

Design of Semiconductor/ Oxide Photoanodes for Effective Light Scattering and Charge Transfers in Dye- Sensitized Solar Cells



*A Dissertation Submitted to the
Indian Institute of Technology Guwahati
as Partial Fulfillment for the Degree of*

DOCTOR of PHILOSOPHY

by

Avishek Banik

**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
GUWAHATI, INDIA
Jan 2019**

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STATEMENT

I hereby declare that the matter embodied in this thesis entitled, “**Design of Semiconductor/ Oxide Photoanodes for Effective Light Scattering and Charge Transfers in Dye- Sensitized Solar Cells**” is the outcome of research work carried out by me under the supervision of Prof. Mohammad Qureshi, at the Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, Assam, India.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made whenever work described here has been based on the findings of other investigators.

IIT Guwahati
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Certificate

Certified that the work described in this thesis entitled “**Design of Semiconductor/Oxide Photoanodes for Effective Light Scattering and Charge Transfers in Dye-Sensitized Solar Cells**” by Mr. Avishek Banik, Department of Chemistry, Indian Institute of Technology Guwahati has been carried out under my supervision and has not been submitted elsewhere for a degree.

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'Time flies'- heard of it so many times, now realizing as I am going to complete a long five year journey at IIT Guwahati. I find these years as one of the most enriching times of my life. I feel I have emerged as a better individual, personally as well as professionally and this could not have been possible without direct and indirect support, inspiration, motivation, and grace of many beautiful souls around me. It's difficult to express in words how grateful I am to these people, till, here is my modest attempt.

At the very onset, I take this opportunity to express my deep sense of gratitude and indebtedness to my thesis supervisor, Prof. Mohammad Qureshi for his proficient guidance, inspiration, creative and scientific ideas, constructive criticism, work ethics and the academic freedom that helped me to explore the domain of my work assembled in this thesis. He, with his great sense of humour could read my mind whenever I am ecstatic or low and showed me right path to hold onto my emotions and move forward with self-confidence and perseverance. Thank you Sir for being there in every situations during my PhD tenure.

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Still many names are missing whose contribution and help is worth mentioning.

Avishek



*Dedicated
To
Maa, Baba
&
Dada*

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Thesis Title:	Design of Semiconductor/ Oxide Photoanodes for Effective Light Scattering and Charge Transfers in Dye- Sensitized Solar Cells
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Thesis Overview

Chapter 1: Introduction

This Chapter addresses the recent advancements in design and development of photoanodes with various semiconductors/oxides of submicron/micron size of diverse morphology with favorable band alignments, which enhances the light harnessing efficiency of the photoanode by increasing the events of interaction between the sensitizer and the incident light as well as hinders the reverse tunneling of photo-injected electrons. A brief discussion on the evolution of photovoltaic technology, basic architecture and working principle of dye-sensitized solar cells are included. Role of submicron/micron size semiconductors/oxides heterostructures in light harvesting through scattering phenomenon have been discussed.

Chapter 2: Experimental

This chapter deals with the detailed synthetic protocols for materials, instrumentation techniques and methodologies used for material characterization, photoanode preparation, and device characterization using specific instrumental techniques/methods. Basic/Specific instrumentation for device characterization e.g. Newport ORIEL Sol3A solar simulator having 450 W Xe-short arc lamp equipped with AM 1.5 G filter connected to a Keithley 2400 sourcemeter for J-V curves, Newport Oriel IQE-200 having 250 W QTH lamp source for incident photon-to-current efficiency measurements and electrochemical impedance spectroscopy (EIS) measurements are also discussed.

Chapter 3: Dual function of silica nanospheres in enhancing the photovoltaic performance in ZnO nanoparticle based dye-sensitized solar cells

