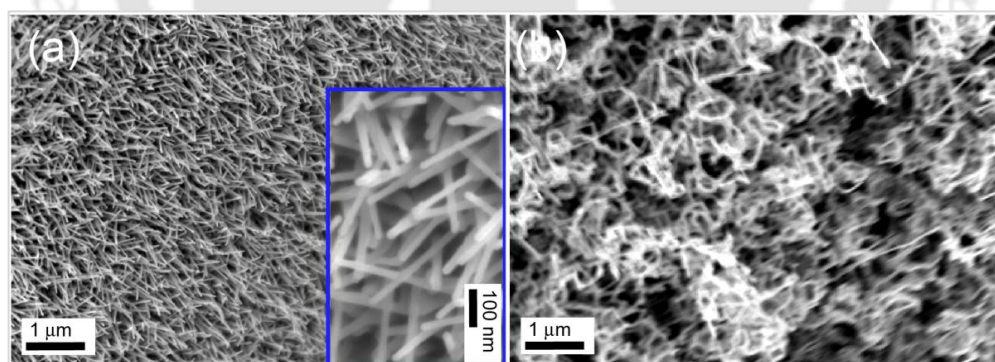


Figure 6.8. FESEM images of various ZnO nanostructures grown on different GR-ZnO and ZnO buffer layer substrates in absence of Au catalyst: (a) GRZ3NW, (b) Z1Z3NW

6.3.2. HRTEM Studies

Further, we have probed the crystalline structure and 1D orientation of the GR-ZnO hybrid NSs grown by Au-catalyst and self-catalytic growth schemes using HRTEM analysis. **Figure 6.9(a)** represents the lattice pattern of a single ZnO NW in GRZN2 sample and **Fig. 6.9(b)** shows a magnified view of region I marked in **Fig 6.9(a)** with a box. The HRTEM image clearly reveals the single crystalline lattice fringes of ZnO NW. The IFFT image shown in the inset reveals a d-spacing of 2.58 Å that is consistent with the strong XRD peak at 34.6° from the (002) plane of ZnO NR/NW.

We have also performed the HRTEM measurements on the ZnO NWs grown in the **Scheme 2**, especially on the GRZ3NW sample to understand the role of ZnO seed layer in the vertical growth of ZnO NWs. It was found that the growth of the NWs is initiated from the ZnO seed layer and no NW growth takes directly on the GR layer. This may be due to fact that graphene has very less surface energy and is a very inert material to nucleate the ZnO on its surface, assuming a low defect density. However, GR layer helps to grow the ZnO NWs vertically on the ZnO seed. It is likely that due to the presence of graphene, no planar growth takes place for the ZnO NWs. In the present case, the vertical growth of NWs can be attributed to the presence of ZnO seed on graphene layer, based on the VS growth mechanism.³ Note that, here we did not observe the growth of ZnO NWs with hexagonal facets, in contrast to the growth **Scheme 1**, where ZnO NRs/NWs were grown using Au NPs as the catalyst and ZnO seed layer.⁶ Thus, epitaxial growth is less effective in the present case.

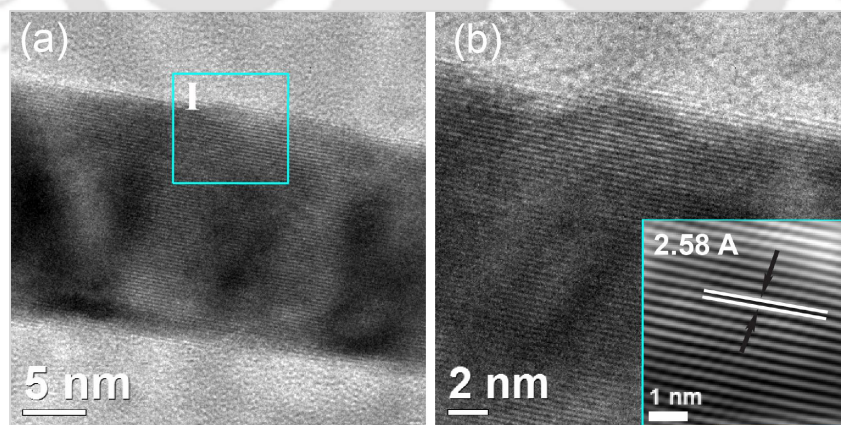


Figure 6.9: HRTEM images of GR-ZnO NWs in GRZN2 sample grown in **Scheme 1**. (a) Lattice fringes of a single ZnO NW. (b) Magnified view of region I marked in (a), depicting the clear lattice fringe for ZnO <002> plane and its d-spacing is shown as inset.

Note that ZnO NWs growth on Z1Z3 is very dense without any vertical alignment (see **Fig. 6.8(b)**). The possible explanation for this observation is that the thick ZnO layer covered with a thin ZnO layer, both have the same surface energy and the density of oxygen atoms is very high on these layers due to presence of oxygen interstitials. These excess oxygen in the substrate help in the planar growth of the NWs ⁶ resulting in no vertical alignment in the NWs. Interestingly, the direct growth of NWs on GR substrate without a ZnO layer (Z3) results in a growth of sparse ZnO NWs. Thus, in a catalyst free growth, self-catalytic seed layer is essential for the aligned growth of the NWs.

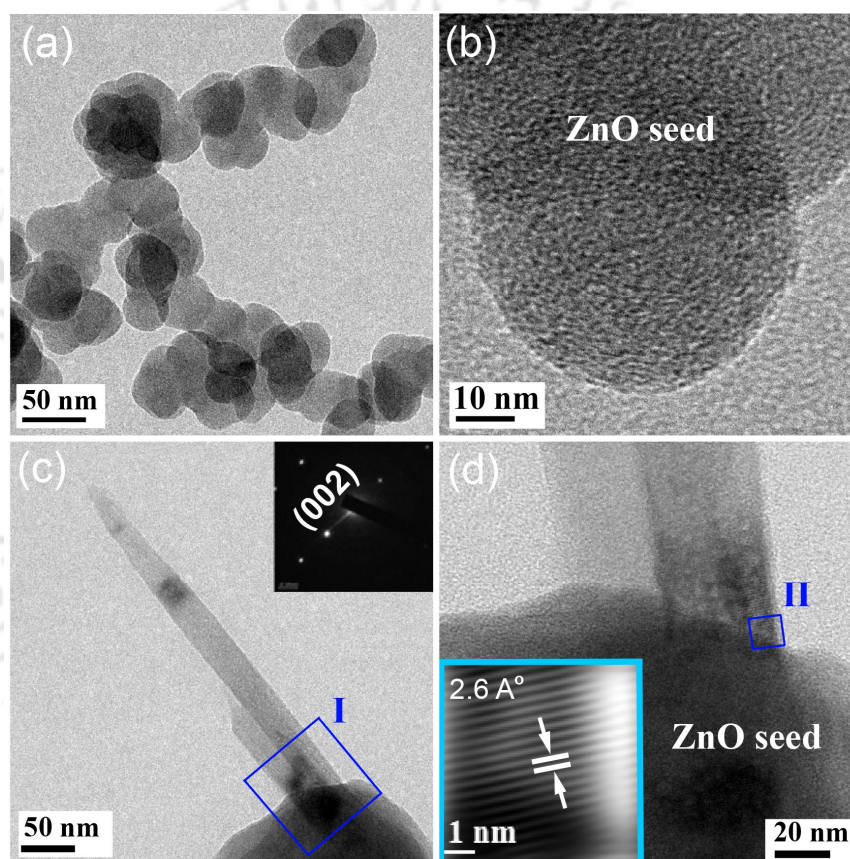


Figure 6.10. (a) TEM image of the ZnO grains grown on SiO₂ with nearly uniform size (~ 40 nm), and (b) the higher magnification TEM image of a spherical ZnO seed. (c) TEM image of a ZnO NW along with the ZnO seed layer in sample GRZ3NW and, the inset shows the corresponding SAED pattern showing (002) plane for the combined layer. (d) Magnified TEM image of region I in (c), which depicts the nucleation of the ZnO NW on ZnO seed and its corresponding lattice fringes showing (002) planes of the ZnO NW with lattice spacing of $2.6\text{\AA}$.

Figure 6.10(a) represents the HRTEM image of the ZnO grains with an average diameter ~ 50 nm. **Figure 6.10(b)** shows the lattice image of a spherical ZnO grain showing the

polycrystalline lattice fringes of ZnO crystals. Further, HRTEM results obtained for the ZnO grains are in close agreement with the XRD results. **Figure 6.10(c)** shows the ZnO NWs grown vertically on the ZnO seed and its corresponding SAED pattern showing the single crystal (002) planes. **Figure 6.10(d)** represents the magnified view of region I in the **Fig. 6.10(c)**, which clearly depicts the nucleation of NW on the ZnO seed and vertical alignment onto (002) planes. The IFFT image in the inset (magnified view of region II) shows the lattice fringes of (002) plane with d-spacing 2.6 Å that strongly supports the Raman data (discussed later).

6.3.3. X-ray Diffraction Studies

We have carried out the XRD studies on the as-grown and 700°C annealed GR-ZnO NSs grown by **Scheme 1**. **Figure 6.11(a)** and **(b)** represents the XRD pattern of the as-grown and 700°C annealed ZnO NRs (GRZN1), NWs (GRZN2), NRBs (GRZN3) on graphene and

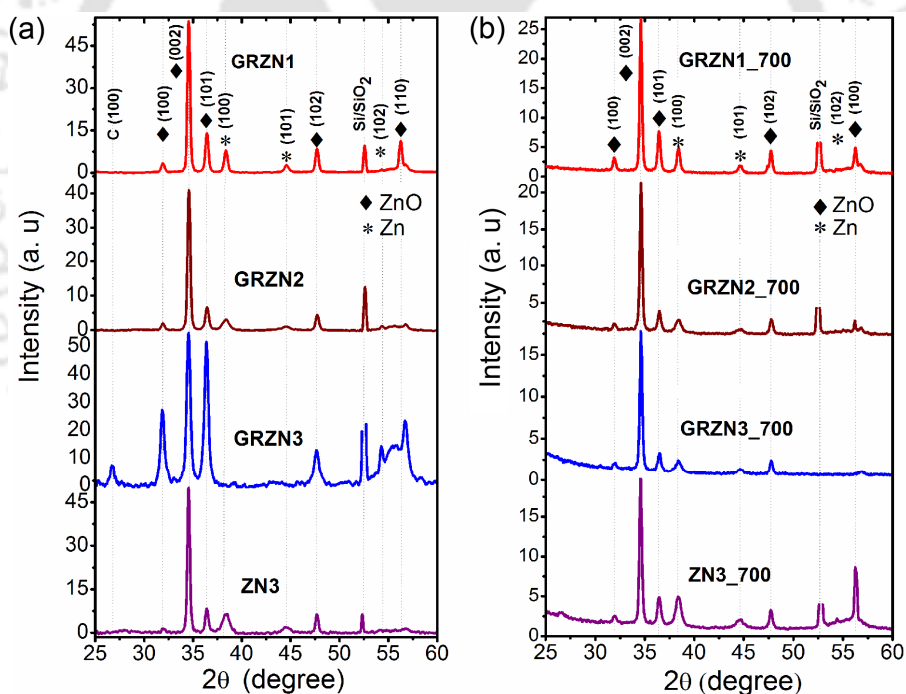


Figure 6.11. (a) XRD patterns of as-grown ZnO NWs showing c-axis orientation of the GR-ZnO hybrid NSs for different substrates grown in the **Scheme 1**. (b) XRD pattern for the post growth annealed GR-ZnO samples at 700°C in Ar atmosphere.

ZnO NWs on graphene-free SiO₂/Au substrate (ZN3). In as-grown GR-ZnO NSs (see **Fig. 6.11(a)**), the intensity of XRD peak at 34.6° from the (002) plane is high for GRZN1,

GRZN2 and ZN3 as compared to that of GRZN3. This implies that the majority of NRs and NWs are (002) or *c*-axis oriented. In case of GRZN3, peaks at 32° (100) and 36.36° (101) are prominent and reveal random orientations of NRB and this is consistent with the FESEM analysis. The weak carbon (002) peak at 26° in the sample GRZN3 originates from the few layer graphene underneath and due to partial coverage of the ZnO NRBs on the substrate, while the absence of this peak in GRZN1 and GRZN2 samples implies a full coverage of the ZnO NRs and NWs on the graphene substrate such that the graphene signal is below the detection limit. Some of the secondary peaks at 38.37° , 44.58° and 54.3° with (100), (101) and (102) orientations, respectively, arise from residual Zn metal NPs, perhaps due to the low temperature growth process adopted in the **Scheme 1**.

The sharp peak at 52.6° (002) arises from the single crystalline Si substrate. Post-growth annealing of GR-ZnO NSs improves the crystalline structure and reduces the excess oxygen and Zn related adsorbents and surface defects as evidenced from the XRD patterns shown in the **Fig. 6.11(b)**. XRD patterns of annealed samples are quite identical to the as-grown ZnO NSs in all the samples except GRZN3_700, in which the secondary peaks of ZnO at 32° (100) and of Zn at 38.37° (100), 44.58° (101) and 54.3° (102) are considerably reduced, while 34.6° (002) remains same. This signifies that the crystalline quality of all the GR-ZnO hybrids is improved after post-growth annealing, which is consistent with the PL results (will be discussed in the next chapter).

6.3.4. Micro-Raman Studies

The crystalline quality of GR-ZnO hybrids grown by **Scheme 1** and **Scheme 2** was further confirmed from the micro-Raman spectroscopy on different graphene substrates based on the peak position, relative intensities and full width at half maxima (FWHM– $\Delta\omega$) of the Raman spectra. **Figure 6.12** illustrates the comparative Raman spectra of all the ZnO NR, NW and NRB samples. The Raman spectrum shows a peak at $\sim 440\text{ cm}^{-1}$ that are grown in the **Scheme 1**, while for the **Scheme 2** it is at $\sim 438\text{ cm}^{-1}$, which corresponds to the $E_2^g(\text{high})$ mode of ZnO NSs significant for the Wurtzite phase. The position of $E_2^g(\text{high})$ and FWHM values have been calculated from the Gaussian peak fit that are labelled in the **Fig. 6.12**. Note that the FWHM of $E_2^g(\text{high})$ mode in the ZnO NSs grown in **Scheme 1** is relatively lower than that of the **Scheme 2** on various graphene substrates. This is in contrast to the strong UV

peak in the PL spectrum (discussed later) indicating a better crystallinity of the ZnO NSs grown in the **Scheme 2**. Note that Z1Z3NW shows relatively lower FWHM indicating better crystallinity of the ZnO NWs. This may be due to the contribution of thick ZnO buffer layer with Raman spectrum. Thus it can be concluded that the ZnO seed layer with GR buffer layer promotes better crystallinity. On the other hand, Au catalyst mediated growth GR-ZnO NSs such as GRZN1, GRZN2 and GRZN3 also have lower FWHM ($\Delta\omega = 8\text{cm}^{-1}$) as compared to the catalyst free growth of ZnO NSs on graphene, which implies the more vertical alignment along c-axis of the ZnO NRs and NWs on GR-Au catalyst substrate. This highlights the superiority of ZnO NSs grown on GR-Au catalyst. However, the Raman signal of graphene is not detected in any of the samples,

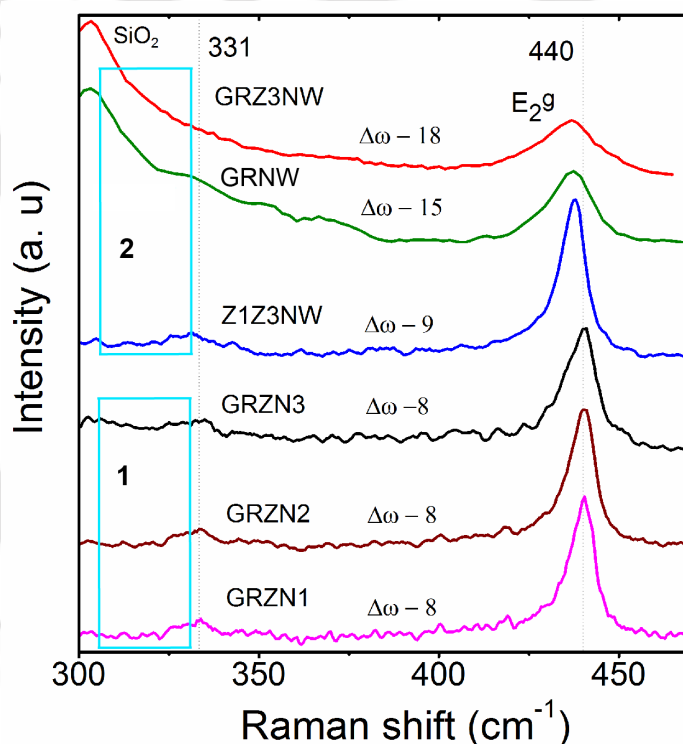


Figure 6.12: Typical Raman spectra of GR-ZnO hybrids grown by Scheme 1 and Scheme 2 are showing a strong E_2^g mode at 440 cm^{-1} , respectively, which indicates the growth of crystalline ZnO NSs with wurtzite structure in both the schemes. Note that the peak positions and FWHM ($\Delta\omega$) are denoted in cm^{-1} unit.

perhaps due to the dense coverage and long NRs/NWs. To confirm the presence of graphene in these samples, we performed the Raman measurements on GRZ3 substrate which we have

discussed in the previous section (see **Fig. 6.2(a)**). E_2^g (high) in GRZ3 reveals the presence of ZnO on the GRZ3 substrate as shown in **Fig. 6.2(b)**.

6.4. Growth Mechanism in Scheme 1

In order to elucidate the growth mechanism of vertically aligned ZnO NRs, NWs and NRBs, individual effect of graphene layer and Au catalyst layers was systematically studied by FESEM, HRTEM and micro Raman analysis. As shown in the schematic of **Fig. 6.6**, vertically aligned ZnO NRs with hexagonal facets are formed with the combined effect of graphene and Au NPs. According to an earlier report, there is no formation of ZnO nanowalls even for high density of Au NPs on graphene.⁷ The novelty of growing well aligned ZnO nanostructures on graphene at a lower temperature in our experiment is the substrate conditions that were different from previous studies. In Chapter 4, we have discussed the defect mediated interaction of Au clusters with graphene before and after RTA treatment based on Raman line shape and HRTEM analysis.

We believe that during the RTA treatment of the substrate at 600°C in Ar atmosphere, Au atoms migrate and segregate at the defect sites to form Au clusters and dewetting (liquid and solid) may be higher adjacent to graphene defects sites. Indeed, we observe distinctly different behavior of Au clustering on SiO₂ substrate and SiO₂/graphene substrates coated with Au layer during the RTA process (see **Fig. 4.12(c) and (d) in Chapter 4**). Spherical Au nanoparticles are formed in the former case, while nonspherical or dumbbell shaped bigger Au NPs are formed in the latter case. The increase in intensity of D band as compared to that of G-band after Au deposition also indicates a plasmonic enhancement of the Raman intensity caused by preferential clustering of the Au atoms specifically at the defect sites in graphene. This provides a very important clue to the crucial role of defect sites on the graphene layer in the catalytic growth of highly aligned ZnO NRs and NWs hybrids. Note that some of the Au atoms may diffuse through the graphene⁸ and form chemical bonds with carbon atoms of graphene as longer Au–C bonds⁹ and this may be responsible for the dumbbell shaped Au NPs. Shape deformation and larger dimension of the Au NPs clearly indicate that large number of Au atoms migrate and cluster preferentially at the defect sites, driven by the dewetting behavior of Au on the graphene layer¹⁰ and for energy minimization of the hybrid system. Due to the dewetting behavior of graphene, bigger size Au NPs form at

the defect sites and highly aligned ZnO NRs and NWs are formed at these sites depending on the density of Au NPs.