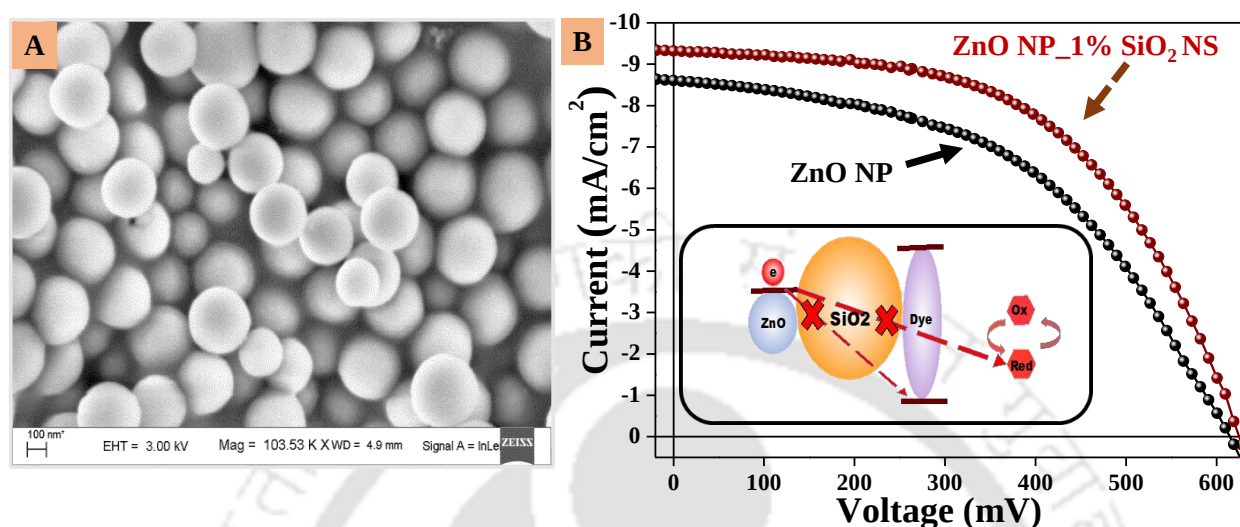


Figure 1. (A) FESEM images of as-synthesized SiO₂ nanospheres (B) J-V curves for the bare ZnO NP and ZS₁ device, Inset to trace B depicts schematic representation of inhibited electron interception at ZnO/dye/electrolyte interface [*Phys. Chem. Chem. Phys.*, 2016, 18, 27818]

This chapter presents the effect of submicron sized insulating silica nanospheres (SiO₂ NS) in a binary hybrid photoanode with zinc oxide nanoparticle. The synthesis of the materials were achieved by easy and cost effective synthetic routes. Optimized photoanode with 1% SiO₂ NS achieved a ~ 22% enhancement in power conversion efficiency (PCE) compared to the reference device. A systematic investigation revealed the bifunctional nature of the silica nanospheres in enhancing the device efficacy compared to its bare counterpart. Enhanced performance of the proposed solar cell can be ascribed to following key factors – i) Better light harvesting efficiency of the photoanode by optical confinement resulting in increased propagation length of incident light by multiple internal reflections furnished by SiO₂ NS ii) Minimum photoinduced electron interception to the redox shuttle (I⁻/I₃⁻) at the working electrode/electrolyte interfaces in presence of insulating SiO₂ NS. Higher recombination resistance (R_{ct}) in case of 1wt% composite indicates that SiO₂ NS serves as a partial energy barrier layer retarding the interfacial recombination (back transfer) of photo-generated electrons at working electrode/ electrolyte interface thus increasing the device efficiency. Figure 1 represents morphological features of as synthesized SiO₂ NS and the J-V curve for the bare as well as best performing photoanode.

Chapter 4: Nanocube assembled SrTiO₃ in enhancing the photovoltaic properties through its energy barrier and light scattering effects

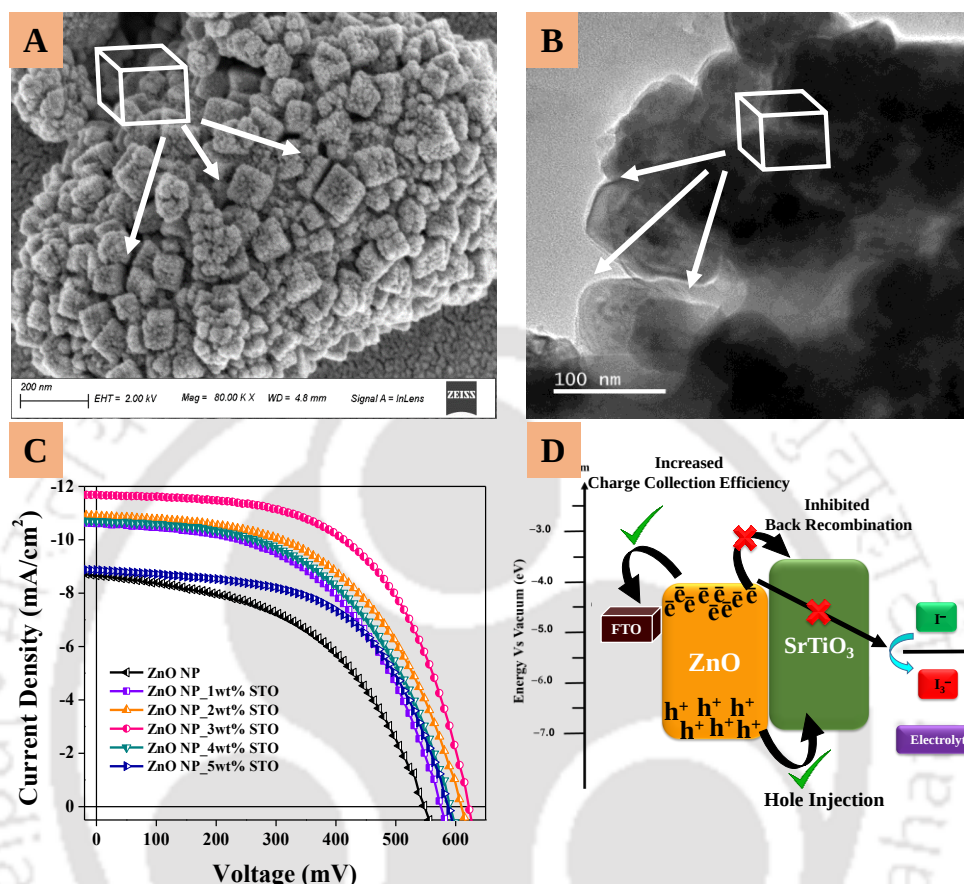


Figure 2. (A) FESEM images of as synthesized STO NCMS (B) Magnified TEM image of STO NCMS (C) *J-V* curves of the fabricated photoanodes (D) Schematic representation the charge transfer processes occurring in the composite devices [*J Phys. Chem. C*, 2018, 122, 16550]

This chapter presents utilization of perovskite ternary oxide, SrTiO₃ microstructure formed by self-assembly of nanocubes (STO NCMS) in the photoanodic section in composite with zinc oxide nanoparticle. Synthesis of STO NCMS was achieved by a two-step hydrothermal route in highly alkaline medium of pH ~12. A **~ 2-fold increase** in the power conversion efficiency (PCE, η) is displayed by ZnO NP_STO NCMS [for an optimized 3% STO NCMS] composite photoanode device compared to pristine device. Improved performance of photoanode with hybrid composite scaffold can be accredited to the boosted optical response in conjunction with impeded reverse tunneling probability of STO NCMS containing photoanode. Enhanced light harvesting through increased interaction of sensitizer with incident light is achieved via optical confinement of incident light by multiple reflections generated from mirror like facets of SrTiO₃ nanocubes as

well as an enhanced light scattering effects from individual entity. IPCE analysis revealed a better absorption of low energy photons that in turn resulted in an enhanced solar to electricity generation for an optimized ratio of STO NCMS. An effective photoinduced charge separation with a uniquely aligned band structure between ZnO and STO NCMS creates thermodynamic driving force and improves electron transfer ability from the LUMO of dye to CB of SrTiO₃ to that of ZnO which increases charge injection efficiency from excited state of dye as well as holes in the valence band of ZnO can migrates to the VB of STO NCMS results in an increased charge collection efficiency of the devices. Moreover, a ~ 200 meV negative CB position of STO acts as a partial energy barrier to the photo-injected electrons thus reducing the back recombination. Morphological features as well as photovoltaic characteristics along with schematic showing the plausible mechanism of electron transfer is depicted in figure 2.

Chapter 5: High quality mirror-like nano cuboidal CeO₂ coupled with reduced Graphene Oxide for superior light harnessing and charge transfer dynamics

This chapter demonstrates exploration of a ternary hybrid composite utilizing nano-cuboidal CeO₂ (CeO₂ NC) and 2D-*reduced* graphene oxide (2D-RGO) sheets in conjunction with ZnO nanoparticle and introduced in the photoanodic segment. Synthesis of CeO₂ NC was achieved via hydrothermal route whereas, RGO was synthesized by an oxidation followed by reduction process. Firstly, Graphene oxide (GO) was prepared utilizing graphite as a precursor. Reduced graphene oxide was synthesized by chemical reduction of graphene oxide. A nearby $\sim 6\%$ power conversion efficiency (PCE) has been achieved for photoanode with optimized CeO₂ NC concentration loaded with 1wt% RGO. A $\sim 30\%$ increase in the short-circuit current density (J_{sc}), $\sim 14\%$ in open circuit voltage (V_{oc}) as compared to bare photoanode is accredited to combination of enhanced light harnessing efficiency as well as better transport of photo-induced charges in the hybrid device. Nano-cuboidal CeO₂ owing to its size and mirror like facets provides a better light harvesting by photoanode through multiple interactions of incident photon with the absorber as well as acts as a partial energy barrier for photoinduced electron interception due to higher conduction band edge position, at the working electrode/electrolyte interfaces. Whereas, an effective photoinduced charge separation with a uniquely aligned band structure between ZnO, CeO₂ via 2D RGO sheets resulted in an increased charge collection efficiency of the devices. A substantial increase in the FF of the devices is resulted from better charge separation, injection as

well as transport offered by RGO sheets having very high electron mobility. Phase characterization, morphological features of as synthesized materials as well as device characteristics are shown in figure (3), (4) and (5).