FESEM image analysis shows that areal density of Au NPs and ZnO NWs on the SiO₂ substrate (without graphene layer) are ~ 117 and $110 \mu\text{m}^{-2}$, respectively. Thus, there is a one to one correspondence between the density of ZnO NWs and the density of Au catalyst on the SiO₂ substrate. In presence of graphene layer, areal density of Au NPs is reduced to $\sim 25 \mu\text{m}^{-2}$ due to bigger size clusters and ZnO NRs grown over it has a density of $\sim 15 \mu\text{m}^{-2}$. Thus, again there is a one to one correspondence between the density of ZnO NRs and density of Au NPs grown on graphene. This reduced density of Au NPs on graphene layer is dictated by the thickness and dewetting behavior of graphene and the density of defects in the graphene layer. Interestingly, Raman analysis shows that average areal density of defects in pristine graphene and GR-Au hybrid layer is in the range 490–860 and 3985–4950 μm^{-2} , respectively. It implies a nearly six-fold increase in defect density after Au deposition by sputtering. On the other hand, Au NP density is only about 5% of the graphene defect density, which is limited by the thickness of the Au layer deposited. Thus, the density of ZnO NRs and NWs are lower than the density of defects and density of Au NPs, as expected.

Further, we noticed a change in the binding energy and increase in the FWHM of C-1s XPS spectrum of graphene before and after Au deposition on graphene (See **Table 4.2** in **Chapter 4**). This signifies a covalent bonding between foreign atoms and graphene¹¹ and structural disorder due to longer Au–C bond length than the C–C bond length in graphene. Due to the higher sticking coefficient of ZnO with Au NPs and lower sticking coefficient with pristine graphene⁷, Zn vapor droplets along with the oxygen migrate from the graphene surface towards most favorable liquid Au droplets; as a result vertically aligned ZnO NRs/NWs were formed by catalytic VLS growth process. In case of Au film on graphene substrate, dense ZnO NWs grow due to the larger density of Au islands on graphene with smaller diameter that makes VLS growth of ZnO NWs with diameters less than 100 nm. Indeed, VLS mechanism of growth is confirmed here from the presence of Au droplets on the tip of the ZnO NRs, as found from FESEM image of the NRs (**Fig. 6.5(e)**). On the other hand, direct growth on graphene substrate follows the VS mechanism, because large quantity of Zn migrates on the surface of the graphene with very low sticking coefficient and continuous supply of Zn leads to Zn adsorption followed by dewetting resulting in randomly

oriented ZnO NRs. Interestingly, the lattice mismatch between the hexagonal ZnO crystal and graphene bond centered sites is very low.⁴ This could lead to epitaxial growth of ZnO NRs on graphene and this is likely to be responsible for the growth of hexagonal faceted ZnO NRs in presence of Au NP catalyst⁴⁻⁵ Munshi et al.⁴ demonstrated epitaxial growth of vertically aligned GaAs NWs on few-layer graphene by the self-catalyzed VLS technique using a molecular beam epitaxy. Hong et al.⁵ showed that high-quality graphene is critical for obtaining vertically well-aligned InAs NWs on graphene substrate with strong van der Waals interaction. However, our results demonstrate that self catalytic growth on graphene layer in absence of Au catalyst does not yield aligned ZnO NWs. It has been pointed out that the perfect epitaxial relation of Au (111) with graphene (002) forces the Au NPs to bind with

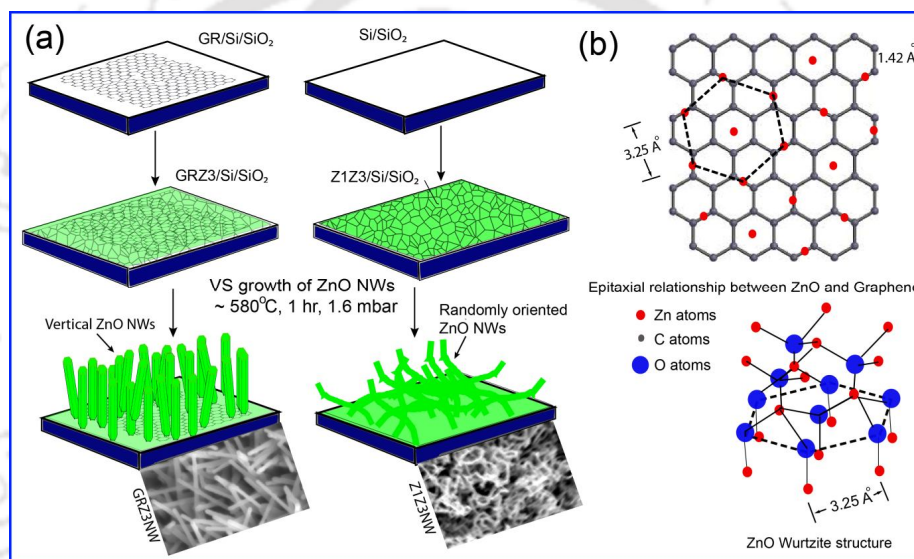


Figure 6.13: (a) A schematic of the growth mechanism of self catalytically grown ZnO NWs on GRZ3 and Z1Z3 substrates in **Scheme 2**. (b) The epitaxial relationship between ZnO in its Hexagonal Wurtzite phase and the bond centered sites of sp^2 hybridized graphene layer.

the graphene layer and aids the growth process¹⁵. We believe that clear hexagonal facets of the as-grown ZnO NRs in presence of graphene may be caused by the hexagonal arrangement of carbon atoms in graphene lattice. During the growth, semiconductor atoms can adsorb above the centre of the hexagonal carbon rings (H- site) or above the bridge between two carbon atoms (B- site), as discussed by Munshi et al.⁴ Thus, the presence of Au catalyst direct the aligned growth of ZnO NRs, while the hexagonal carbon ring in graphene helps to attain a hexagonal facet of the ZnO NRs. Note that due to a relatively low

temperature growth process adopted here, self catalytic growth may be less efficient and as a result, unreacted Zn and O remain in the final product. Nevertheless, the demonstration of graphene assisted low temperature growth of high quality ZnO NRs and NWs on graphene is a significant step in the fabrication of integrated optoelectronic devices involving two powerful optical materials, namely, graphene and ZnO nanostructures.¹² We will demonstrate the graphene enhanced UV photodetection from GR-ZnO hybrid NSs in the next chapter.¹³

6.5. Growth Mechanism in Scheme 2

Note that in Scheme 2, Au catalyst is not used during the growth process. Based on the results obtained in the growth **Scheme 2** in comparison with **Scheme 1**, we proposed the mechanism of self catalytic growth of ZnO NWs on graphene substrate, as shown in the **Figure 6.13**. **Figure 6.13(a)** is a schematic representation of the morphology of the ZnO NWs grown on both GRZ3 and Z1Z3 substrates. In absence of Au catalyst vapor solid (VS) growth mechanism is believed to takes place. When VS growth of ZnO NWs is performed simultaneously on both substrates, well aligned ZnO NWs are formed in the case of GRZ3 substrate, while dense and randomly oriented ZnO NWs are formed in the case of Z1Z3 substrate as noted before. FESEM image for each case is also been included for comparison. Our results, indicates that the presence of graphene promotes the vertical alignment in ZnO NWs. The mechanism behind this can be understood from **Fig. 6.13(b)** which shows the epitaxial relationship between ZnO in its hexagonal Wurtzite phase and bond centered sites of C-C bonds present in the sp^2 hybridized graphene layer. The red shift (13 cm^{-1}) of 2D band in the Raman spectra of GRZ3 substrate supports our assertion on the strong interaction between the GR and ZnO layers and the artificial lattice matching (see **Fig. 6.2(a)**), which results in the growth of aligned ZnO NWs.

6.6. Summary

In this chapter we have demonstrated a new growth strategy for the graphene assisted controlled fabrication of well aligned 1D ZnO nanostructures such as NRs, NWs and NRBs at a relatively low temperature on single and few-layer graphene. A Systematic study on the specific role of graphene, Au catalyst and ZnO seed layer in the growth of vertically aligned ZnO NRs and NWs were undertaken to understand the growth mechanism. It was revealed

that the combined effect of the graphene with Au NPs and ultra-thin ZnO seed layer leads to the formation of high quality well aligned ZnO NRs and NWs, while direct growth on graphene substrate yielded randomly oriented ZnO NRBs and nanotetrapods.

Detailed analysis of microstructure and crystalline quality of GR-ZnO hybrids involving HRTEM, micro-Raman spectroscopy, X-ray diffraction techniques were presented. The important findings of this chapter are summarized below.

1. Various types of ZnO NSs were grown on single layer graphene using PVD technique with Au catalyst and catalyst free growth methods and the growth mechanism was elucidated for the first time.
2. The crucial role of in-plane defects in the pristine graphene and clustering of Au atoms at the defect sites on the growth of highly crystalline ZnO NRs/ NWs with clear hexagonal facets was investigated from HRTEM and micro Raman techniques. We believe that hexagonal faceted ZnO NRs results from the epitaxial growth of NRs on the graphene bond centered sites and Au NPs catalyze the vertical growth.
3. Catalyst free growth of ZnO NWs on ZnO seed layer substrates in the presence/absence of graphene layer was successfully demonstrated. Dense array of aligned ZnO NWs was formed in the case of RTA treated ZnO ultra-thin film on graphene, while the absence of graphene yield randomly oriented sparse ZnO NWs.
4. HRTEM and micro-Raman studies revealed the good crystalline quality of the ZnO NWs grown on GR-ZnO buffer layer substrate in comparison with ZnO NWs grown on ZnO seed layer substrates.
5. A growth mechanism was proposed based on the artificial epitaxial relationship between ZnO crystals and graphene.

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Photoluminescence and Photoconductivity Studies on Graphene-ZnO Hybrid Nanostructures

In this chapter, we discuss the results of UV-vis absorption, photoluminescence (PL) and photoconductivity (PC) studies on GR-ZnO nanostructures (NSs). Role of graphene on the enhanced UV-visible PL from as-grown and annealed (500 and 700 °C) ZnO NRs, NWs and NRBs under vacuum and Ar gas atmosphere was investigated to explore the origin of various visible and NIR PL emissions from GR-ZnO hybrid NSs. Graphene enhanced UV photodetector (PD) with GR-ZnO NW hybrids was demonstrated that shows superior UV sensitivity of the order of 10^2 as compared to that of bare ZnO NWs. A GR-ZnO thin film UV PD was fabricated to evaluate the enhancement of photocurrent in ZnO film due to the underlying graphene layer. High responsivity (1100×10^3 A/W) was achieved from the cyclic photoresponse measurements at different bias voltages with UV ON/OFF conditions. We evaluated various device parameters such as response time, responsivity and PC gain in self-catalytically grown GR-ZnO NWs and bare ZnO NWs as well GR-ZnO thin film hybrids.

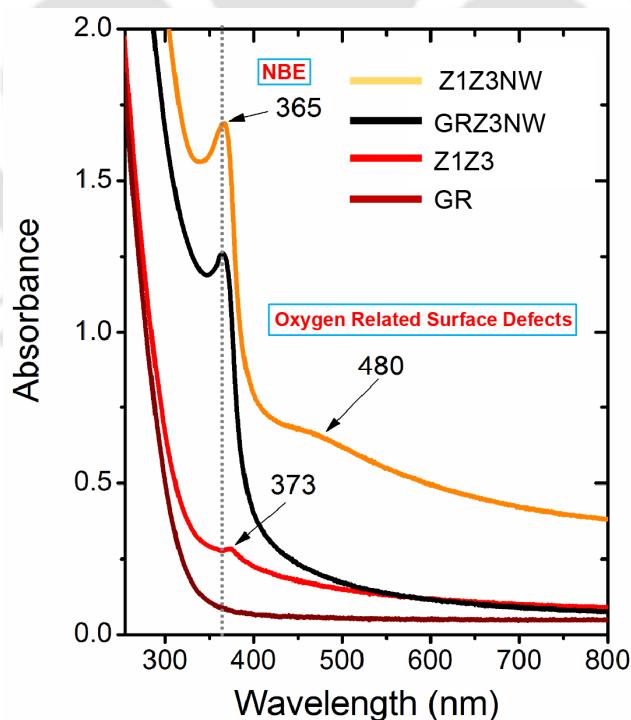
7.1. Optical Absorption Studies

In-order to estimate the strong interaction of ZnO and graphene directly, we have presented the optical absorption measurements of catalyst free grown ZnO NWs on graphene (**Scheme 2**). Note that the details of the GR-ZnO Hybrids grown by **Scheme 1** and **Scheme 2** are shown in the **Table 7.1**. GR-ZnO Hybrids are grown on the quartz substrates for the absorption measurements. **Figure 7.1** represents the absorption spectra of ZnO NWs grown on thick ZnO seed layer (Z1Z3) and ultra-thin ZnO seed layer coated on the graphene (GRZ3) transferred on to quartz substrates. The absorption spectra of pristine graphene (GR) and Z1Z3 substrates are also shown for the comparison. After the growth of ZnO NSs on graphene, a very strong absorption peak at ~ 365 nm is clearly visible, which implies the growth of vertical ZnO NWs. On the other hand, GR and Z1Z3 substrates show no significant UV absorption and a very weak UV absorption band at 373 nm, respectively. The UV absorption band intensity is significantly higher by a factor of 6 and 10 in GRZ3NW and Z1Z3NW, respectively when compared with Z1Z3. The high UV absorption may be due to

Table 7.1: Details of the substrate and morphology of the resulting ZnO nanostructures grown by Scheme 1 and Scheme 2.

Scheme	Sample code	Base Substrate	Description of Substrate	ZnO nanostructures
Scheme 1	GRZN1	SiO ₂	Graphene/AuNP, RTA	NRs, aligned, hexagonal
	GRZN2	SiO ₂	Graphene/Au film	NWs, aligned
	GRZN3	SiO ₂	SiO ₂ /graphene	NRBs, random
	ZN3	SiO ₂	Au NP, RTA	NWs, random
Scheme 2	GRZ3NW	SiO ₂ , Quartz	10 nm ZnO on graphene, RTA	Vertical NWs
	Z1Z3NW	SiO ₂ , Quartz	10 nm ZnO on 300 nm ZnO layer, RTA	NWs, Random
	GRNW	SiO ₂ , Quartz	Graphene layer only	Sparse NWs, Random

the large surface area and dense array of ZnO NWs. The absorption data is consistent with the enhanced UV PL emission and PC from the GR-ZnO NWs hybrids (discussed later). Note that there is an additional broad absorption band identified in the visible region centred at ~ 480 nm in Z1Z3NW sample, which is attributed to the oxygenated defect (either oxygen vacancy (V_o) or oxygen interstitials (O_i)) states that are formed due to the low temperature PVD growth.¹

**Figure 7.1:** Comparison of absorption spectra for ZnO NWs grown on graphene and ZnO coated quartz substrates. For comparison, spectra of GR and ZnO film prior to the growth of NWs are shown. The absorption peaks are denoted in nm unit. Note that these samples are prepared by the Scheme 2.

We discuss the UV-visible PL properties of the as-grown GR-ZnO NSs such as NRs, NWs, NRBs and ZnO NWs grown on SiO₂ substrates that were fabricated based on the Au-catalyst and self-catalytic growth processes (**Scheme 1** and **Scheme 2**) in the following sections. Further we present the effect of annealing at two different temperatures at 500 and 700°C in Ar gas atmosphere on UV-visible-NIR PL characteristics of GR-ZnO hybrids.

7.2. UV-visible Photoluminescence Studies

7.2.1. Graphene-ZnO Hybrids Fabricated in Scheme 1

Optical properties of the as-grown GR-ZnO NSs were investigated by PL spectroscopy. **Fig. 7.2** represents the room temperature PL spectra of as-grown GR-ZnO NSs in GRZN1, GRZN2, GRZN3 and ZN3 samples with 325 nm laser excitation. The symbols refer to the experimental data and the solid lines correspond to the Gaussian peaks fitted with the experimental data. In each case, the UV peak at ~ 375 nm is due to the near band edge (NBE) emission from ZnO and the broad visible band centered at ~ 500 nm arise from the defects in ZnO nanostructures.

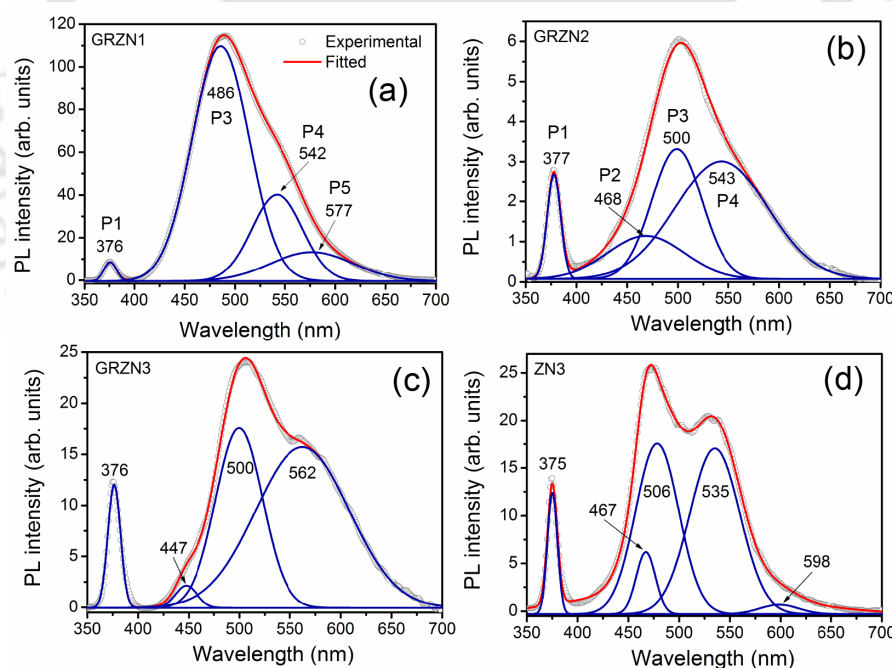


Figure 7.2: Room temperature PL spectra of as-grown GR-ZnO hybrid nanostructures fabricated by **Scheme 1**: (a) GRZN1, (b) GRZN2, (c) GRZN3 grown on graphene layer, (d) ZnO NWs grown without graphene layer (ZN3). Solid blue lines are the Gaussian curves fitted to the experimental data (symbols).

Due to the asymmetry in the line shape of PL spectra, multiple peaks are fitted with Gaussian line shape and the **Table 7.2** summarizes the peak parameters extracted from the fitting for as-grown samples. The possible identities of each peak are also mentioned in the **Table 7.2**,

based on our observations and the literature reports. The sharp NBE peak varying between 375 and 378 nm is significant in all the samples and it is due to the free excitonic transition. The intensity of the UV peak is nearly equal in GRZN1, GRZN3, and ZN3, while it is about 5 times lower in GRZN2. On the other hand, the visible band is strongest in GRZN1 and weakest in GRZN2. Note that the center of the visible PL peaks differs from sample to sample, though the UV peak position remains unchanged. Strong and sharp UV peak in these samples indicates reasonably good crystalline quality of the as-grown ZnO NRs, NWs and NRBs. The broad peak in the visible region is well known for the intrinsic defects in ZnO, such as oxygen vacancies (V_o),² deep interstitials of oxygen (O_i)³ or Zn (Zn_i) and antisite oxygen (O_{Zn})⁴⁻⁵ that may be formed on the surface of the ZnO nanostructures during the growth process. In the as-grown ZnO nanostructures, several green and yellow emissions were identified at different wavelengths, as shown in the **Table 7.2**.

Table 7.2: Details of the PL peaks fitted with Gaussian line shape for the near band edge (NBE) and defect emissions for as-grown GR-ZnO NSs grown by **Scheme 1**. The center of each peak (P1, P2 and P3) is denoted in nm unit. A21, A31, A41 and A51 denote the ratio of integrated intensity of peak P2, P3, P4, P5 to peak P1, respectively.