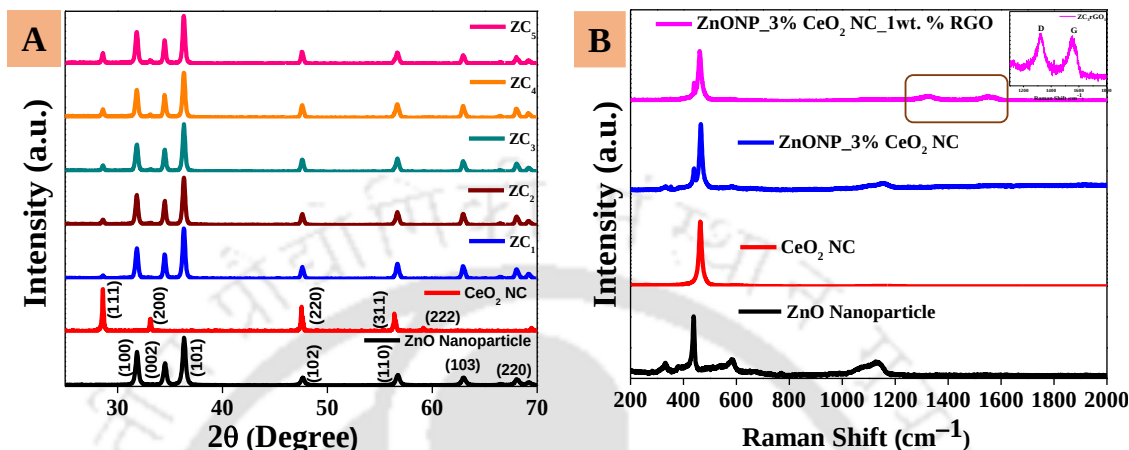


Figure 3. (A) PXRD spectra of ZnO NP, CeO₂ NC, and composites ZC_x (x=1-5) (B) Raman Spectra of ZnO NP, CeO₂NC, ZC₃ and ZC₃RGO₁. (Manuscript Submitted)

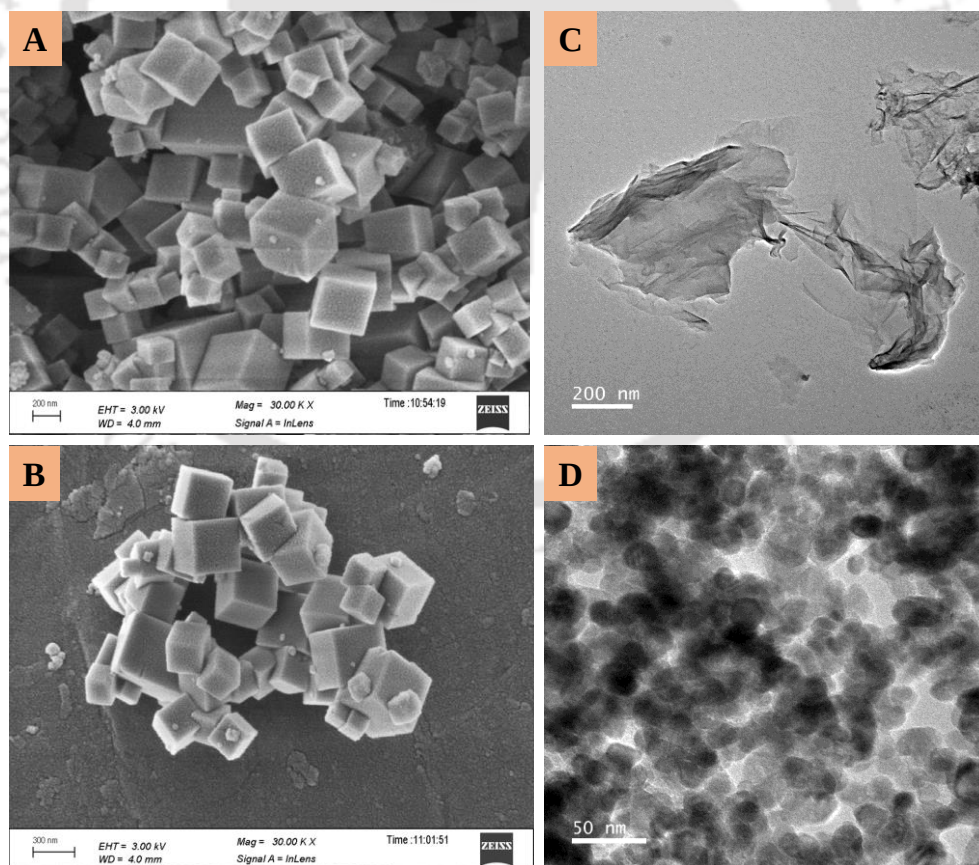


Figure 4. (A) FESEM and (B) Magnified FESEM images of CeO₂NC (C) TEM image of RGO and (D) TEM image of ZnO NP (Manuscript Submitted)

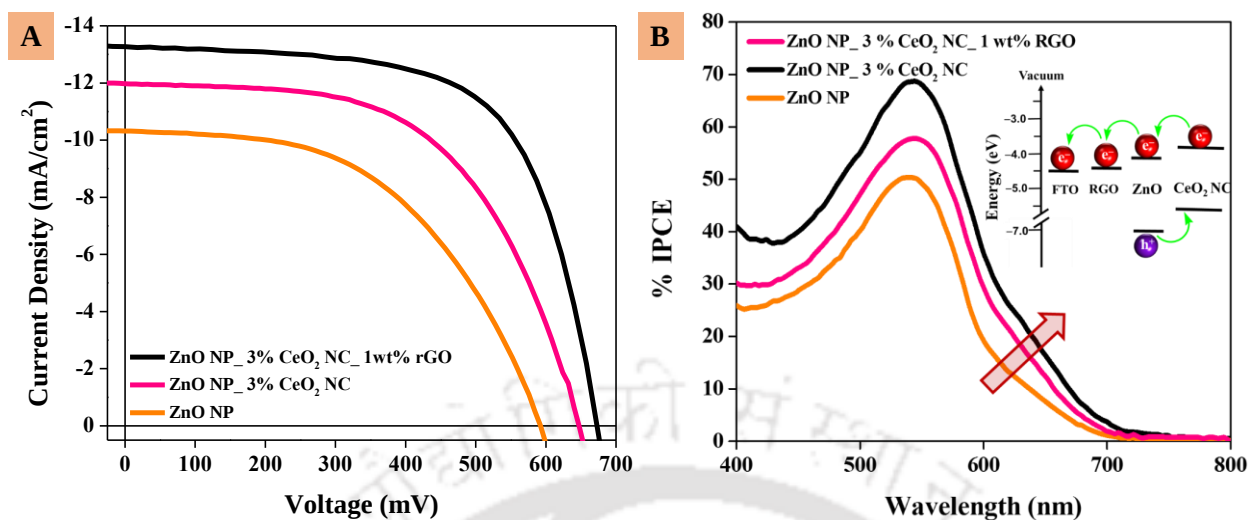


Figure 5. (A) J-V curve (B) IPCE plot of fabricated ZnO NP, ZnO NP_3% CeO₂ NC, ZnO NP_3% CeO₂ NC_1wt% rGO photoanode based devices (Manuscript Submitted)

Chapter 6: Nano-amassed mesoporous zinc oxide hollow microspheres as synergy boosters for efficient energy harvesting in SnO₂ based dye- sensitized solar cell