Sample	As-grown								
	P1	P2	P3	P4	P5	A21	A31	A41	A51
GRZN1	376	–	486	542	577	–	55.5	18.2	9.9
GRZN2	377	468	500	543	–	2.3	4.6	7.73	–
GRZN3	377	447	500	–	562	0.3	5.37	–	9.57
ZN3	375	467	506	535	598	3.87	0.97	6.77	0.3
Identity	NBE	V_{Zn}^{2-}	V_o/V_{Zn}	O_i/O_{Zn}	Deep O_i				

In the present case, the samples were grown at a relatively low substrate temperature (540°C) with a Zn source in presence of oxygen flow. Thus, O_i and V_{Zn} are more likely to be present in these samples, contrary to the usually reported V_o defects in ZnO nanostructures. Interestingly, recent calculation predicts that the sequence of formation energy of defects in ZnO is $V_{Zn} < O_i < O_{Zn} < V_o$ at low growth temperatures.⁵ Based on the earlier reports and the XPS analysis (discussed later) on the ZnO NWs/NRs, the PL peak arising in the range 447-468 nm in different samples may be attributed to the doubly ionized Zn vacancies (V_{Zn}^{2-})⁴⁻⁵. Note that the as-grown GRZN1 does not exhibit this peak. The PL peak observed in the range 483-506 nm is the commonly observed green emission from the vapor deposited ZnO

NWs. Theoretical calculation on the defect formation of ZnO shows that the origin of strong green emission is likely to be either V_o or V_{Zn} .^{4, 6-8} Most of the previous experimental reports suggested that the origin of this emission could be the recombination of photo generated holes with the electrons belonging to V_o states on the surface of the NWs.^{6, 9} Thus, the PL peak observed in the range 483-506 nm is tentatively attributed to the V_o states. On the other hand, the PL peaks in the range of 528–543 nm arise from deep level defects, either O_{Zn} or neutral O_i .^{3, 5, 10} Further, the observed yellow emission in the range of 561–598 nm may be attributed to the ionized O_i induced transitions.¹⁰ Note that under the present growth conditions, deep interstitial defects are expected in ZnO along with the oxygen vacancy related surface defects. Due to large surface area of the ZnO NWs and NRs, the surface states related visible PL is significant in these samples, despite a good crystalline core as evidenced by the XRD and HRTEM analysis discussed in **Chapter 6**. Willander et al reported strong UV and visible PL from highly crystalline aligned ZnO NRs grown on p-4H-SiC by vapor deposition method. They went on to demonstrate white light emitting diodes based on these ZnO NRs.¹¹ Though there have been debate regarding the origin of various visible peaks, it has been suggested that different samples have different defect configurations due to different growth conditions. The peak profile of the defect emission band is dependent on the relative density of the radiative defects. It has been reported that ZnO can exhibit different emissions in the visible range including violet, blue, green, yellow, and orange-red, which are associated with intrinsic and extrinsic defects in the material.¹¹

7.2.2. Graphene-ZnO Hybrids Fabricated in Scheme 2

UV and visible PL studies are conducted for the as-grown and RTA treated ZnO NWs samples by room temperature PL measurements at 325 nm excitation. Note that we have not observed any significant change in the UV and visible PL spectra after the RTA treatment of the ZnO NWs as compared to the untreated NWs. Hence, for further discussions the PL data are presented for the RTA treated samples. **Figure 7.3(a-c)** illustrates the PL evolution in ZnO NWs grown on graphene and ZnO seed layer substrates and the corresponding Gaussian fitting components for UV and visible emissions. Note that the PL spectra is acquired at an excitation wavelength 325 nm. The Symbols represent the experimental data, while the solid lines correspond to the fitted data. The PL spectra show a sharp UV emission peak at 380 nm attributed to the near band edge (NBE) emission and a broad visible emission band centered at ~ 500 nm in self catalytically grown GR-ZnO NSs. It is interesting to note that the ratio of

Table 7.3: Details of the PL peaks fitted with Gaussian line shape for the near band edge (NBE) UV emission and defect related visible emissions for each sample. The center of each peak (P1, P2, P3, P4 and P5) is denoted in nm unit. A12, A13, A14 and A15 denote the ratio of integrated intensity of peak P1 to P2, P3, P4 and P5, respectively.

Sample Code	UV PL	Visible PL peaks				Ratio of UV/Visible PL intensity		
	P1	P2	P3	P4		A12	A13	A14
Z1Z3NW	382	493	536	584		1.2	0.5	0.7
GRZ3NW	382	499	538	580		1.3	0.6	0.4
GRNW	382	494	532	573		0.07	0.03	0.03
Identity	NBE	V_o / V_{Zn}	O_i / O_{Zn}	Deep O_i / O_i^-				

integrated intensity of UV to visible PL is relatively high in both Z1Z3NW and GRZ3NW as compared to GRNW sample. The integrated intensities and the ratios of UV and visible PL for all the samples are shown in the **Table 7.3**. This implies that the crystalline quality of the NWs grown on GRZ3 substrate is significantly high. Note that the density of the NWs is high in case of Z1Z3NW and the substrate ZnO thick layer may contribute to the UV and visible PL. Thus, randomly oriented ZnO NWs in Z1Z3NW may not possess high crystalline quality, though the observed PL intensity is comparable to that of the aligned NWs grown on the graphene layer.

Further, a comparative analysis was made on the PL data to understand the effect of ZnO seed layer (Z3), thickness of the ZnO buffer layer (Z1), graphene (GR) layer on the PL efficiency of the ZnO NWs from Gaussian fitting analysis. The visible PL features are found to be similar in all the cases and intensity is very high in GRNW sample as compared to GRZ3NW and Z1Z3NW samples. Presence of Z3 layer leads to a sharper and intense UV peak with a lower intensity visible band in GRZ3NW and Z1Z3NW samples. Thus, the Z3 layer plays a crucial role in the catalyst free growth of ZnO NWs. Due to the dissimilar peak positions and asymmetric line shape, UV emission was peaked at 382 nm and three PL peaks were fitted for the broad visible emission band in each case. As compared to the GRNW, the intensity of UV PL in Z1Z3NW and GRZ3NW is higher by a factor of 17 and 3, respectively (**Fig. 7.3(a)** and **(b)**). Higher intensity UV PL in Z1Z3NW is most likely due to the contribution of the thick ZnO seed layer in the UV PL. On the other hand, in GRNW the integrated intensity of the fitted visible peaks at ~ 494 , 532 and 573 nm are higher as compared to Z1Z3NW and GRZ3NW, which signifies more number of oxygenated defects (V_o/O_i) in the ZnO NWs due to the absence of Z3 layer (see **Fig. 7.3(c)**). Note that the two visible PL peaks at ~ 530 and 580 nm are common in all the samples, which signifies the

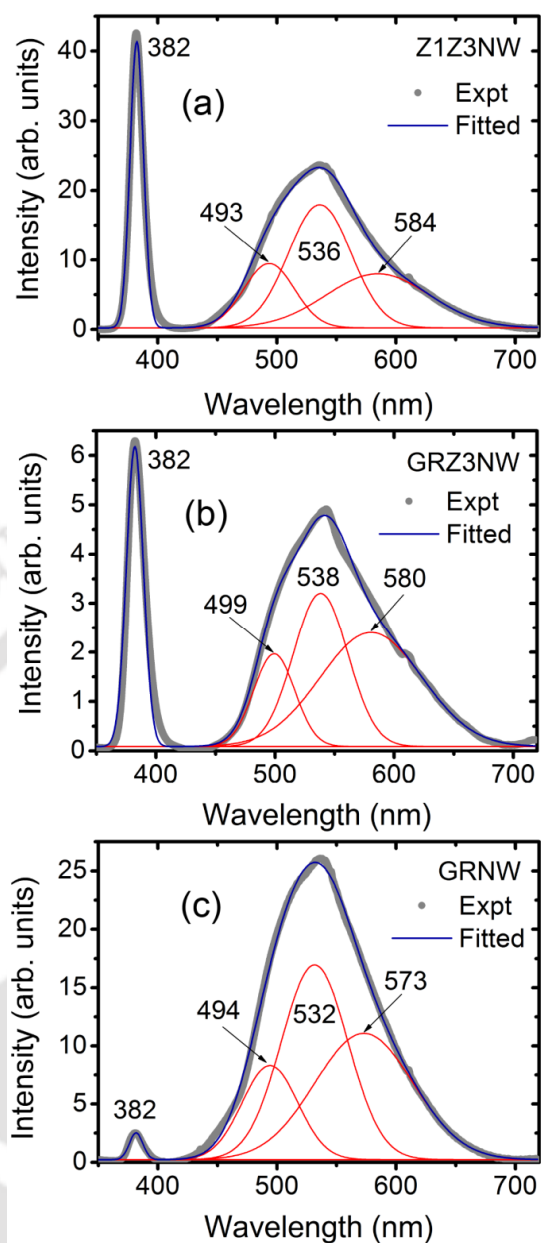


Figure 7.3: PL characteristics of self catalytically grown ZnO NWs on graphene in (Scheme 2) and their Gaussian line shape fitting: (a) Z1Z3NW, (b) GRZ3NW, and (c) GRNW. The symbols represent the experimental data and solid lines correspond to the fitted data. The peak centers are denoted in nm unit.

formation of neutral O_i defects.⁴ Nevertheless, Z1Z3NW and GRZ3NW samples have strong UV emission and relatively lower intensity of visible emission. The detailed peak parameters and possible assignments of the defect emissions are presented in **Table 7.3**.

7.2.3. Effect of Annealing on UV-visible-NIR Photoluminescence

Here, a systematic study on UV, visible and NIR PL characteristic of GR-ZnO NSs was performed after annealing at 500 and 700°C in Ar gas atmosphere. Note that the NIR PL studies was performed only for the ZnO NRs and NWs grown on graphene.

7.2.3.1. UV-visible Photoluminescence

Figure 7.4(a-f) illustrates the effect of post-growth annealing at 500 and 700°C on the PL spectra of the ZnO NSs. The solid lines represent the Gaussian line shape fittings to the experimental PL spectra. We notice a significant improvement in the intensity of UV as well

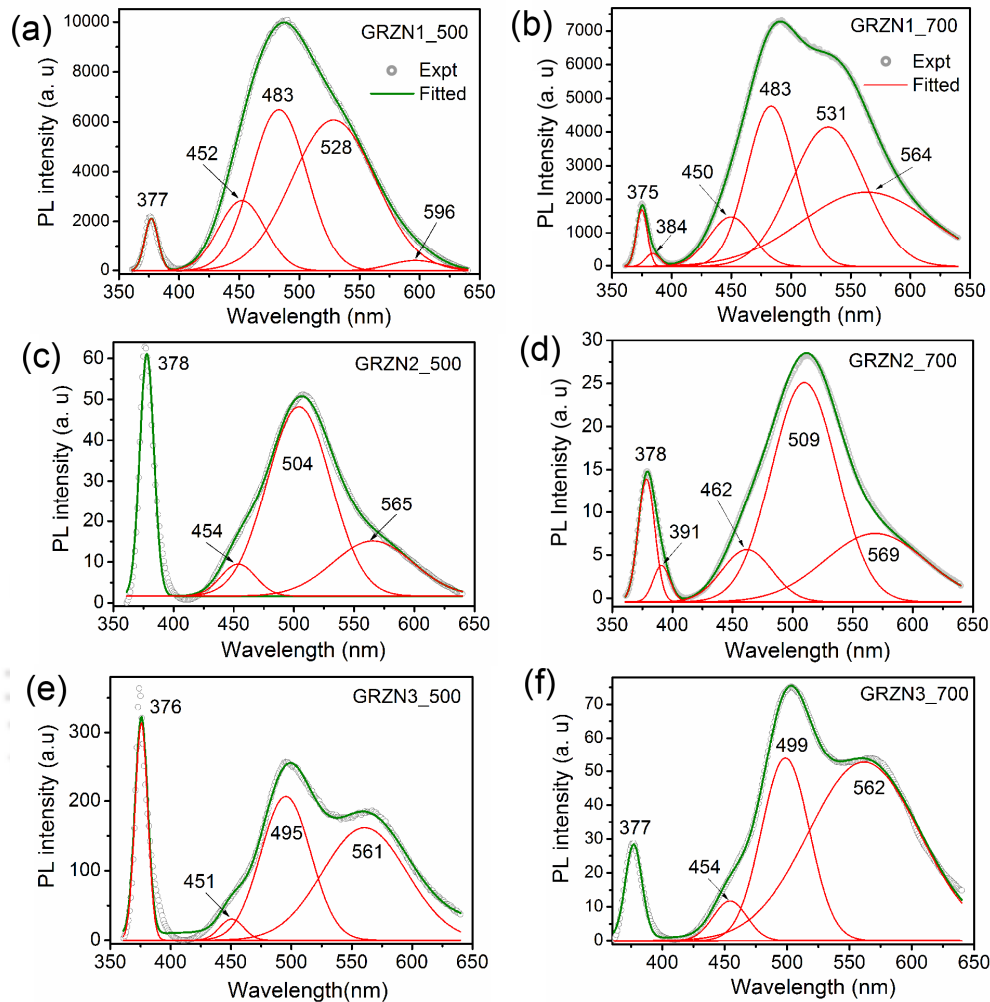


Figure 7.4: PL spectra of GR-ZnO hybrid systems after post-growth annealing at 500°C and 700°C: (a-b) NRs (GRZN1), (c-d) NWs (GRZN2), (e-f) NRBs (GRZN3) hybrids. Gaussian fitted peaks are shown with solid lines with peak centres in nm unit.

as visible PL, though no significant shift in the NBE emission occurs after the annealing. In case of GRZN1, the NBE PL intensity is enhanced by more than two orders of magnitude and the visible PL emission is enhanced by about two orders of magnitude after annealing. **Figure 7.4(a)** shows that a PL peak appears at ~ 450 nm in GRZN1 after annealing, while it was absent before annealing. In case of both GRZN2 and GRZN3, the enhancement in UV and visible PL intensity is about 20 and 10 times, respectively (see **Fig. 7.2**). Thus, UV PL intensity is significantly improved by post-growth annealing at 500°C in all samples indicating improvement in crystalline quality and reduction of nonradiative defect centers

upon annealing. Analysis of PL data further shows that the intensity ratio of 2nd green emission (483 nm) to UV emission is reduced by a factor of 4.43 in GRZN1, 3rd green emission (528 nm) to UV emission is nearly unchanged and the yellow emission (596 nm) to UV emission is reduced by a factor of 13.75 after annealing. On the other hand, in GRZN2 and GRZN3, the intensity ratio of both 1st and 2nd green emission to UV emission was reduced by a factor of 7.7, 3.0 and 1.3, 1.5, respectively after annealing. The intensity ratio of yellow emission to UV emission for both these samples is reduced by a factor of 6.2 and 2.8, respectively.

Thus, reduction of surface defect density after post-growth annealing is more prominent in ZnO NWs and NRBs as compared to the ZnO NRs. However, ZnO NRs in GRZN1 shows strongest UV as well as visible PL after annealing due to activation of more radiative channels than the nonradiative channels. Note that an additional PL peak at ~ 450 nm was observed in GRZN2 and GRZN3 after annealing at 500°C. Since Zn to O ratio is nearly 0.5 in all the samples, V_{Zn} is quite likely to be present in our samples. However, more studies are needed to pinpoint the exact origin of different visible PL peaks in the graphene-ZnO hybrid nanostructures. We have found that further annealing at higher temperature at 700°C does not improve the PL characteristics any further, as shown in the **Fig. 7.5(b, d, f)**. UV and visible PL characteristics of the 700°C annealed GR-ZnO NSs are further compared with the as grown and 500°C annealed samples. The crystalline quality improved after annealing that was clearly revealed from XRD studies discussed in **Chapter 6**. It is observed that after 700°C annealing, the intensity ratio of UV to visible PL band decreases to some extent. Centre of the visible PL band differs from sample to sample, while the center of the UV peak is almost identical in all the samples after annealing at 500 and 700°C. Note that after 700°C annealing, besides the NBE peak, the UV band shows a small peak at 384-391 nm, probably related to the surface states.¹² It appears that the surface states become more active and nonradiative channels are reduced after annealing. The various PL peaks and probable identities of each peak are summarized in the **Table. 7.4**, based on our analysis and literature reports.

The intrinsic defects are formed during the growth of the ZnO NWs, particularly due to the adoption of relatively lower growth temperature (540°C) in the present work. In GRZN1, we observed about two order of magnitude enhancement in the intensity of visible PL after 700°C post-growth Ar annealing, while in the case of GRZN2 and GRZN3 it is enhanced by a factor of 5 and 32, respectively. Interestingly, UV PL intensity is enhanced in

Table 7.4: Details of the PL peaks fitted with Gaussian line shapes for the UV and visible emission bands after 500 and 700 °C Ar annealing. The centre of each peak (P1- P5) is denoted in nm unit.

Sample	Annealed at 500°C				Annealed at 700°C					
Peaks	P1	P2	P3	P4	P1	P1*	P2	P3	P4	P5
GRZN1	377	452	483	528	375	384	450	483	532	557
GRZN2	378	454	504	-	378	391	462	509	-	569
GRZN3	376	451	495	-	377	-	454	499	-	562
Identity	NBE	$V_{Zn^{2-}}$	V_o / V_{Zn}	Deep O_i / O_{zn}			$V_{Zn^{2-}}$	V_o / V_{Zn}	Deep O_i / O_{zn}	Deep O_i

all samples and the ratio of intensities of UV to various visible PL emissions was significantly increased after annealing. In particular, the relative intensity of peak P1 with respect to peak P4 and P5 are increased by about one order of magnitude in GRZN1 after annealing, as shown in the **Table 7.3**. It implies that after annealing, there is a reduction of nonradiative defects in the ZnO NRs/NWs. However, the density of intrinsic radiative defects is increased considerably after annealing, as evidenced from the overall increase in the visible PL intensity. Note that these defects are very stable in the ZnO NRs/NWs, since the visible PL intensity is high even after 500 and 700°C annealing. Due to broad band visible PL emission at room temperature from these ZnO NRs, NWs and NRBs, these structures are suitable for white light display and other optoelectronic device applications.

7.2.3.2. Near Infrared Photoluminescence

In order to investigate the nature of defects and their exact identity in GR-ZnO NR/NW hybrids, we have conducted the PL measurements with below band-gap excitation on both as-grown and annealed samples. We used a 405 nm sub-band gap laser excitation to monitor the visible-NIR PL spectra at room temperature. **Figure 7.5** shows the room temperature PL spectra of the as-grown and 700°C Ar annealed GRZN1 (**Fig. 7.5(a-b)**), GRZN2 (**Fig. 7.5(c-d)**) and ZN3 (**Fig. 7.5(e-f)**) samples. Note that sub-band gap excitation gives rise to large number of visible PL bands and additional NIR PL bands from the hybrid nanostructures. Due to the asymmetry in the line shape and its evolution, each PL spectrum is fitted with multiple Gaussian peaks. The symbols correspond to experimental data and the solid green line refers to the fitted peak. The PL spectrum for each sample with above band-gap and below band-gap excitation show common peaks in the range 400 to 650 nm. Since we used a cooled CCD Si detector for monitoring PL spectrum with sub-band gap excitation,

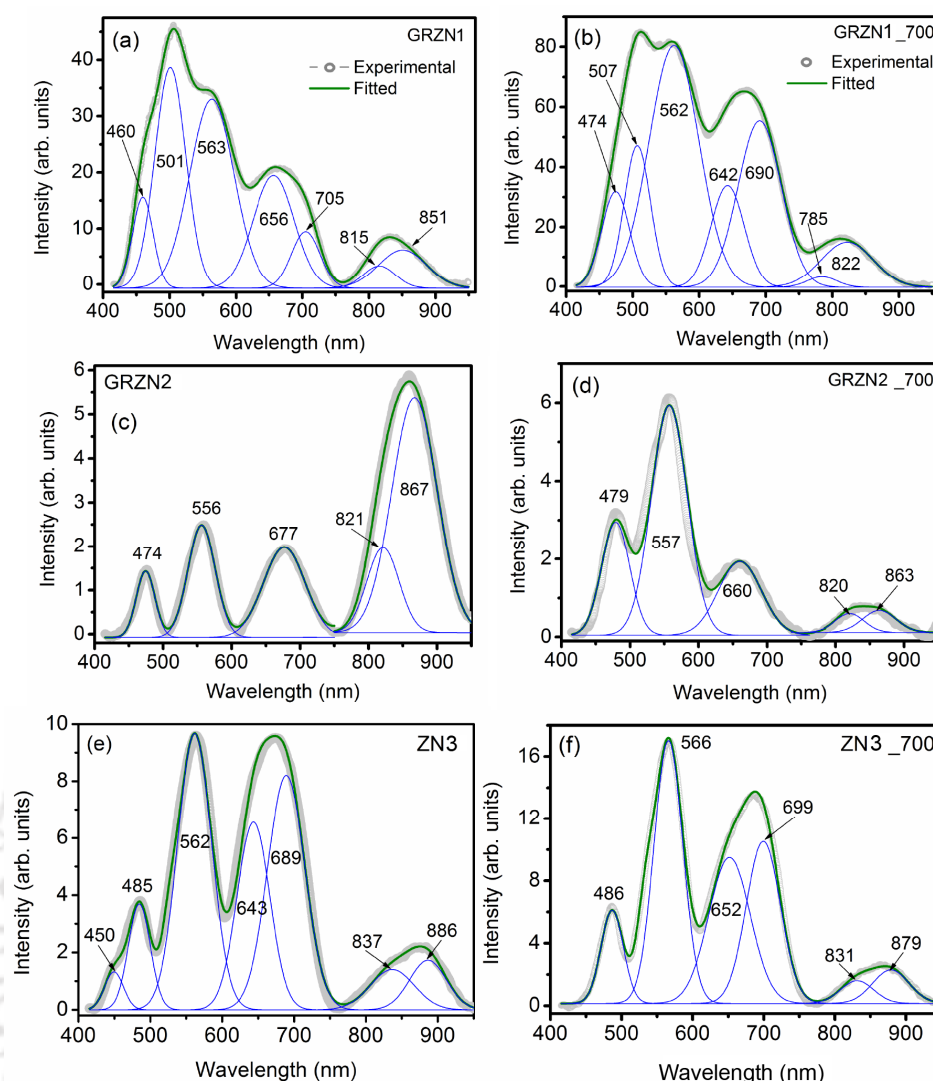


Figure 7.5. Comparison of the visible-NIR PL spectra recorded with 405 nm excitation (sub-band gap) from GR-ZnO NRs/NWs before and after annealing at 700°C in Ar gas: (a–b) GRZN1, (c–d) GRZN2, and (e–f) ZN3 samples. Various peaks are fitted by Gaussian line shape; the symbols represent the experimental data and solid line shows the fitted data.

additional distinct peaks are observed in the range 650–900 nm. With 405 nm excitation, the blue, green, and orange–red emissions centered at ~ 450 – 486 , ~ 500 – 563 and ~ 640 – 700 nm, respectively, are strong in all the as-grown as well as annealed samples. Note that the intensity of the orange–red emission is nearly doubled in GRZN1 and ZN3, while it is not changed significantly in GRZN1 after annealing. The summary of the peak positions and their possible identities, based on the discussion in the previous section, are presented in **Table 7.5**.

Interestingly, a new PL emission band in the NIR range 785–886 nm is observed in all the samples with the 405 nm sub-band excitation. The center of the peak for the NIR band

slightly changes from sample to sample, due to contributions mainly from two components. Due to asymmetric line shape of the PL band, two Gaussian peaks are fitted in each case (see **Fig. 7.5**). Note that both NIR peaks appear above 800 nm, which is not reported earlier. Previous report on NIR PL in ZnO discussed about a peak at ~ 756 nm only.⁶ Our results are distinctly different, due to the use of sub-band gap excitation and the methodology of different growth methodology of ZnO NRs/NWs. After annealing (Ar gas), the NIR PL band in GRZN1 sample is nearly doubled, while it is reduced in the GRZN2. Note that the relative intensities of two peaks are changed after annealing, with a minor change in the peak positions. The difference in peak positions for different samples may be due to their distinct

structural morphology and the local environment of the defects in ZnO lattice. Note that some groups^{18,22} have reported NIR PL at ~ 750 nm (1.65 eV) in ZnO, though we observed NIR PL bands above 800 nm and the NIR band in general has received far less attention. In some cases, the NIR PL band is ascribed to the second order diffraction of UV luminescence, as it can only be observed in the ZnO films with a strong UV luminescence. However, it also has been postulated that the NIR luminescence originates from the oxygen related defects similar to those responsible for the red luminescence in ZnO.^{18,22}

Table 7.5: Details of the visible and NIR PL peaks fitted with Gaussian line shape obtained with the sub-band gap excitation (405 nm) for each sample before and after 700°C Ar annealing. The center of each peak is denoted in nm unit. Identity (tentative) of each peak is written as per the standard notations used in the text.

Sample	As-grown							700°C Annealed						
Peaks	P1	P2	P4	P5	P6*	P7*		P1	P2	P3	P4	P5	P6*	P7*
GRZN1	460	501	563	656	705	815	851	474	507	562	642	690	785/ 822	-
GRZN2	474	-	556	-	677	821	867	479	-	557	660	-	820	863
ZN3	450	485	562	643	689	837	886	-	486	566	652	699	831	879
Identity	V_{Zn}^{2-}	V_o / V_{Zn}			Zn_o / V_o	O_i	O_i	V_{Zn}^{2-}	Vo / V_{Zn}	O_i / O_{Zn}	Zn_o	Zn_o / V_o	O_i	O_i

Possibility of second order diffraction of UV PL manifesting as a NIR band is completely ruled out here, since we used a 405 nm excitation along with a filter in the present study. Based on the XPS analysis, the possibility of NIR PL originating from the oxygen related defects is quite likely in the present case. Interestingly, as-grown GRZN2 shows a strong NIR PL band at 867 nm and its intensity is strongly reduced (by about 5 times) after annealing in Ar ambient, which may be due to reduction of neutral O_i defects in the annealed samples.^{8, 13}

The two PL components with centers at 820–830 nm and 863–879 nm are tentatively attributed to O_i^- and neutral O_i , respectively.⁸ Despite the post-growth annealing, the defect related PL intensity is strong in GRZN1 sample because of high oxygen content and a large surface area of ZnO NRs with broken tips that may contain high density of traps on the surface.

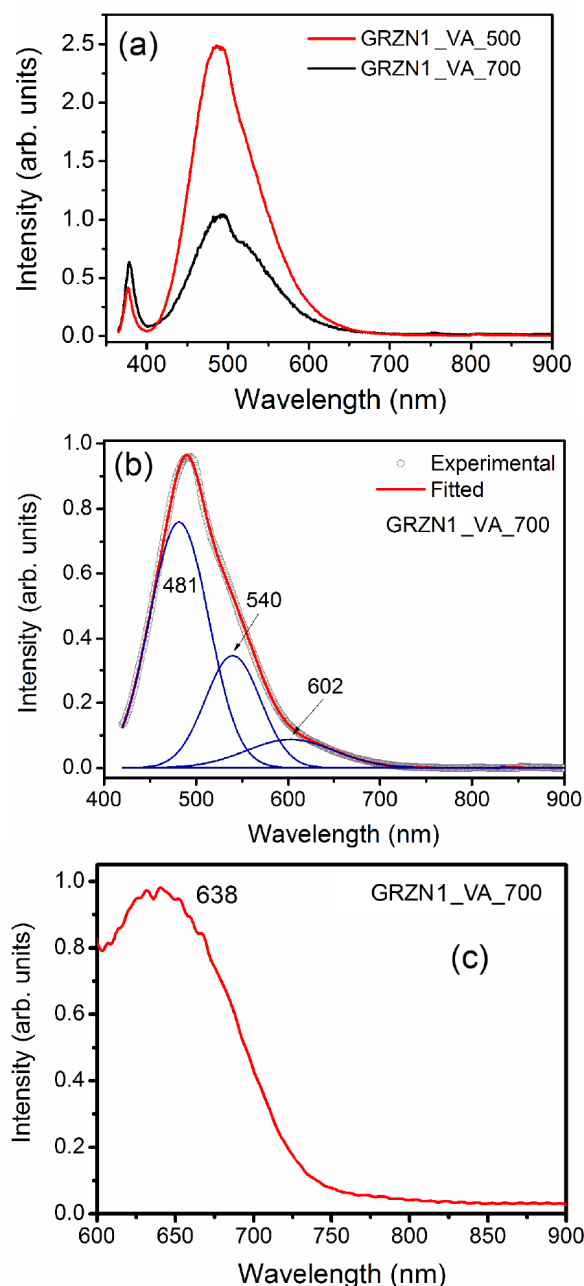


Figure 7.6: (a) Comparison of PL with 325 nm excitation for 500 and 700°C vacuum annealed samples. (b) Fitting of the PL spectrum of 700°C annealed GRZN1 excited with 405 nm laser. Symbols represent the experimental data and the solid lines show the fitted peak. (c) PL spectrum of 700° vacuum annealed GRZN1 excited with 488 nm sub-band gap laser. Peak position is denoted in nm unit. Note that no NIR PL was detectable after vacuum annealing.

To clarify further the origin of NIR PL and its relation to O_i induced defects in ZnO NRs/NWs, vacuum annealing of GRZN1 samples was conducted and PL emission was studied with both above band-gap (355 nm) and below band-gap (405 and 488 nm) excitations to monitor the evolution of PL bands. **Figure 7.6(a)** shows the comparison of PL spectra recorded with 355 nm excitation for GRZN1 sample after vacuum (1.0×10^{-5} mbar) annealing at 500 °C and 700 °C annealing. The data clearly shows that there is a systematic reduction in intensity of the green emission and enhancement in intensity of the UV band higher temperature of vacuum annealing. Interestingly, no NIR PL band could be detected in the vacuum annealed sample, indicating deactivation/ partial removal of the associated defects. **Figure 7.6(b)** shows the PL spectrum of 700°C annealed sample recorded with 405 nm excitation and the broad asymmetric PL peak could be fitted with three Gaussian peaks centered at 481, 540 and 602 nm. The visible PL bands are found to be consistent with that of **Fig. 7.5**. In fact, the major reduction in the O_i induced peak (~ 540 nm) of GRZN1 after vacuum annealing is consistent with our argument that the NIR PL arises from the O_i defects in ZnO. Absence of NIR PL was further confirmed from the vacuum annealed GRZN1 sample excited with the 488 nm laser, as shown in the **Fig. 7.6(c)**. It shows only a visible PL band at 638 nm and no NIR PL was detectable. Thus, the vacuum annealing partially removes the O_i defects in the ZnO NRs/NWs and our PL assignments are suppressed by the annealing results. The nature and origin of various PL emission bands discussed above can be summarized by a schematic energy band diagram shown in the **Fig. 7.7**, following the report by Wang *et al.*⁶ The presence of large number of highly stable defect centres emitting in the visible and NIR region makes the GR-ZnO hybrid suitable for bright display applications. We have demonstrated the tunability of the PL emission bands through controlling the growth and post-growth processing conditions.

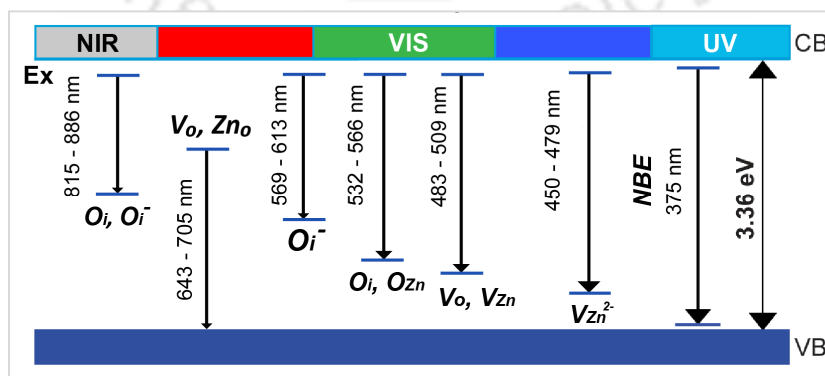


Figure 7.7: A schematic of energy band diagram showing various defect states in the band gap of ZnO NRs/NWs and corresponding PL emission wavelengths observed in our samples.

7.3. XPS Studies

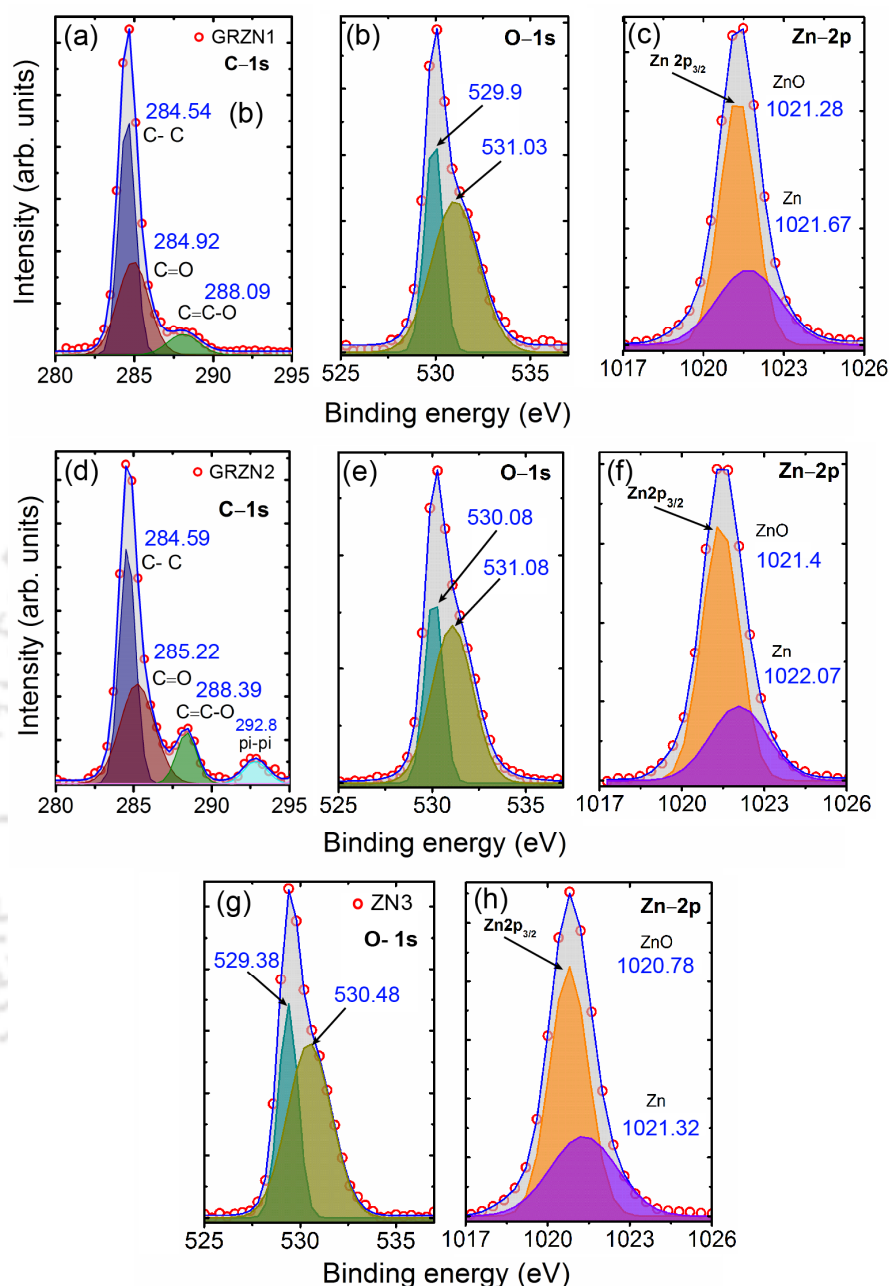


Figure 7.8: Core level XPS spectra of (a) GRZN1 (b) GRZN2 (c) ZN3 samples showing the deconvoluted C1s peaks arising from graphene and O1s, Zn2p peaks from ZnO. Peak positions in each case are denoted in eV unit. Integrated intensity (area) of individual components of fitted peaks in each spectrum is significant for the contribution of elements and their bonding in the respective sample.

XPS measurements are carried out to identify the elemental composition and local environment of defects in the as-grown and post-growth annealed GR-ZnO NR/NW hybrids. The characteristics XPS features for GRZN1, GRZ2 and ZN3 samples are shown in **Fig. 7.7**. It represents the core level spectra of graphene (C- 1s) and ZnO (Zn- 2p, O- 1s) in GRZN1

(Fig. 7.7(a–c)), GRZN2 (Fig. 7.7(d–f)) and ZN3 (Fig. 7.7(g–h)). The corresponding fitting parameters for the XPS spectra are shown in **Table 7.6**. Interestingly, all the samples show very high oxygen content as compared to the Zn content. Thus, excess oxygen may be present in the form of O_i and O_{Zn} in the as-grown and annealed ZnO NRs/NWs. Note that the PL data showing strong visible PL in all the samples may be due these excess oxygen related defects in the ZnO lattice, as revealed from the XPS analysis. XPS analysis (see **Table 7.6**) shows that GRZN1 contains highest percentage of excess oxygen among all three samples. Interestingly, PL data showed very high intensity of visible as well as NIR PL in the GRZN1 sample as compared to the GRZN2 and ZN3 samples. The peaks at lower binding energy (Peak 1 at 530.2 eV) in the O-1s core level spectrum can be attributed to the O^{2-} of the wurtzite structure of the hexagonal Zn^{2+} ion array, and the O^{2-} ions are surrounded by zinc atoms with the full supplement of nearest-neighbour O^{2-} ions. The higher energy peak at 531.33 eV (Peak 2) is associated with the O^{2-} ions in the oxygen-deficient regions within the ZnO matrix.¹⁴

Table 7.6: Details of the fitting parameters for O 1s and Zn 2p core level XPS spectra in graphene–ZnO hybrid nanostructures. Atomic percentage of O and Zn in various samples as determined from XPS data is shown for comparison.

Sample	O-1s		Zn-2p		Atomic percentage	
	Peak1 (eV)	Peak2 (eV)	Peak1 (eV)	Peak2 (eV)	O1s (%)	Zn2p (%)
GRZNR	530.2	531.33	1021.58	1021.97	70.3	29.7
GRZNW	529.53	530.42	1021.7	1022.37	67.1	32.9
ZNW	529.68	530.48	1021.08	1021.6	63	37
Identity	O^{2-}	V_o	Zn-O	Zn metal		

Thus, the XPS spectrum reveals that as-grown ZnO NRs/NWs have oxygen rich as well as oxygen deficient regions present in the same sample. Due to low formation energy, oxygen vacancies are easily formed in ZnO crystals. The deconvolution of core level spectrum of Zn-2p_{3/2} shows two peaks at 1021.28 and 1021.78 eV for GRZN1, as shown in **Fig. 7.7(c)**. Similar deconvolution is shown in **Fig. 7.7(f)** and **(h)** for GRZN2 and ZN3, respectively. The lower energy and higher energy components in each sample represent Zn in oxide form and Zn in metal form, respectively.¹⁴ Centre of the XPS peaks and their respective identity are presented in **Table 7.6**. The ratio of relative area of peak 2 to peak 1 in GRZN1 is slightly higher (0.54) than that in GRZN2 (0.44), i.e., Zn in the form of metal nanoparticles and/or Zn interstitials (Zn_i) are present in higher concentration in GRZN1. This is fully consistent with

the XRD results discussed in the **Chapter 6**. Thus, despite good crystallinity and hexagonal facets of the ZnO NRs, as-grown ZnO NRs and NWs show high concentration of oxygen and zinc related defects. In particular, intrinsic defects O_i , O_{Zn} , V_o and V_{Zn} may be high in these samples. Due to the relatively low growth temperature adopted here, the surface defect density might be high in these samples and defects are responsible for the strong visible PL in the GR-ZnO Hybrids.

7.4. Photoconductivity Studies

7.4.1. Graphene-ZnO NW Hybrid UV Photodetector

In order to evaluate the photoresponse of the GR-ZnO hybrids, we have performed the PC measurements at a fixed bias voltage (2V). For PC measurements, silver (Ag) contacts were deposited by thermal evaporation technique under high vacuum on top of the ZnO NWs surface by keeping a shadow mask with a channel width and length $\sim 0.1 \text{ mm} \times 0.1 \text{ mm}$. The thickness of the Ag layer is about 100 nm. A schematic of the device configuration is shown in **Fig. 7.9(a)**. **Figure 7.9(b)** and **7.9(c)** represent the dark and photocurrent response as a function of voltage in the GRZ3NW and Z1Z3NW, respectively, with UV ($\sim 365 \text{ nm}$) excitation. The corresponding time response of the photocurrent in each case is shown in **Fig. 7.7(d)** and **(e)**, respectively. Note that the PC of the ZnO NWs grown on Z1Z3 layer is very less as compared to the NWs grown on the GRZ3 layer. The PC was enhanced by a factor of 20 in the GRZ3NW as compared to the Z1Z3NW. The enhancement in case of graphene layer is probably resulting from the Schottky barrier formation between the bunch of vertically aligned ZnO NWs and graphene layer. This increment might be due to the efficient separation of electrons and holes at the junction of graphene and ZnO NWs interface due to the junctional potential in case of GRZ3. The dark I-V curve is found to be nonlinear due to the presence of the traps/defects (see **Fig. 7.9(b)**) and the PC is about two orders of the magnitude lower than the case of GRZ3NW (see **Fig. 7.9(c)**). Thus, graphene layer enhances the UV photocurrent sensitivity of the ZnO layer on it. This is an interesting observation and it can be exploited in future optoelectronic devices.