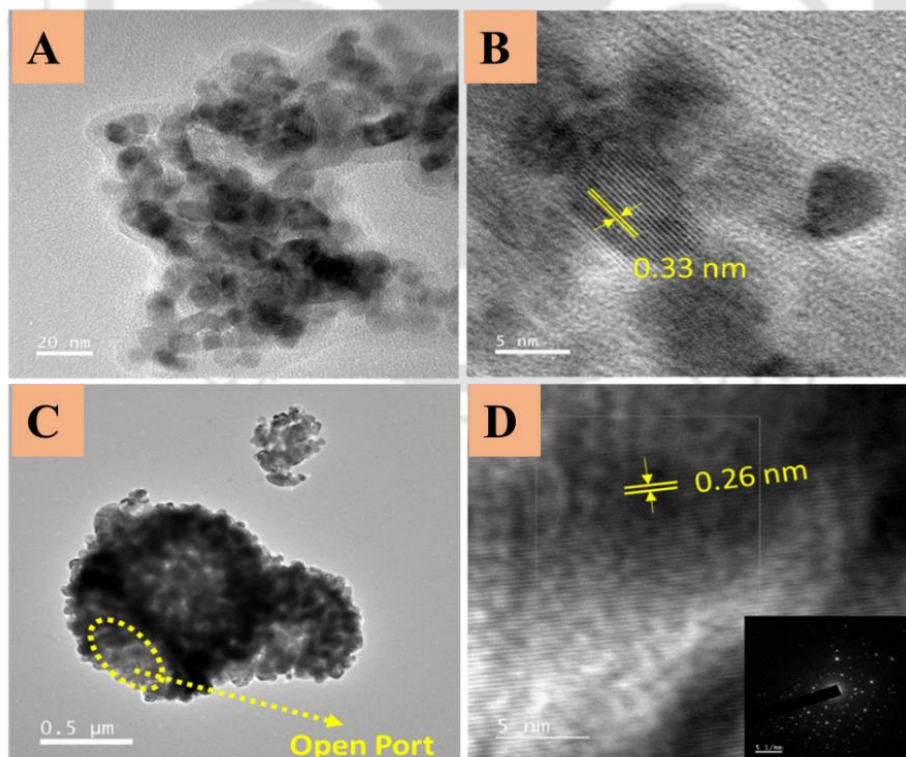


Figure 6. TEM and HRTEM images of (A) SnO₂ NP and (B) ZnO HS [ACS Omega, 2018, 3, 14482]

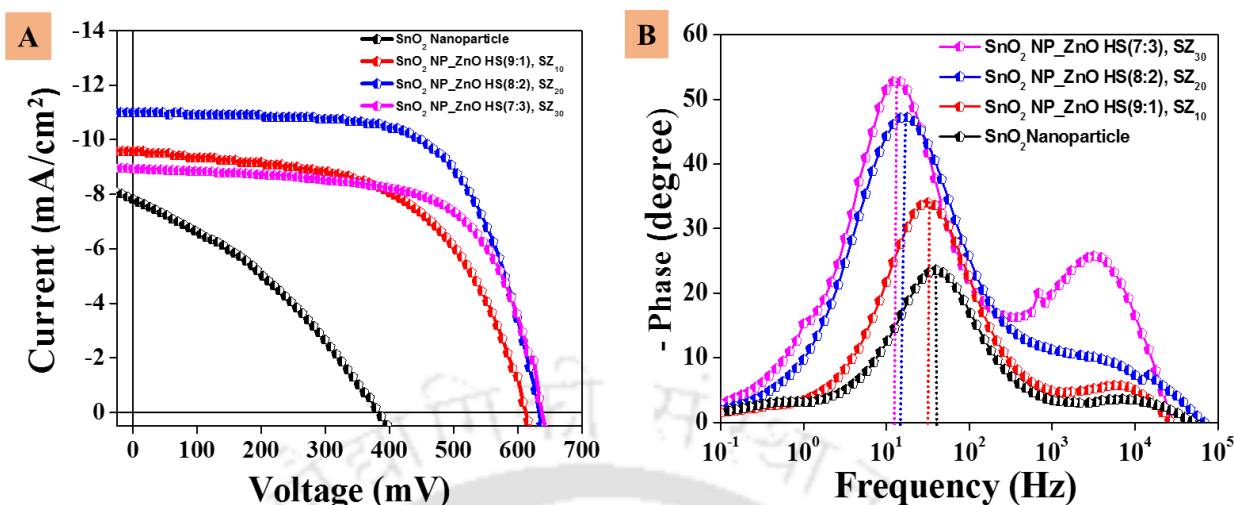
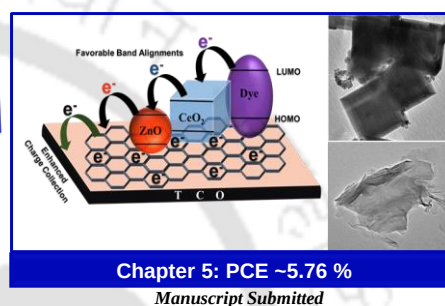
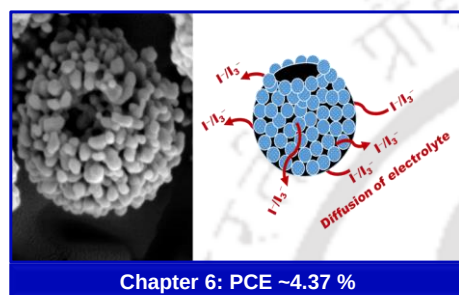
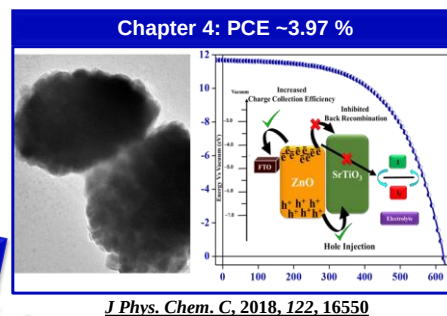
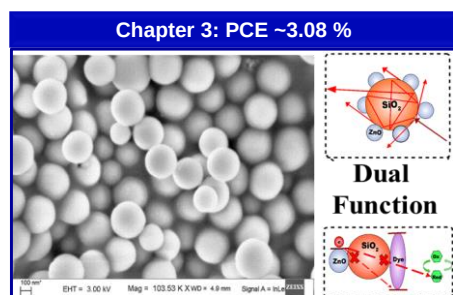