Further, we have investigated the PC growth and decay behavior of ZnO NWs by fitting with bi-exponential function, following the report by Dhara *et. al.*¹⁵ PC growth can be expressed as:

$$I_{ph}(t) = I_1 + A_1(1 - e^{-t/\tau_1}) - A_2e^{-t/\tau_2} \quad \dots\dots (7.1)$$

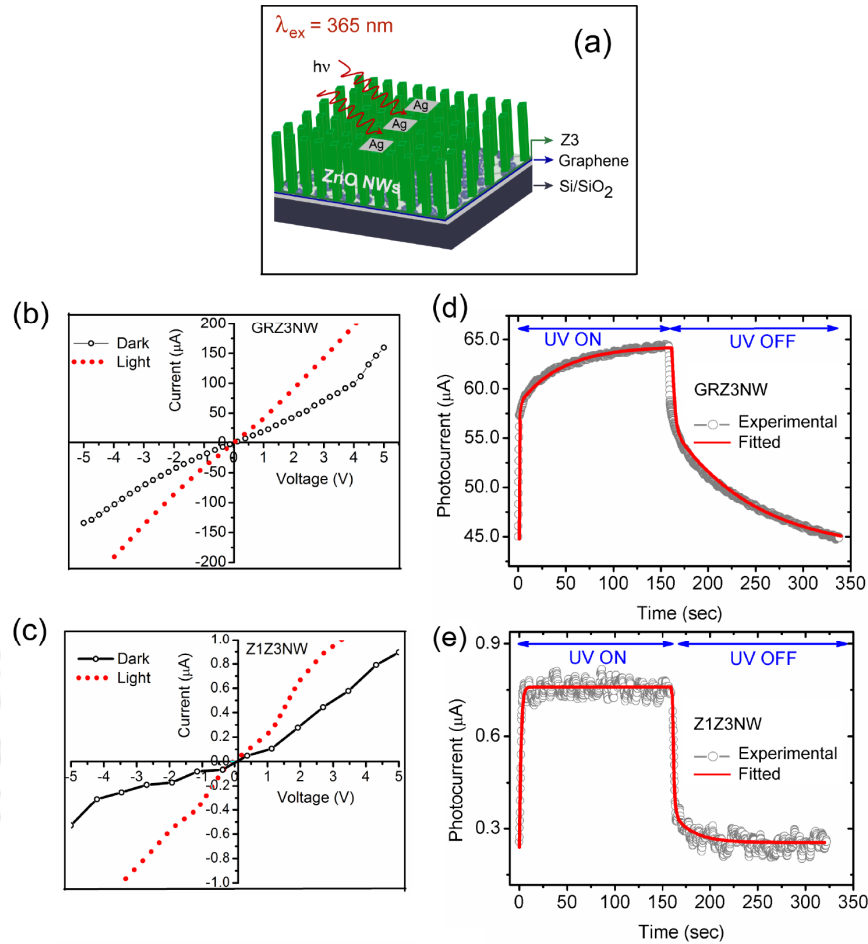


Figure 7.9: (a) A schematic of the Ag contact made on the ZnO NWs array for the photoconductivity (PC) measurement, illuminated with UV light (365 nm). (b-c) Dark current and photo current as a function of voltage in GRZ3NW and Z1Z3NW, respectively. (d-e) The time response of the respective photocurrent in GRZ3NW and Z1Z3NW at a fixed bias voltage (2V). The symbols represent the experimental data and the solid lines correspond to the fitted data in each case.

Here I_1 , A_1 and A_2 are the constants. τ_1 and τ_2 are the time constants, which are calculated from the fitting. For GRZ3NW and Z1Z3NW the time constants of PC growth are found to be $\tau_1 = 45.0s$, $\tau_2 = 3.7s$ and $\tau_1 = \tau_2 = 1.6s$, respectively. PC decay is expressed as:

$$I_{ph}(t) = I_{ph}(\infty) + A_3 e^{-t/\tau_3} + A_4 e^{-t/\tau_4} \quad \dots (7.2)$$

Here A_3 and A_4 are the constants. τ_3 and τ_4 are calculated as 2.5s, 88.5s in the case of GRZ3NW and 1.4s, 20.8s in Z1Z3NW, respectively. Note that the $I_{ph}(\infty)$ represent the photocurrent after long time, in no light connection, which is equal to the dark current. Thus, the time response of the photocurrent is relatively slow in GRZ3NW as compared to that of Z1Z3NW, though GRZ3NW possesses higher sensitivity. The time response is mainly controlled by the intrinsic defects in the ZnO layer. One can focus the optimization of growth conditions and GR-ZnO seed layer substrates with lesser defects may reveal the exact

role of underlying graphene on the response and recovery times of the PD. Besides the surface defects, GR–ZnO hetero–interface may be partly responsible for the slow response of the PD.

7.4.2. Graphene-ZnO Film Ultrasensitive UV Photodetector

In-order to assess the role of graphene in the photoresponse enhancement, we have fabricated a set of PD devices that are made up of ZnO thin film on GR (GRZ3) and Z1Z3 substrates only. **Figure 7.10(a)** and **(b)** represent the device structure of the GRZ3 and Z1Z3 layers. Note that the fabrication of Ag contacts were made by the thermal evaporation, as discussed in the previous section. Prior to the PC measurement, presence of underlying graphene and crystalline quality of ZnO seed layer was confirmed from the micro-Raman and XRD, as shown in the **Fig. 7.10(c)** and **(d)**, respectively. Presence of strong D band and broad G, 2D bands reveal that the underlying graphene have non-uniformity and disorder on the surface due to the coverage of ZnO film on it. From **Figure 7.10(d)**, it is evident that ZnO grains are single crystalline and have *c*-axis orientation in (002) plane with perfect Wurtzite structure. Note that the ultra-thin ZnO film (10nm) was deposited at substrate temperature 200°C.

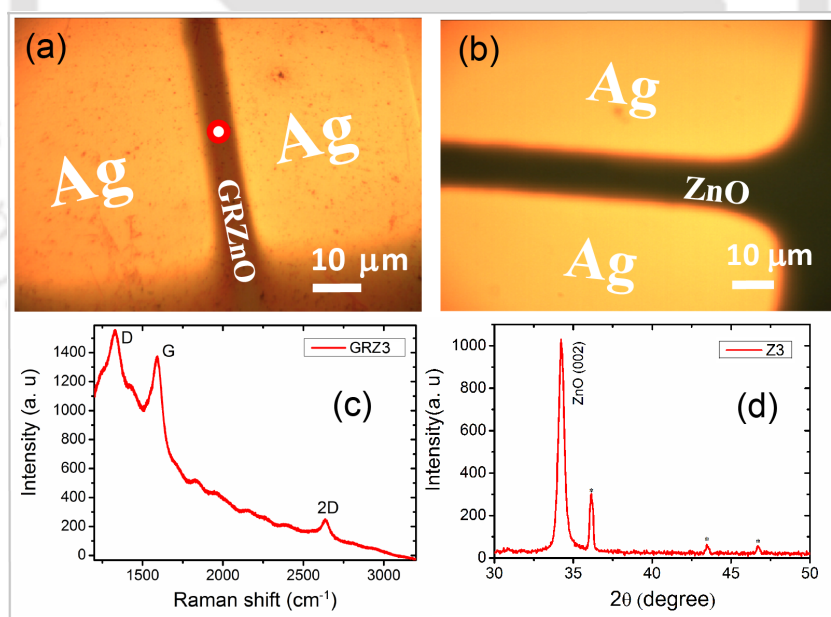


Figure 7.10: Optical microscope images of the (a) GR-ZnO (GRZ3) and (b) ZnO thin film (Z3) UV photodetector (PD) device. (c) Raman spectra of GRZ3 PD, which is taken at the marked location between the two Ag contacts. (d) XRD pattern for the Z3 film significant for a single crystalline ZnO grains with *c*-axis orientation along (002) plane.

We have also performed the UV-vis absorption on GRZ3 and Z3 substrates in-order to confirm the absorption of light in presence of graphene. **Figure 7.11(a)** represents the optical

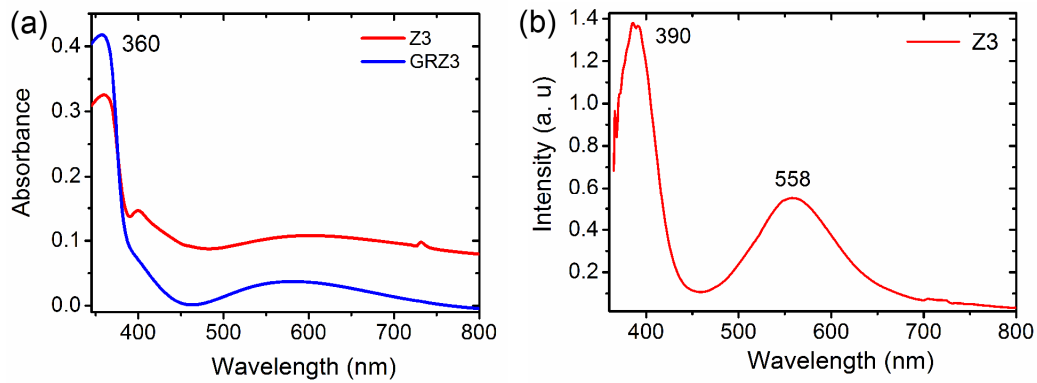


Figure 7.11: (a) UV-visible absorption from Z3 and GRZ3 layers coated on quartz substrates showing a strong UV absorption (360 nm) and a broad visible absorption significant for the oxygenated defects on ZnO surface. (b) PL spectra of Z3 layer. Excitation wavelength used for the PL measurements is 355 nm. Note that all the PL peaks are denoted in the nm unit.

absorption spectra of the GRZ3 and Z3 layers coated on quartz substrates and PL spectra of Z3 layer is shown in **Fig. 7.11(b)** ($\lambda_{\text{ex}} = 355\text{nm}$). Both GRZ3 and Z3 show a strong UV absorption band at 360 nm and a broad visible absorption band related to the oxygenated surface trap centres on ZnO thin film. A strong UV absorption band in both the samples is significant for the single crystalline nature of ZnO grains, which is consistent with the micro Raman and XRD results. The PL spectra for the Z3 layer shows a strong NBE emission at ~ 390 nm. A broad visible emission centred at 558 nm in Z3 layer is attributed to the V_o/O_i related defects on the surface of the ZnO thin film. Further, we have measured the dark and photo I-V characteristics of graphene and ZnO and GR-ZnO films. **Figure 7.12(a)** represent the dark I-V characteristics of graphene at different bias voltages. It shows a perfectly linear/ohmic nature of the charge transport in the graphene. It is to be noted that the high currents (mA) at a low bias voltage identified in the graphene transferred on to a SiO_2 is significant for the semi metallic nature of a graphene layer. Further dark and photo I-V curves of GRZ3 and Z3 layers are shown in the **Fig. 7.12(b)**. Here the excitation wavelength used for the photoconductivity studies is 375 nm. **Figure 7.12(c)** and **(d)** represent the UV photoresponse for the Z3 and GRZ3 layers at fixed bias voltage ($V_{\text{bias}} = 3\text{ V}$). Note that the behaviour of photocurrent growth and decay profiles were fitted by biexponential growth and decay functions, as discussed in the previous section. The dotted line signify the experimental data and solid redline corresponds to fitted data.

We estimated the time constants for each cycle of UV ON/OFF state from the corresponding time response curves in the Z3 and GRZ3 samples, as shown in **Fig. 7.12(c)** and **(d)**. The time constants in Z3 for the photocurrent growth and decay profiles are found to

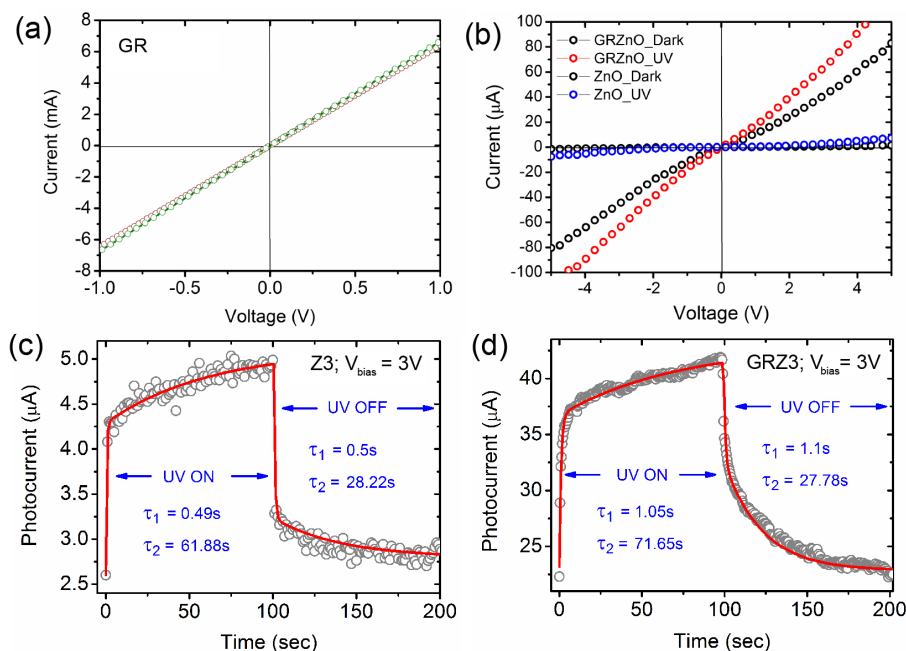


Figure 7.12: (a) Dark I-V characteristics of CVD graphene. (b) Dark and photocurrent (I-V) characteristics of the ZnO and GR-ZnO thin film hybrids excited with 375 nm wavelength. UV photocurrent from the (c) ZnO and (d) GR-ZnO thin film UV PDs. Growth and decay curves at UV on and off conditions are fitted with the bi-exponential function. Note that the dotted lines represent the experimental data and solid line corresponds to the fitted data.

be $\tau_1 = 0.49s$; $\tau_2 = 61.88s$, and $\tau_3 = 0.5s$, $1.1s$; $\tau_4 = 28.22s$, respectively, while that of $\tau_1 = 1.05s$; $\tau_2 = 71.65$ and $\tau_3 = 1.1s$; $\tau_4 = 27.78$, respectively. We achieved a faster response and recovery times in Z3 and GRZ3 UV PDs as compared to that of GRZ3NW and Z1Z3NW cases. Interestingly, the UV photoresponse of GRZ3 is enhanced by a factor of 10 than that of Z3, which signifies the high photosensitivity of the ZnO layer in presence of graphene. In order to understand the nature of UV sensitivity of the GR-ZnO hybrid, we have performed the cyclic photocurrent measurements on Z3 and GRZ3 PDs. **Figure 7.13(a)** and **(b)** represent the cyclic UV photoresponse characteristics recorded at different bias voltages, 1-5 V. Note that the response time for the UV PC in Z3 and GRZ3 are 200 and 100 sec, respectively. **Figure. 7.13(d)** represents the UV responsivity as a function of bias voltage. Responsivity of a PD decides the rate of photogenerated free charge carriers with respect to the power of incident light at applied bias voltage.¹⁶⁻¹⁷ Responsivity (R_s) of both Z3 and GRZ3 UV PD was calculated as a function of bias voltage. The R_s is defined as

$$R_s = \frac{I_{light}}{P_0 \times A} \quad \dots\dots\dots (7.3)$$

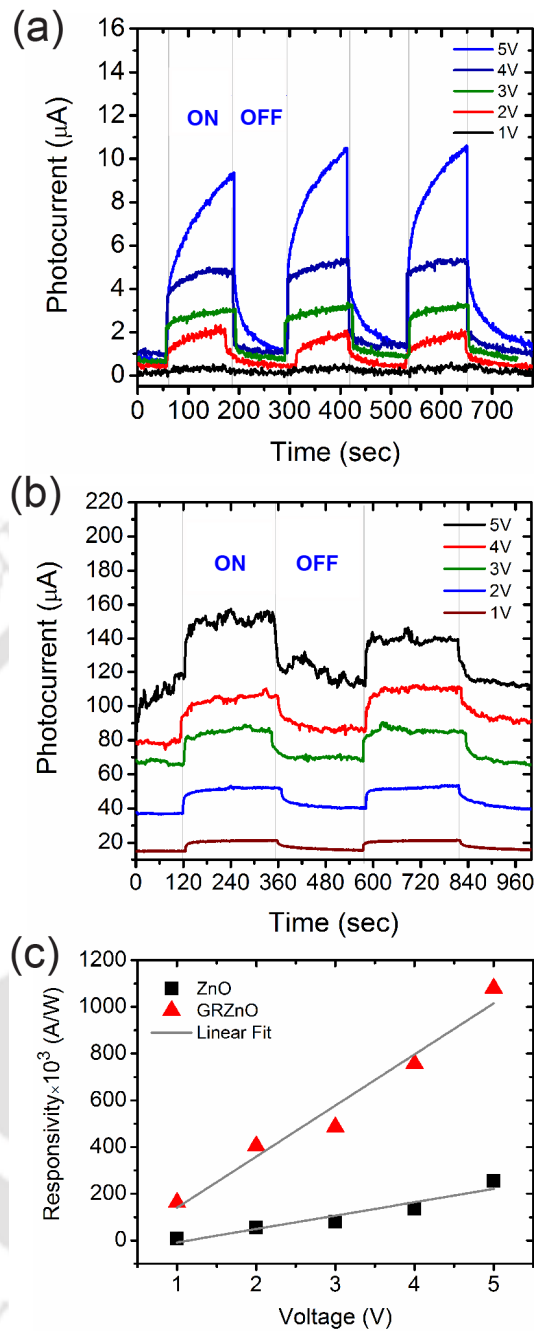


Figure 7.13: Cyclic photoresponse from ZnO and GR-ZnO thin film hybrid PDs: Cyclic photoresponse characteristics of: (a) Z3 and (b) GRZ3 layers at different bias voltages. (c) Photoresponsivity as a function of bias voltage in Z3 and GRZ3 hybrid PD. Note that the dotted line represent the experimental data and solid line corresponds to fitted data.

Where, P_0 is illumination power of incident light (0.405 mW/cm^2), A is the Effective device area ($0.1 \text{ mm} \times 0.1 \text{ mm}$) and I_{light} is the photocurrent. The R_s values for both the PDs were fitted with a 1st order linear equation. The responsivity of GRZ3 and Z3 PDs were found to be $1100 \times 10^3 \text{ A/W}$ and $250 \times 10^3 \text{ A/W}$, respectively at 5V bias. This clearly reveals that the responsivity of GRZ3 is higher by a factor of 4 than that of Z3 layer, which may be due to the

Schottkey barrier formation between graphene and ZnO layer coated on it. In conclusion, the cyclic photoresponse measurements reveal that the high mobility of graphene reduces the recombination rate of photogenerated carriers; as a result, the life-time of the photogenerated carriers was greatly increased.¹⁷

7.5. Summary

In this chapter we demonstrated the UV-vis-NIR absorption and PL properties of the GR-ZnO NSs grown by the metal catalyst method and catalyst free growth process. We investigated the origin of UV-vis-NIR PL in as-grown and post-growth annealed (500 and 700°C) GR-ZnO NR, NW, and NRB hybrids and reported new oxygen related deep level defects. Further evolution of the UV and visible PL was studied and correlated with effects of ZnO buffer layers on graphene substrates in the aligned growth of ZnO NWs with high crystalline quality. Highly enhanced UV photocurrent was achieved in the case of ZnO NWs grown on graphene, which is consistent with the PL results. Further enhanced UV photosensitivity of GR-ZnO hybrids were evaluated from the cyclic photoconductivity studies. Important achievements of this chapter are summarized below.

1. Strong UV-vis-NIR PL and its origin was reported in GR-ZnO hybrids.
2. A new NIR PL emission band is identified in the range between 815-886 nm (1.52-1.40 eV) in GR-ZnO hybrids and it is tentatively assigned to the oxygen interstitial (Oi) defects, detected experimentally for the first time.
3. Two orders of magnitude enhancement in UV PC was achieved in GR-ZnO NW as compared to bare ZnO NWs.
4. Cyclic photoconductivity measurements of GR-ZnO thin film hybrid revealed the role of graphene in the enhancement of UV photosensitivity (1100×10^3 A/W).

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Chapter 8

Origin and Tunability of Visible Photoluminescence from Chemically Derived Graphene Thin Films

In this chapter, we demonstrate the synthesis of chemically derived graphene (CDG) functional materials, such as graphene oxide (GO), reduced graphene oxide (rGO), and graphene oxide nanoribbons (GONRB) by chemical exfoliation techniques. Subsequently, we have fabricated the CDG thin films using simple spin coating technique. Identification of various in-plane and edge oxygenated functionalities was carried from the evolution of visible PL through oxygenation and hydrogenation studies, for the first time. The origin of various visible PL peaks were investigated from TGA/DTG and FTIR analyses in the CDGs and are correlated with the micro-Raman analysis. Tunability of blue and green PL emission was extensively investigated by controlled hydrogenation and oxygenation of CDGs.

8.1. Synthesis of chemically Derived Graphene

The CDGs were synthesized by chemical exfoliation techniques using a graphite as source material for GO and rGO, while GONRB prepared from multiwall carbon nanotubes (MWCNTs). The schematic process of CDG fabrication is illustrated in the **Fig. 8.1(a)** and preparation steps are discussed in the following sections. Note that the details of the synthesis and characterization of GR and DGR were discussed in the chapter 3.

8.1.1. Preparation of GO

GO was prepared by the modified Hummers method.¹ Initially the high purity (99.98%) bulk graphite with average flake size $\sim 500\ \mu\text{m}$ (ASBURY CARBON, USA, carbon content $>98\ \text{wt}\%$) 10 g and sodium nitrate (5 g) were mixed with sulphuric acid (230 ml, 98 wt%) in an ice bath, and potassium permanganate (30 g) was slowly added to prevent the temperature from exceeding 293 K. The reaction was conducted at 308 K for 30 min with gas release, and then de-ionized water (460 ml) was gradually added, bringing about violent effervescence. The temperature of the water bath was increased to 371 K and the reaction was maintained

for 40 min in order to increase the oxidation degree of the GO product. The resultant bright-yellow suspension was diluted and further treated with a H_2O_2 solution (30 ml, 30%), followed by centrifugation and careful washing to clean out the residual salt. The wet GO was dewatered by vacuum drying at 323 K.

A GO suspension in water (2mg /ml, 200 ml) was treated in an ultrasonic cleaner (KQ-100, 40 kHz, 100 W) for 30 min, followed by high-speed centrifugation (10000 rpm, 20 min) to remove impurities, which only resulted in a slight precipitation. The stable graphene oxide hydrosol was heated at 353 K for a short period (around 20 min for a 5 mm thick membrane and 40 min for a 10mm thick membrane) in a thermostatic water bath; during this time a smooth and condensed thin film was formed very rapidly at the liquid/air interface. The under surface suspension was then transferred into another beaker, and the membrane left at the bottom was dried at 353 K for 8 h and torn off.

8.1.1. Preparation of rGO

First, the GO was prepared using the method discussed in the previous section. Next, chemical reduction at room temperature using a strong reducing agent hydrazine mono hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$) produces agglomeration and RGO is quite unstable and is difficult to filter as uniform film. Here, we have performed reduction of GO at low temperature and room temperature, and it is observed that at 2-5 °C homogenous RGO has been formed rather than agglomeration formed at room temperature. This is convenient to make ultra-thin films by spin coating for any device fabrication.

8.1.3. Preparation of GONRB

For the preparation of GONRB, commercially procured MWCNTs (diameter ~ 60-100 nm, length ~ 10-15 μm , purity >95%) are used as a source material. The vertical unzipping had been carried out by treating these MWCNT with KMnO_4 and H_2SO_4 followed by mild reduction with hydrazine monohydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$). MWCNT (20 mg) were suspended in 20 ml of concentrated H_2SO_4 for 1 h to 12 h. KMnO_4 (100mg for 20 ml solution of MWCNT/ H_2SO_4) was then added and the mixture allowed stirring for 1 h at room temperature. The reaction mixture was then heated in an oil bath at 55 °C for 30 min. The completeness of the reaction was confirmed from the colour identification test of the reaction mixture, as reported by Kosynkin et al.²

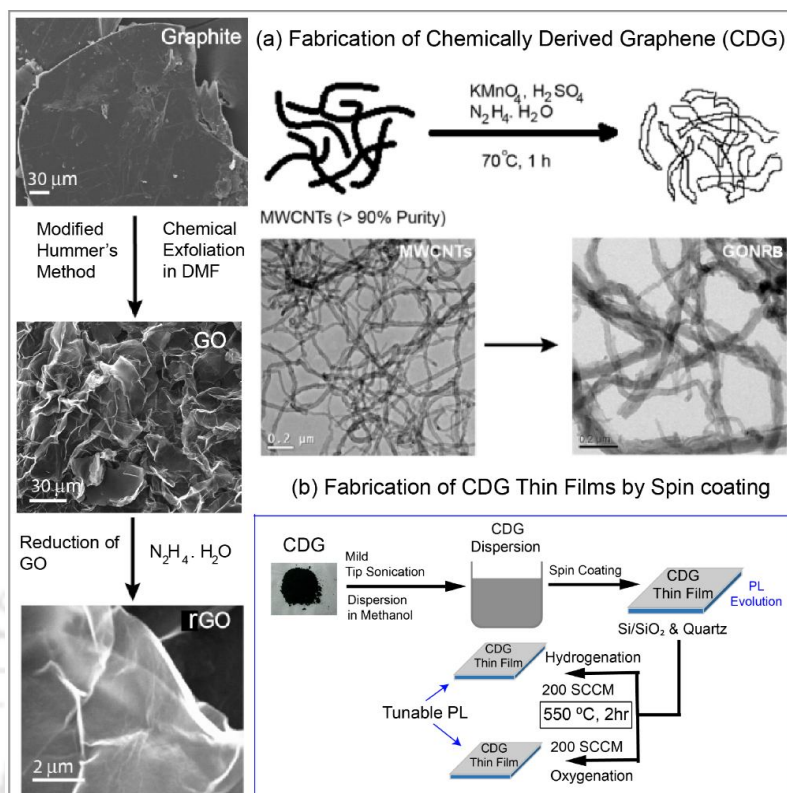


Figure 8.1: (a) Schematic shows the synthesis of CDGs such as GO, rGO and GONRB. (b) Fabrication of CDG thin films using simple spin coating technique.

When the reaction appeared complete, the temperature was increased to 70°C and the solution was allowed to stabilize. Upon stabilization to 70°C , the reaction chamber was removed from the heat source, allowed to cool to room temperature by adding 100 ml of ice containing 1.25 ml of 30% H_2O_2 in order to prevent the precipitation of insoluble MnO_2 . After vacuum filtration through a PTFE membrane (Pore size $\sim 5.0\ \mu\text{m}$), the solid was removed and stirred in 20 ml of water for 30 min, and then bath-sonicated for 15 min. The material was then mixed with 20 vol% concentrated HCl (5 ml). The solid was then filtered through a PTFE membrane. The product was removed and stirred in 20 ml of ethanol for 30 min, then bath-sonicated for 15 min. The material was mixed with 100 vol% diethyl ether (20 ml) followed by filtration through a PTFE membrane. The final product was washed twice with ether (5 ml each time) and dried in oven to get graphene oxide nanoribbons (GONRB). GONRB aqueous solution was subjected to mild tip sonication for 30 min.²

8.1.4. Preparation of Thin Films of CDG

A schematic for the fabrication of CDG thin films by simple spin coating technique is shown in **Fig. 8.1(b)**. As prepared CDGs were dispersed in a polar solvent (methanol) followed by a

mild tip sonication for controlled dispersion. The CDG solution was spin coated on the quartz and SiO₂ substrates for uniform thickness. The quality of thin films has been assessed primarily by micro-Raman spectroscopy analysis.

8.1.5. Hydrogenation and Oxygenation of CDG Samples

For a better understanding of in-plane and edge functional groups on the evolution of PL spectra from CDGs, we have performed the hydrogenation and oxygenation of the powder and thin film samples of CDGs including CVD graphene under the controlled flow of high purity H₂ and O₂ gas, respectively. The samples were kept in an alumina boat and loaded in a tubular quartz chamber inside a muffle furnace. GO and rGO coated on SiO₂ and quartz substrates were annealed under identical conditions. Initially, the chamber was pumped down to a pressure of 4.0×10^{-4} mbar, and the temperature was ramped up to 550 °C with heating rate 6 °C/min. The temperature was maintained at 550 °C during the annealing in H₂/O₂ flow. The flow rate for both the gases used for annealing was 200 SCCM for the duration of 2 h. Note that the sample codes used for the oxygenated and hydrogenated samples of CDGs are represented by a suffix 'O' and 'H', respectively. For example, GOO refers to oxygenated GO, GOH refers to hydrogenated GO etc.

8.2. Structural Studies of CDGs

8.2.1. Raman Spectroscopy Studies

In chapter 3 we evaluated the crystal structure, sp^2 hybridization, structural imperfections arising from the intrinsic defects in GR and DGR from micro Raman spectroscopy. From Raman finger-prints and Lorentzian line-shape analyses, we have probed the structural imperfections arising from the intrinsic defects and oxygenated functionalities on graphene basal plane and edges. The intrinsic defects are naturally grown during the CVD growth process and are unavoidable. In case of CDGs, various oxygenated functional groups selectively nucleate on the basal plane as well as at the edges of CDGs during the oxidation/reduction with KMnO₄, H₂SO₄ and HNO₃. This creates a continuous disruption of π network on the basal plane and graphene interlayers depending upon its sp^2 and sp^3 crystallite size. In general, the covalent attachment of these functionalities preferentially takes place at the defect sites and sp^3 carbon domains.

Figure 8.2 presents a comparison of Raman spectra for GR, DGR and CDG functional materials. Note that the Raman spectra are scanned with 514.5 nm laser excitation for all the

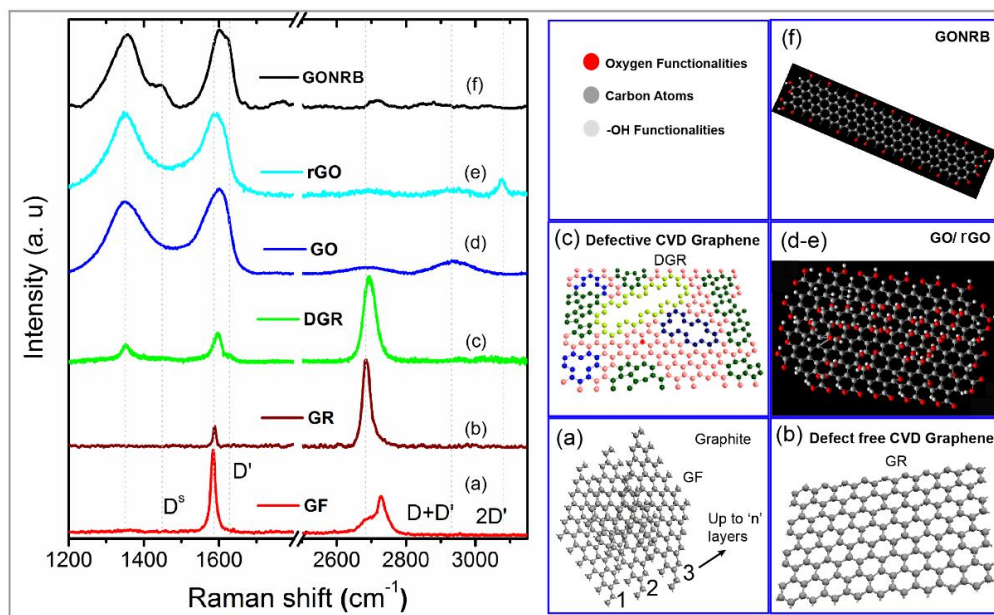


Figure 8.2: Raman characteristic modes of different CDG materials: (a) graphite flake (GF), (b) pristine GR, (c) DGR, (d) GO, (e) rGO and (f) GONRB. The Raman signatures are denoted as D, D^s (Oxygen functionalized sp^3 carbon), G, D', 2D, D+D' and 2D' bands. Note that all the spectra were recorded with 514.5 nm laser excitation. The right hand panel shows the corresponding molecular models of each sample elucidating the various functional groups and extended defects formed during the preparation process.

samples at room temperature. The atomic models of CDGs corresponding to each spectrum are presented on the right side panel of **Figure 8.2**. These atomic models were simulated from Atomistic Tool Kit (ATK 11.8.2, Quantumwise) software. The Raman spectrum of bulk graphite film (GF) is shown in the **Fig. 8.2(a)** for comparison. Note that the absence of D band and a sharp symmetric G band in GF imply the highly ordered graphitic layers (sp^2 hybridized) present in the starting carbon precursor. The nature of intrinsic defects in the CVD grown GR is shown in **Fig. 8.2(b)** and (c). The most commonly identified in-plane and edge defects that are formed in the CVD growth are carbon vacancies (e.g., single, bi- and multiple), extended defects (line, edge reconstruction due to the weak dangling bonds leading to formation of pentagon and heptagon defects). Various kinds of such defects are schematically represented by the atomic models, as shown in **Fig. 8.2**.³

Further, the characteristic Raman features of GO, rGO and GONRB, such as broad D (1350 cm^{-1}), G (1595 cm^{-1}), D' (1620 cm^{-1}), 2D (2700 cm^{-1}), D+D' (2940 cm^{-1}) and 2D' (3240 cm^{-1}) bands are shown in **Fig. 8.2(d, e, f, g)**, respectively and these bands signify the presence of both sp^2 and sp^3 carbons. In CDGs, the variation of these carbon bonds is associated with the oxygenated surface functionalities. Interestingly, in the case of GONRB,

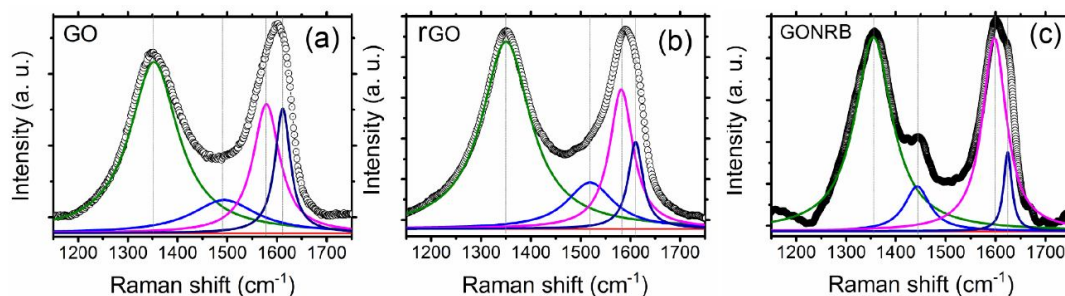


Figure 8.3: Typical Raman spectra (symbols) of (a) GO, (b) RGO and (c) GONRB showing D and G bands and its spectral deconvolution (lines) showing the evolution of various functional groups formed as a result of chemical exfoliation of graphite.

an additional sharp feature (D^s) at the higher frequency side of the D band at $\sim 1450\text{ cm}^{-1}$ has been found, for the first time (see **Fig 8.2(f)**) and it is tentatively assigned to the covalently attached carboxyl (COOH) and carbonyl (C=O) functional groups at the edges of GONRB. Note that D^s band is absent in case of GO and rGO samples. Our FTIR studies along with the TGA/DTG studies reveal that the COOH functional groups can be removed partially after oxygenation/hydrogenation, while C=O functionalities can covalently rearrange due to weak dangling bonds of carbon atoms. This might be due to the lower thermal stability of COOH compared to that of the C=O functionalities.⁴

In general, the carbon atoms present at the graphene edges are bonded with weak dangling bonds that usually take part in the edge reconstruction. Edge atoms are primarily observed in GONRB due to their edge confinement at the weakly bonded C–C edges.⁵⁻⁶ Tuning these edge sites with oxygen or nitrogen by controlled chemical or physical functionalization will allow wide range of PL in the visible to NIR wavelength in GONRB samples.^{5,7} In the present case, GONRB samples show a strong green PL emission due to the attachment of COOH and C=O functionalities at the edges. Note that the COOH and/or C=O functionalities are distinguished based on their FTIR signatures and the thermal stability of the functional groups at the edges in pristine and hydrogenated CDGs through the TGA analysis.⁸ However, Raman features of GO and rGO show the broad line shape of D and G bands that reveal the high degree of disorder due to the continuous in-plane disorder and inter layer disruption and plenty of in-plane oxygen functional groups on the basal plane (sp^3 defect sites).

The contribution of various in-plane and edge oxygen functionalities and surface defects in each sample was quantified with Lorentzian line shape analysis of D, G, D' and 2D Raman bands, as shown in **Fig. 8.3**. The D and G bands are fitted with two Lorentzian peaks each,

namely D, D^s (new Raman feature at $\sim 1450\text{ cm}^{-1}$), G and D' bands (see **Fig. 8.3**). Note that in all the CDG samples, the D band is broader than that of the GR, which significantly denote the disorder due to in-plane oxygenated functionalities attached at the sp^3 carbon sites. Interestingly, edge confinement effect due to COOH or C=O functional groups is understandable from the evolution of D^s band in GONRB. Attachment of these functional groups is more probable with edge carbon atoms due to the presence of weak dangling bonds leading to the continuous edge reconstruction.³ Note that the FWHM of D^s band is nearly double for GONRB as compared to that of GO and rGO, which implies the nucleation of oxygen functionalities significantly at the edges, mostly due to the COOH and C=O functional groups. This Raman signature is fully consistent with the strong green PL emission from the GONRB, which is significant for the sub-band gap energy states of COOH and C=O. Further, the change in the position of G-band ($\sim 1590\text{ cm}^{-1}$) due to the in-plane lattice strain and disorder caused by the functionalization of graphene sheets and presence of D' (at $\sim 1620\text{ cm}^{-1}$) band are attributed to the intrinsic edge reconstructed defects.³ In addition, D+D' and 2D' band features are strong in case of GO and rGO, while these are weak GONRB (see **Fig. 8.2**). These two features reveal a higher interlayer distance between the graphene layers in GO and rGO due to covalent attachment of in-plane epoxy/OH functional groups and formation of extended defects, respectively.

8.2.2. HRTEM Studies

The spatial uniformity and disorder due to defects on the basal plane and edges of the GR layer and CDGs are extensively investigated from the HRTEM analyses. Crystalline quality and in-plane and edge defects of GR were discussed in chapter 3. **Figure 8.3(a)** represents the HRTEM image of the cross section of multilayer GO (~ 30 layers) showing the distribution of layers and the lattice distortion present in the layers. The IFFT image (upper right inset) is extracted from the region of I, which clearly shows the layer distortions among the GO sheets and the shaded region may be due to the oxygenated functionalities and disorder in the layers of GO. The multiple electron diffraction spots arise from the GO basal plane, as shown in the lower right inset of **Fig. 8.4(a)**. **Figure 8.4(b)** shows a TEM image of rGO sheet and corresponding SAED pattern shown in the inset signifies the few-layer graphene sheet. The TEM image of the GONRB prepared from the MWCNT is shown in **Fig. 8.4(c)**. The Inset shows a HRTEM image of the GONRB and arrows indicate the unzipped portion of the MWCNT during the oxidation/reduction process. Note that the dark regions denote the presence of metal catalyst NPs and amorphous carbon.

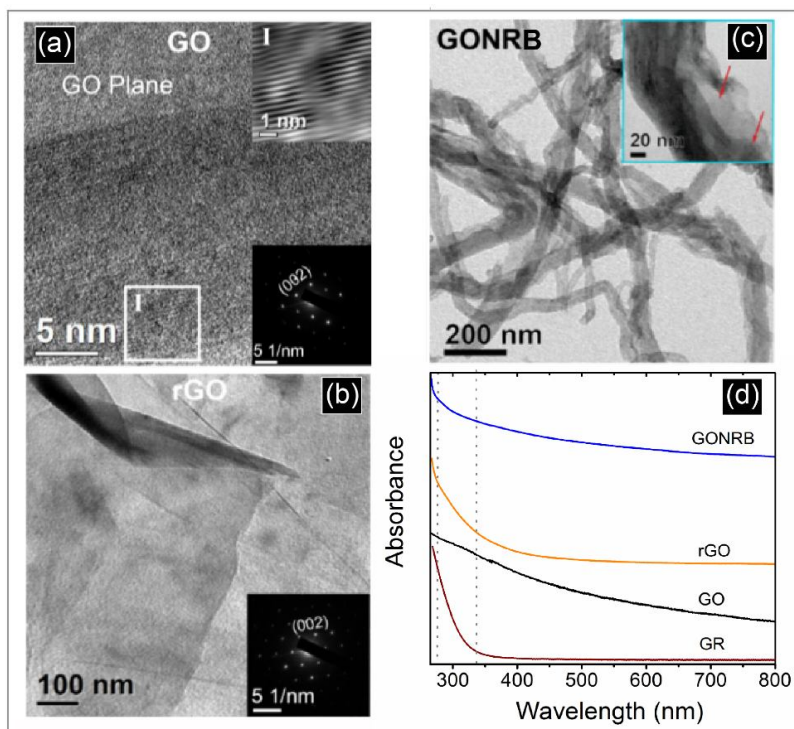


Figure 8.4: HRTEM images of various forms of CDGs: (a) Cross section of the multilayer GO sheets. Upper inset is a magnified view of the region of I, which shows the interlayer separation of graphene layers, and the lower inset shows the corresponding SAED pattern taken on the GO basal plane. (b) Few layer rGO and corresponding SAED pattern (inset). (c) TEM image of GONRB grown from MWCNTs. Inset shows the unzipped NRs and arrows indicate the unzipped portions. (d) Comparison of optical absorption spectra of CVD graphene and CDGs: GR, GO, rGO and GONRB. The vertical dotted lines represent the absorption peaks corresponding to the π - π^* transition and sub-band energy states (due to edge functionalization with COOH and C=O), respectively. The curves are vertically shifted for clarity.

8.3. Optical Absorption Studies

Optical absorption measurements have been carried out on GR and CDG materials in order to understand the effect of surface functionalities and intrinsic defects on graphene. Comparison of the absorption spectra from different graphene samples coated on quartz substrates is shown in **Fig. 8.3(d)**. It is evident that the GR is completely transparent over the entire range of visible–NIR region as compared to the CDG materials showing some absorption in the visible region. We have also measured the absorption spectra in DGR, which is almost identical to that of GR, though it contains intrinsic defects on the basal plane and at the edges. Note that GO, rGO and GONRB show a broad visible absorption. Visible absorption from the CDGs signifies two important contributions, i.e., transition from π - π^* electronic states of graphene basal plane formed by partially overlapped p-orbitals in the sp^2 hybridised carbon

and stacking of various in-plane oxygenated functional groups corresponding to defect induced intermediate energy states (sub-bands), i.e., transition from $n-\pi^*$ states.^{6, 10}

8.4. Photoluminescence Studies of CDG Thin Films

The PL spectra from all the CDG thin films have been acquired with 355 laser excitations. In general, CDG samples may show the excitation wavelength dependent PL due to the distribution of various conjugated aromatic rings of sp^2 crystallites with different sizes, separated by the sp^3 matrix which are associated with $\pi-\pi^*$ energy states and sub-band energy states ($n-\pi^*$) of oxygen functionalities.⁸⁻⁹ **Figure 8.5(a-c)** illustrates the room temperature PL features of GO, rGO and GONRB thin films, respectively, with 355 nm laser excitation. The PL spectrum in each case was fitted with the three Gaussian peaks, namely one blue and two green emissions, peak P1 at $\sim 437-440$ nm, peak P2 at $\sim 497-500$ nm and peak P3 at $\sim 537-551$ nm. Interestingly, P1 and P2 are common to all CDG thin films, while relative position and intensity of P3 changes from sample to sample. Note that the solid blue line represents the fitted curve and symbols correspond to the experimental data. The peak positions and line shapes are dissimilar in different cases due to the difference in nature of in-plane and edge functionalities in the CDG thin films.

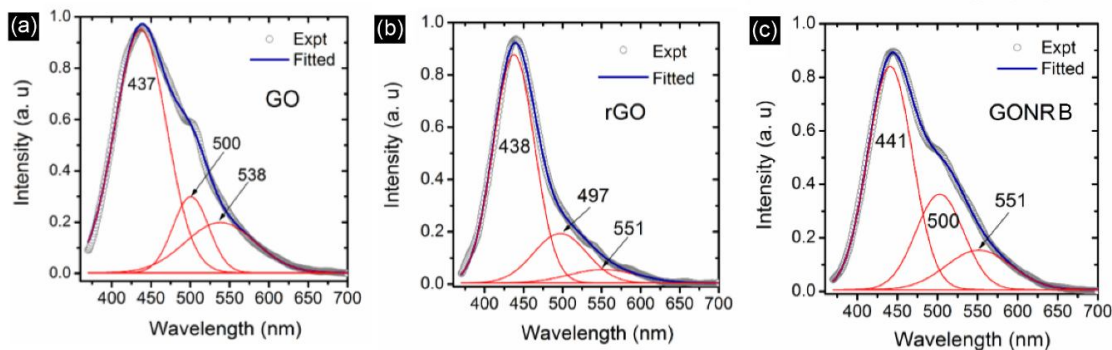


Figure 8.5: Room temperature PL spectra from CDG thin films excited with 355 nm laser: (a) GO, (b) rGO, (c) GONRB. The symbol refers to the experimental data and the solid blue line corresponds to the fitted data in each case; centres of the fitted peaks are denoted in nm unit.

The origin of blue PL emission (P1) from GO related functional materials is studied well in the literature and it arises from the localised energy states of crystalline sp^2 domains separated within the sp^3 matrix.¹⁰ P1 at ~ 440 nm from disordered GO is a representative of π states of crystalline sp^2 clusters within the sp^3 carbon sites. These sp^3 sites are associated with in-plane oxygenated functionalities on the graphene basal plane, mostly epoxy and CO related functionalities. The nature of blue emission also depends on the degree of in-plane

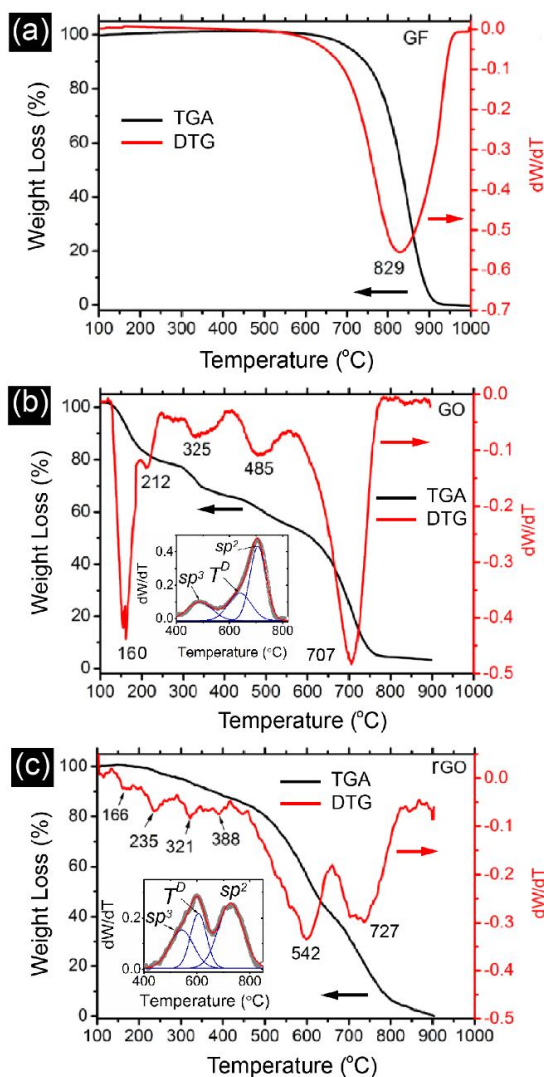


Figure 8.6: TGA/DTG thermogram profiles of CDG materials measured in high purity oxygen atmosphere: (a) GF (b) GO, (C) rGO and. The DTG peaks are denoted in degree °C unit.

oxygenated functionalities nucleated at the sp^3 sites.¹¹ In the present case, the line shape of the P1 peak does not change significantly for different CDG samples. On the other hand, P2 and P3 peaks are likely to originate from the defect induced sub-band energy states, which are mostly confined at the edge sites of the CDGs.⁵⁻⁶ These sub-band energy states may arise from the covalent attachment of COOH and C=O functional groups at the edges, which is consistent with the new Raman band at 1450 cm^{-1} (D^s). The line shape of the PL from these sub-bands may be different in different CDG samples due to the variation in COOH and C=O functionalities. Note that the P2 and P3 emissions are strong in case of GONRB, where edge states are likely to be dominant. Interestingly, the evolution of P1, P2 and P3 with

annealing reveals that the in-plane and edge functionalization (COOH and C=O) of CDGs give rise the sub-band gap energy states.

The precise nature and evolution of oxygenated functionalities on the in-plane and edge sub-band gap emissions were monitored by the controlled hydrogenation and oxygenation (annealing) experiments and the results are discussed later.

8.5. TGA/DTG Studies

A quantitative understanding of the in-plane and edge functional groups in CDGs was developed from the analysis of the TGA/DTG results, as illustrated in **Fig. 8.6**. The nature of the functional group defects has been assessed from the thermal stability behaviour of each CDG sample analysed from TGA and DTG curves (black and red curves), as depicted in **Fig. 8.6(a-c)** for GF, GO and rGO, respectively. The oxidation temperatures (T_0) and the ratio of sp^2 , sp^3 and functionalized sp^3 carbon (T^D) content in all the CDG samples were calculated using Gaussian line shape fitting of DTG peaks (see the insets of **Fig. 8.6**) and it provides a clear picture on the evolution of the specific in-plane oxygen functionalities and COOH or C=O edge functional groups.

Table 8.1. Summary of the DTG profiles of the different CDGs before and after hydrogenation treatment. The peaks in the range 160–400 °C are attributed to the various oxygenated functional groups attached to the sp^3 sites of graphitic structure and those in the range 400–900 °C represent sp^3 , sp^2 and oxygen functionalized sp^3 carbon (T^D). Here, T_1 , T_2 ,.... T_6 represent the successive oxidation temperatures obtained from the DTG peaks in each sample. The ratio of sp^3/sp^2 and T^D/sp^2 were calculated from the integrated intensities of Gaussian line shape fitting of the DTG peaks of sp^3 , sp^2 and T^D .

Sl. No	Sample	Functional Groups				sp^3	sp^2	T^D	sp^3/sp^2	T^D/sp^2
		T_1	T_2	T_3	T_4	T_5	T_6			
1	GF	–	–	–	–	–	829	–	–	–
2	GO	160	212	325	–	485	707	638	0.38	0.53
3	rGO	166	235	321	388	542	727	606	0.56	0.54
4	GOH	160	212, 295	337	437	541	658	616	0.84	0.59
	rGOH	–	–	–	416	533	650	611	1.73	0.91
Functional Group Identity (Tentative)		H_2O	$-OH$	$-COOH$ $/C-O-C$	$C-OH/$ $C=O$	$C-C$	$C=C$	Functionalized sp^3 Carbon (This work)	–	–
		12	12	12	12-13	12	12			

The complete details of the DTG peak position, integrated area and the ratio of sp^3 , functionalized sp^3 (T^D) to sp^2 carbon and functional group identity (tentative) are presented in the **Table 8.1**. The T_0 for GF is very high (829 °C), which is attributed to the highly ordered graphitic layers with covalently bonded sp^2 hybridised crystalline carbon. On the other hand, GO and rGO show much lower decomposition temperature (DTG peaks) for sp^2 and sp^3 carbon that may be due to the interlayer distortions and in-plane/edge oxygenated functional groups (see the **Fig. 8.4(a)**). The multiple DTG peaks in the range of 100 and 400 °C can be ascribed to the in-plane and edge oxygenated functionalities. A sudden drop in the weight % of GO at 160 °C arises from the evaporation of water (hydroxyl– OH) and weakly bonded in-plane epoxy (–O–) functional groups.¹²

Various peaks of DTG profiles for different samples are extracted from Gaussian fitting and are tabulated in the **Table 8.1**. Note that rGO shows higher oxidation temp (T_5 , T_6) for sp^2 and sp^3 carbon (see **Fig. 8.6(b)**) as compared to that of GO. These results are consistent with the evolution of blue PL emission in GO and rGO and enhanced green emissions in GONRB after hydrogenation and oxygenation, respectively.

8.6. FTIR Studies

Identity of various in-plane and edge oxygen functional groups in CDGs is further confirmed from the FTIR analysis. The FTIR bands associated with the various CO related oxygen functional groups and sp^2 (C=C) and sp^3 (C–C) carbons can be distinguished from the spectra shown **Fig. 8.7**. These features are compared for as-grown and hydrogenated CDG samples. All the CDG samples show the characteristic IR active vibrational modes of covalently bonded carbon and oxygen atoms, besides the sp^2 and sp^3 hybridized carbon. The complete details of the FTIR bands for each sample and their physical significance are presented in **Table 8.2**. The two weak modes at 2886 and 2936 cm^{-1} signify the C–H stretching at the edge of the graphene layer. It can be clearly seen that these modes are prominent in GONRB, while in case of GO and rGO they are insignificant due to the saturation of oxygen species on the basal plane.¹⁴

Interestingly, a key feature of the functionalization on the basal plane of the graphene was obtained from the important vibrational feature of sp^2 crystalline carbon at 1589 cm^{-1} , and it is attributed to the in-plane stretching of covalently bonded carbon atoms of CDGs. This band is common to as-prepared GO and rGO, and after hydrogenation (at 550°C) it is

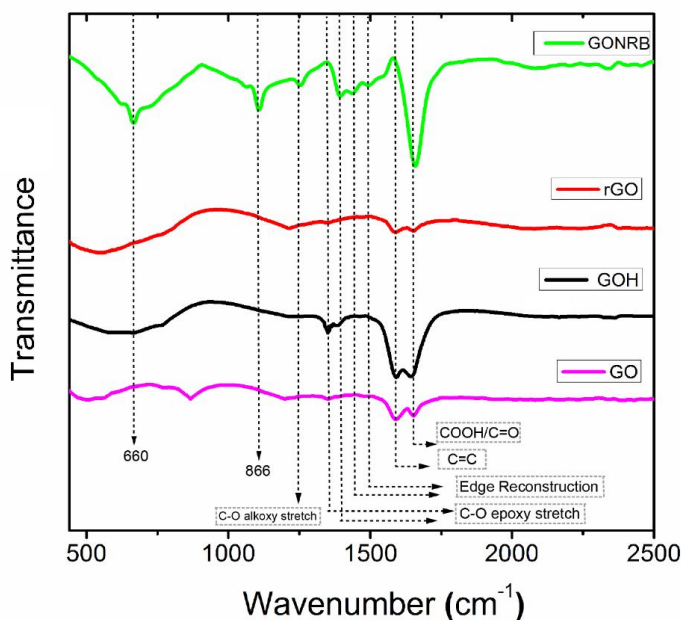


Figure 8.7: FTIR spectra of GO, GOH, rGO and GONRB showing the presence of covalently attached oxygen functional groups, sp^2 (C=C) and sp^3 (C-C) carbon attached on the basal plane and edges of CDGs.

significantly enhanced due to the removal of in-plane covalent oxygen functionalities. Another mode at 1655 cm^{-1} was observed in GO and rGO and after hydrogenation, it becomes stronger. Interestingly, the 1655 cm^{-1} band is strong and sharp in case of GONRB, and it is attributed to the COOH or C=O functionalization at the edge sites. Note that the C=C (1589 cm^{-1}) mode is not prominent in GONRB due to strong presence of COOH and C=O edge functional groups. Additionally, the evidence for the contribution of C=O is revealed from the enhancement of 1655 cm^{-1} mode after hydrogenation of GO, while the strong vibrational modes at ~ 1105 , 1254 and 1393 cm^{-1} in GONRB are attributed to the C–O related alkoxy and epoxy stretching vibrations at the edge sites. However, attachment of OH functional groups is more significant during the initial stage of oxidation in the CDG materials. The continuous oxidation treatment leads to the formation of COOH and C=O functionalities along with the enhanced sp^3 carbon content due to the intercalation of the graphene layers.¹² The formation of covalent COOH/C=O functionalities are more favourable in case of GONRB, which is evidenced from the higher sp^3/sp^2 ratio and it's consistent with the FTIR analyses.¹¹⁻¹² The two additional bands at 660 and 866 cm^{-1} may be attributed to the residual C=O related vibrations on the graphene basal plane. Thus, the FTIR results reveal the actual nature of edge functionalities, such as COOH or C=O in GONRB samples and the evolution of in-plane oxygenated functionalities in GO and rGO, which are fully consistent

Table 8.2. Summary of the vibrational modes of the various carbon and oxygen covalent functionalities in different CDG materials extracted from the FTIR spectra.

Peak Position (cm ⁻¹)				Peak Assignment	Ref.
GO	rGO	GOH	GONRB		
1197	–	–	1108	C=O stretching of alkoxy groups	15
–	1210	–	1254	C-O (1260) epoxy stretching	14-15
1350	1350	1350, 1382	1395	C-O (1389) epoxy deformation	15
–	–	–	1436	Edge reconstruction (Tentative) (skeletal vibration of graphene)	This Work
–	–	–	1494	Edge reconstruction (Tentative)	–
1589	1588	1590	1589	C=C in-plane stretching	16, 17
1653	1652	1643	1658	-COOH	14
–	–	2820	–	-CH ₂ symmetric	17
–	–	2938	2930	-CH ₂ asymmetric	17

with the PL results discussed later. FTIR results reveal that the GONRB have additional functional groups as compared to that of GO and rGO due to domination of the edge sites. This is consistent with the higher intensity of green PL in GONRB after annealing (discussed later).

8.7. Micro-Raman and TGA/DTG Studies of Hydrogenated CDG

The evolution of oxygen functional groups with hydrogenation treatment was substantiated from the Raman signatures of CDGs and these results are compared with the TGA/DTG analyses. **Figure 8.6(a)** represents a comparison of Raman characteristic bands of various hydrogenated CDGs and the hydrogenated GR. The ratio of integrated intensities I_{2D}/I_G and I_D/I_G reveals considerable reduction in the oxygenated functional groups on the graphene basal plane as well as at the edges and improves the sp^2 crystallinity of GO and rGO after hydrogenation, as evidenced by the sharp G and 2D band shown in **Fig. 8.8(a)**, in comparison to the as pristine CDG samples (see **Fig. 8.2**). Note that a weak 2D band was found in the hydrogenated GONRB sample. (see **Fig. 8.8(a)**). The absence of D+D' and 2D' bands in hydrogenated CDGs is an evidence for the reduction of in-plane and interlayer epoxy/COOH functional groups. Presence of D+D' band in GONRBH may be due to the C=O functionalities. The Raman analysis is consistent with the changes in PL spectra of

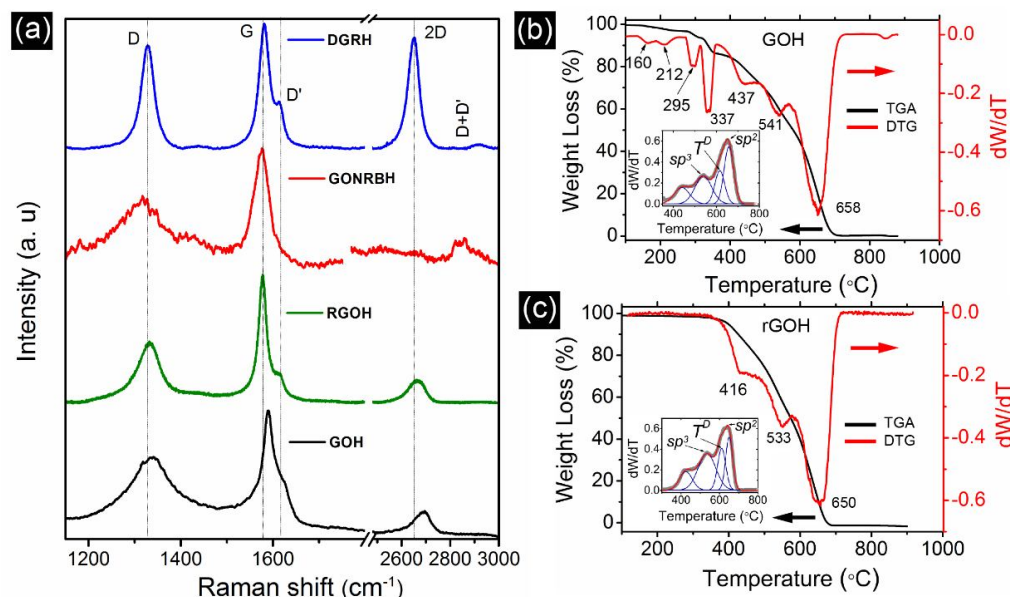


Figure 8.8: (a) Characteristic Raman spectral features of defective graphene (DGR) and CDG samples after H_2 annealing showing distinct D, G, D' and 2D bands and corresponding integrated intensity ratios of I_D/I_G , I_{2D}/I_G are labelled for each sample that are calculated from the Lorentzian line shape fittings. The excitation wavelength used here is 632.8 nm. The TGA/DTG profiles of (b) GOH and (c) rGOH. The units of DTG peaks are in $^{\circ}\text{C}$. The inset in each case represents the Gaussian line shape fitting for the DTG peaks of sp^3 , sp^2 and functionalized sp^3 carbon (T^D).

hydrogenated CDGs, as discussed below. The disappearance of D^s band (at $\sim 1450 \text{ cm}^{-1}$) in hydrogenated and oxygenated GONRB clearly reveals the removal of COOH functionalities and the asymmetry in the line shape may be due to the presence of residual $\text{C}=\text{O}$ at the edge sites of GONRB that enhances the green PL emissions (discussed below).

Further, the above Raman results were correlated with the TGA/DTG analysis of hydrogenated CDG samples. **Figure 8.8(b)** represents the thermal analysis of hydrogenated GO and rGO extracted from the TGA/DTG profiles. Inset in each case represents the deconvolution of sp^3 , sp^2 and functionalized sp^3 (T^D) carbon DTG profiles with Gaussian line shape fitting. Here, two important observations can be made on GOH and rGOH: (i) an increase in the ratio of sp^3/sp^2 , (ii) a reduction in the T_0 (ΔT_0 — 49 $^{\circ}\text{C}$ for GO and ΔT_0 — 77 $^{\circ}\text{C}$ for rGO) signifying the removal of in-plane epoxy/OH related functionalities on the graphene basal plane. Here ΔT_0 is the change in the oxidation temperature of sp^2 carbon before and after hydrogenation. An additional DTG peaks at 437/416 $^{\circ}\text{C}$ for GO/ rGO and a sudden weight loss at 337 $^{\circ}\text{C}$ were observed. These observations imply that the additional DTG peak might be due to the residual $\text{C}=\text{O}$ functionalities, which is fully consistent with the FTIR result of hydrogenated GO sample. Note that the PL emission intensity was strongly

reduced after hydrogenation that might be due to the large number of sp^2 crystallites within the sp^3 domains. This may be due to the high temperature of annealing that may have removed the covalently bonded oxygen functionalities. These results help us to identify the specific PL bands from in-plane and edge functionalized CDGs.

8.8. Photoluminescence Studies on Oxygenated and Hydrogenated CDG

The contribution of in-plane and edge functional groups to the visible PL was investigated from the PL studies on the oxygenated and hydrogenated CDG samples. **Figure 8.9(a-c)** represents the room temperature PL spectra from various CDG thin films before and after the oxygenation/hydrogenation treatment. **Figure 8.9(d-f)** represents the Gaussian line shape fitting of the PL spectra for oxygenated and hydrogenated GONRB samples. A comparison of the relative change in PL intensity is made on the basis of the Gaussian peak fitting of the PL data. Note that all the samples show strong blue emission before annealing and it is highly reduced in GO/ rGO after H_2 annealing, which might be due to the removal of in-plane oxygenated functional groups from the GO/rGO basal plane during the high temperature annealing (550 °C) (see **Fig. 8.6(b) and (c)**).⁴ Though there is an overall reduction in the PL intensity after oxygenation, the relative intensity of blue PL is high with respect to the green PL in rGO, while the blue PL intensity is very low in GO. Improved sp^2 crystallinity was observed from the annealed CDGs, which were evidenced from the FTIR, micro-Raman and TGA/DTG results. The evolution of COOH and C=O functionalities in the GONRB correlates well with the evolution of the PL peak intensity. The peak parameters and their physical origin (tentative) are presented in **Table 8.3**. These assignments are supported by the FTIR and Raman results discussed in the previous section. Note that the peak positions of the blue P1 and green emissions (P2 and P3) lie in the range of 437–443, 497–502 and 534–551 nm, respectively. The hydrogenation and oxygenation of CDG samples reveal the improved sp^2 crystallinity in case of GO and rGO, while in case of GONRB evolution of COOH and C=O functionalities were observed. The Gaussian line shape parameters for the GONRB reveal a considerable increase in the C=O functional groups after oxygenation, while COOH functionalities were less in the case of annealed GONRB (see **Table 8.3**). **Table 8.3** shows that after annealing, relative intensity of P1 reduces with respect to that of P2 and P3. Recent report on the photo thermal reduction of GO showed the reduction of defect induced emissions based on the gradual movement of PL peak from blue to red along with narrowing of line width.⁹ Based on our experimental observations and literature reports on the PL

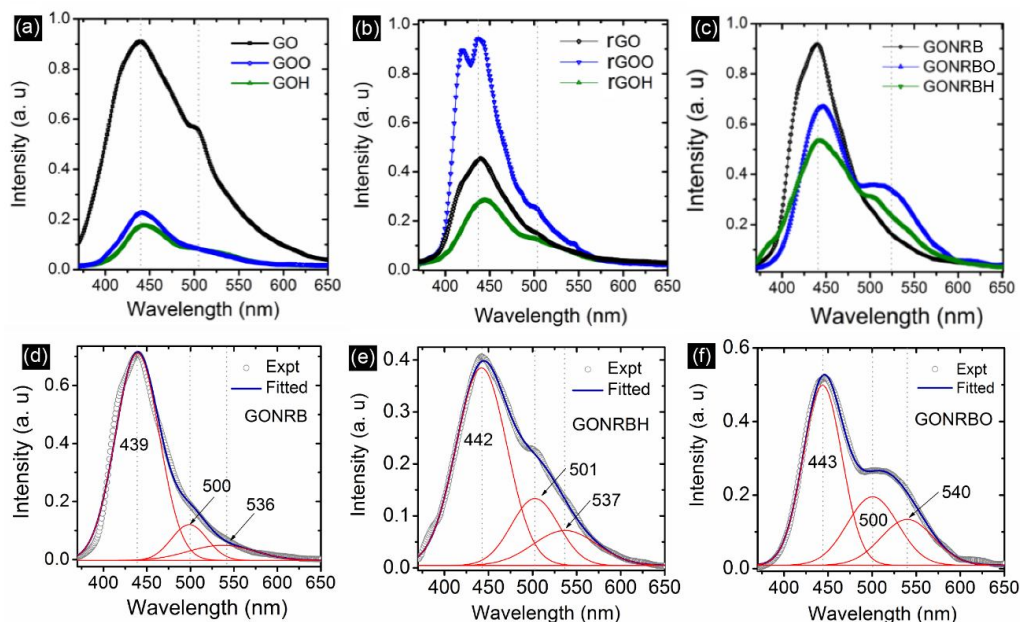


Figure 8.7: Effect of oxygenation and hydrogenation on the PL spectra from different CDG samples: (a) GO, (b) rGO and (c) GONRB. Gaussian line shape fitting for the (d-f) GONRB samples to compare the evolution of COOH and C=O edge functionalities before and after oxygenation and hydrogenation.

evolution of CDGs, we have tailored the blue and green emissions by monitoring the sp^2 crystallinity and monitoring the COOH and C=O functionalities at the edge site of CDG materials. We tentatively assign the two green emissions: P2 at ~ 497 – 502 nm and P3 at ~ 534 – 551 nm in CDG materials to the defect induced energy states of COOH and C=O functionalities, respectively.

8.9. Summary

1. CDG functional materials were synthesized and their thin films were fabricated using simple spin coating.
2. The spatial distribution and identification of intrinsic and functional group defects at the in-plane and edge sites in graphene and CDG materials were established from the micro-Raman, FTIR and HRTEM analysis to elucidate the origin of blue and green PL emissions from the CDG thin films.
3. The contribution of in-plane and edge functional groups to the visible PL was further investigated from the TGA/DTG analysis for the first time. The evidence for the specific functionalities at the edges and basal plane that gives rise to the blue and green emission in

CDGs have been identical from the combined analysis of micro-Raman and TGA/DTG results from the as-grown, hydrogenated and oxygenated CGDs, for the first time.

4. The defect induced two green emissions from the CDG materials at $\sim 497\text{--}502\text{nm}$ and $\sim 534\text{--}551\text{nm}$ are assigned to COOH and C=O functionalities, respectively, while the blue emission is attributed to the localised states of sp^2/sp^3 domains and epoxy related in-plane functional groups.



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Summary and Conclusions

This chapter presents a summary of important contributions of the thesis and highlight the new findings on the fabrication of large area single layer graphene and graphene based transition metal (TM) plasmonic and ZnO hybrid nanostructures (NSs) and their applications in photocatalysis, SERS sensor and UV photoconductive detectors. Scope of the future works related to this thesis is presented at the end of the chapter.

9.1. Summary and Highlights of the Contribution

In this thesis, I have presented about the fabrication of high quality, large area single layer graphene (SLG) by chemical vapor deposition (CVD) and chemically derived graphene by wet chemical synthesis. Further, I have developed the graphene (GR) transition metal (TM) plasmonic hybrid NSs from by a physical functionalization technique. A quantitative analysis of defects and defect mediated interaction of TM NPs with graphene was investigated using HRTEM and resonance Raman spectroscopy, for the first time. Further, I implemented these GR-TM plasmonic hybrids for the application of efficient visible light photocatalysis and SERS detection. Next, I demonstrated a new growth strategy for the graphene assisted controlled growth of vertically aligned 1D ZnO nanostructures such as nanorods (NRs), nanowires (NWs) and nanoribbons (NRBs) at a relatively low temperature using physical vapor deposition (PVD) technique on single layer and few-layer graphene. The explicit role of graphene, Au catalyst and ZnO seed layer in the growth of vertically aligned ZnO NRs and NWs were investigated systematically. I have fabricated a graphene enhanced GR-ZnO NW hybrid UV photodetector, which shows a high UV responsivity of the order of 10^2 and fast response/recovery times as compared to that of bare ZnO NWs. The role of graphene in the enhancement of the UV responsivity was correlated from the cyclic photocurrent (PC) photoresponse measurements of the GR-ZnO thin film hybrid.

The important contributions of the present thesis work are summarized below.

A. Critical Growth Parameters for Large Area Defect Free Single Layer Graphene

Control of several growth parameters, such as gas precursors and preannealing of copper (Cu) foil prior to the growth process of graphene, which decide the nucleation of large area coverage of the SLG was studied systematically in this thesis. Control of defects in SLG was achieved by both preannealing and CVD process conditions. We found that the longer duration of preannealing of Cu foil yields the defect free SLG coverage at atmospheric pressure growth conditions. The methodology of clean transfer of graphene on to different substrates was performed successfully, such that the as-transferred graphene does not have any nonuniformity and surface corrugation. Besides the CVD growth, we have fabricated the chemically derived graphene (CDG) functional optical materials to correlate the structural and functional group defects associated with the sp^2 and sp^3 carbon. To understand the origin of visible photoluminescence from CDGs, we have performed the controlled hydrogenation and oxygenation studies and identified various in-plane and edge oxygenated functional groups, for the first time.

B. Defect Mediated Efficient Physical Functionalization of Graphene with Transition Metals

A quantitative study on the interaction of TM NPs with in-plane and edge defects of graphene was performed. We optimized the physical functionalization process for the formation of GR-TM hybrids preserving its sp^2 crystallinity. Raman studies in conjunction with HRTEM imaging provide direct evidence of defect enhanced strong interaction of Au with the defect sites in graphene and physical functionalization of graphene at room temperature, without involving any chemical reaction. Local SPR and SERS effect at the GR-TM interface was identified from a strong enhancement of the D and D' Raman modes and enhancement of SPR peak in the absorption spectra. Raman mapping, HRTEM analyses provided evidence for strong bonding of Au NPs at the defect sites in graphene. The inter-defect distance and areal defect density calculated from the Raman analysis on GR-TM are in excellent agreement with the HRTEM analysis. Further these results are supported with the XPS analysis. Raman line shape analysis further suggested that ultra-thin Au coated SLG behaves like a pristine bi-layer graphene lending support for strong interaction between Au and graphene layer. The excitation wavelength dependent Raman features of graphene and GR-TM hybrids before and after rapid thermal annealing (RTA) reveals the surface dewetting and diffusion of TM atoms through in-plane defects and edge defects. A wide

range of visible absorption was found in GR–TM hybrid system from UV to NIR wavelength region. This is significant for the reduction in the SERS signal after annealing, which was observed from the wavelength dependent Raman spectra and Raman mappings.

C. Visible Light Photocatalysis and SERS Applications of Graphene-Transition Metal Plasmonic Hybrids

A wide range of UV–vis–NIR absorption from the GR–TM plasmonic hybrids provides us a clue to exploit it for the enhanced visible photocatalysis. GR-TM hybrid plasmonic hybrids are implemented as visible light photocatalysts for the degradation of the environmental pollutants in aqueous media. We achieved enhanced visible light photocatalytic activity from physically functionalized graphene and graphene oxide (GO) with gold nanoparticles (Au NPs). Role of intrinsic and oxygenated functional group defects in the visible photodegradation of methylene blue (MB) was qualitatively analysed from the micro–Raman, HRTEM and UV-visible absorption studies. Enhancement in the photocatalytic activity of GR-Au and GO-Au plasmonic hybrids reveals the defect mediated interaction of the Au NPs with GR and GO, which was established from SPR and SERS. The enhanced visible light photodegradation of MB up to 77% and 85 % with first order rate constants 8.26×10^{-4} and $6.87 \times 10^{-4} \text{ min}^{-1}$ was achieved in case of Au functionalized GO and defective graphene, respectively. This is a significant achievement and it may be due to the superior charge transfer from graphene based plasmonic hybrids incorporated with structural defects and oxygenated functionalities.

We prepared large area graphene and GR-Au Hybrids for the SERS sensing to detect the Raman signal from the organic dye molecules with different dye concentrations. We found the enhanced charge transfer between the dye molecule and the GR-Au plasmonic substrate, as compared to bare SiO_2 substrate. The Raman enhancement of the order of 10^3 is achieved from this GR-TM plasmonic hybrids.

D. Graphene Assisted controlled growth of Graphene-ZnO Hybrid Nanostructures

We implemented the SLG as a versatile 2D platform for the growth of well aligned 1D ZnO nanostructures using Au catalyst and catalyst free growth approaches at a relatively low growth temperature. It was revealed that the combined effect of the graphene and Au NPs

leads to the formation of high quality well aligned hexagonal faceted ZnO NRs and NWs, while direct growth on graphene substrate yielded randomly oriented ZnO NRBs. In-case of catalyst free growth, vertical growth of ZnO NWs take place on GR–ZnO thin film substrate, while randomly oriented ZnO NWs are grown on ZnO seed layer in absence of graphene layer. A growth mechanism was proposed for both the schemes based on the pseudo epitaxial relationship between ZnO and graphene lattice at the bond-centred sites. This epitaxial growth mechanism was supported by the characteristic Raman line shape features, in which the change in the relative intensities of 2D and D band Raman modes and a red shift in 2D band ($\sim 13 \text{ cm}^{-1}$) after RTA treatment in ZnO coated graphene substrate was revealed.

E. Tunable UV-Visible-NIR Photoluminescence from Graphene-ZnO Hybrid Nanostructures

Strong and tunable UV-visible-NIR photoluminescence (PL) was achieved at room temperature from the as-grown and annealed GR-ZnO hybrids. Several new visible and NIR PL bands were identified from these hybrid nanostructures that were tentatively attributed to the intrinsic defects associated with the oxygen rich growth conditions. PL studies on the as-grown and post-growth annealed GR–ZnO NRs, NWs and NRBs hybrids by Scheme 1 show sharp UV emission that was substantially improved upon post growth annealing at 500°C . Several visible PL bands were identified from these hybrid nanostructures that were attributed to the oxygen related defects in ZnO. Conclusions from PL analysis are fully supported by the XPS analysis. HRTEM and Raman studies reveal the good crystalline quality of the ZnO NWs grown on GR–ZnO buffer layer substrate in comparison with ZnO NWs grown on ZnO seed layer and GO–ZnO buffer layer substrates.

F. Improved UV Photodetector Based on Graphene-ZnO NW and Graphene-ZnO Film hybrids

We fabricated the graphene enhanced UV photodetector based on graphene-ZnO hybrid with an enhancement factor of two orders magnitude in the UV photosensitivity as compared to bare ZnO NWs. We evaluated the role of graphene in the enhancement of UV sensitivity by fabricating a GR-ZnO thin film hybrid. We found fast response and recovery time constants from the exponential growth and decay profiles of UV PC ON/OFF conditions, due to increased charge transport of graphene in GR-ZnO hybrid. The cyclic photoresponse

measurements reveal that, the high mobility of graphene reduces the recombination rate of photogenerated carriers. As a result, the lifetime of the photogenerated free charge carriers was greatly increased. Cyclic photoconductivity measurements of GR-ZnO thin film hybrid revealed the distinct role of graphene in the enhancement of UV sensitivity (1100×10^3 A/W).

9.2. Scope of Future Work

Present thesis is focused on the controlled growth of large area graphene followed by fabrication of graphene integrated hybrid nanostructures with TM plasmonic NSs and ZnO NSs and their photocatalysis, SERS and photoconducting applications. The present work can be extended in several ways, as described below.

1. More studies on comparison on the physical functionalization versus chemical functionalization with TM NPs can be performed and optimized for different applications.
2. As-transferred SLG can be exposed to the low RF plasma for the controlled functionalization with in various gas environments to introduce the band gap in the pristine graphene.
3. Graphene can be transferred on to an array of semiconductor NWs or 2D semiconducting layered crystals that are present on dielectric, flexible and transparent substrates. These kind of hybrid structures may show enhanced optoelectronic properties, which have enhanced light matter interaction even in the absence of external bias.
4. There are several other 2D materials that are semiconducting in nature and that have immense optical response in the visible light spectrum. These kind of 2D semiconducting materials are called layered transition metal dichalcogenides (TMDCs). Most of the semiconducting TMDCs can be grown (or) transferred directly on to the graphene to form 2D heterostructures, which have new perspectives for the optoelectronic applications.
5. Due to large surface area, carrier mobility, mechanical strength of the graphene, incorporating with other nanomaterials can provide improved functionalities for various self- energy harvesting applications.

6. Since carbon is abundant in the nature, CDG composites with conventional photocatalytic materials can be implemented as a visible photocatalysts for the removal of environmental pollutants for water purification water.
7. Growth of Graphene –ZnO hybrid can be optimized for the application in white light emitting diodes and other display applications.
8. Heterostructures of graphene and graphitic carbon nitride with tunable band gap can be made for exploitation in diverse range of applications.