Figure 7. (A) *J-V* curve (B) EIS (Bode Phase Plot) plot of SnO₂ NP and SZx (x=10, 20, 30%) photoanode based devices [*ACS Omega*, 2018, 3, 14482]

This chapter demonstrates a practical strategy to boost efficiency in sparsely studied SnO₂ nanoparticle based photoanode by using nano-amassed micron sized mesoporous zinc oxide hollow spheres (*meso*-ZnO HS). SnO₂, one of the promising material suffers in terms of efficacy due to its inherent issues such as faster electron recombination and low fill factors and been a dire issue to deal with. A binary hybrid photoanode utilizing nano-amassed micron sized mesoporous zinc oxide hollow spheres (*meso*-ZnO HS) in conjunction with SnO₂ nanoparticle (NP), i.e. SnO₂ NP_ ZnO HS [for an optimized weight ratio (8:2)] displayed a near ~4–fold increase in the power conversion efficiency as compared to pristine SnO₂ NP device. *Meso*-ZnO HS are synthesized by an Ostwald ripening process in reflux conditions using Zn (NO₃)₂.6H₂O and PEG 200. Enhanced device performances in case of composite based photoanodes [SnO₂ NP_ ZnO HS] have been explained on the basis of better light harvesting capability of the composite photoanode as well as impeded reverse tunneling probability of photo-induced electron at semiconductor/dye/electrolyte interface. Around ~100% increase in the fill factors in case of composite based devices is due to facilitated diffusion of electrolyte through the pores of *meso*-ZnO HS, thus increasing the regeneration probability of oxidized dye. Moreover, a type II band alignment formed between well matched band positions of SnO₂ and ZnO heterostructures results in a charge carrier separation (electrons on SnO₂ and holes on ZnO) leads to reduced recombination and thus increases charge carrier lifetimes. Phase characterization, morphological features of as synthesized materials as well as device characteristics are shown in figure (6) and (7).

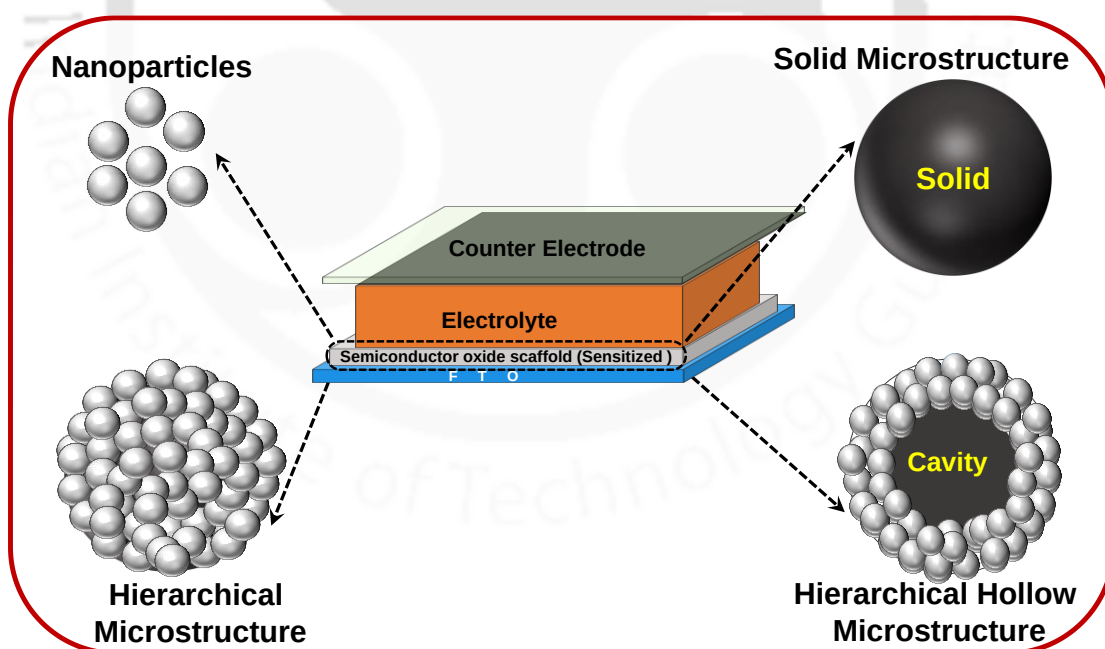
Thesis Overview:



**Light Harvesting
&
Charge Transfer
Dynamics**

Introduction

This chapter briefs about the development of photovoltaic technology, working principle of dye- sensitized solar cells, basic concepts about light scattering and its application in DSSC. Different photoanodic architecture, with diverse morphological features of light scattering materials in light harvesting over the conventionally used nanoparticle based photoanodes have been discussed. The chapter is concluded with a brief literature survey of current state-of-the art scenario and challenges related to the utilization of light scattering materials in dye-sensitized solar cell.



1.1 DEVELOPMENT OF PHOTOVOLTAIC TECHNOLOGY: AN OVERVIEW

The greatest challenge for current global society is to find means to replace the inevitably vanishing fossil fuels by clean and renewable energy resources to avoid adverse environmental and health hazards from the current energy system.¹⁻³ With ~ 13 TW global energy consumption rate in the year 2000 it is statistically projected that there will be a need of ~ 28 TW of energy by 2050, keeping the population growth and consumption of energy constant. Among all renewable energy resources, i.e., wind energy, solar energy, bio-energy, marine energy etc., solar energy is most abundant and has the potential to satisfy the future energy demand to build a globally sustainable society.⁴⁻⁵ Solar energy supplied to the earth, i.e., 3×10^{24} joules a year is gigantic and around 10,000 times more than the current energy demand.⁶ However, development of economic and highly efficient devices with earth abundant materials remains an enormous challenge. “Photovoltaics” promises to be an alternate avenue for efficient solar-to-electricity generation utilizing solar cells. Numerous efforts were made by the researcher across the globe to fabricate solar cells that can harvest solar energy efficiently.⁷⁻⁹ However, long energy payback time, high cost, toxic substances involved in processing etc., limits the real world applications of photovoltaics in a large scale.¹⁰ Figure 1.1.1 shows (A) distribution of global energy potential (renewable) vs world total energy consumption and (B) Growth of photovoltaic technology since 1992 in terms of power generation.

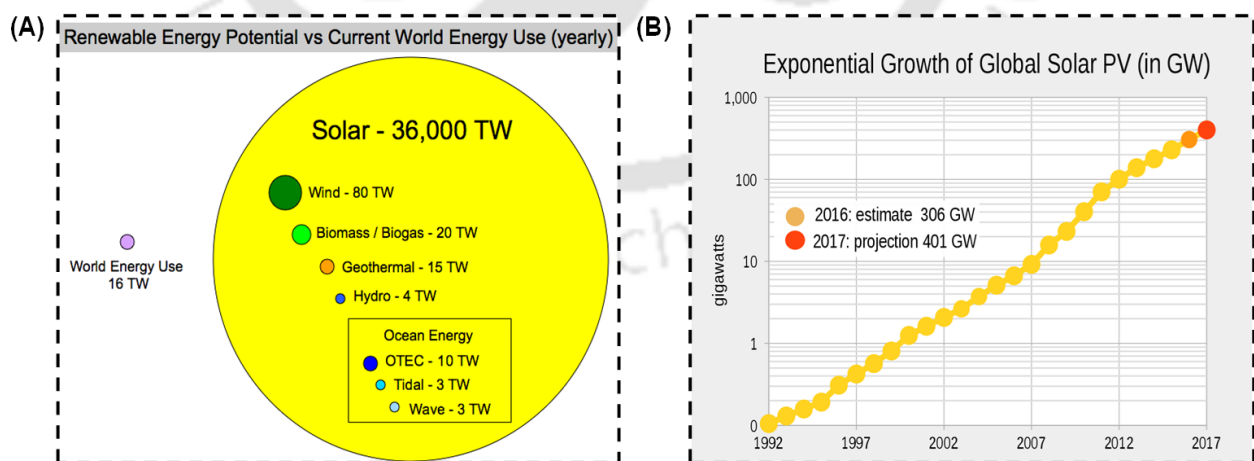


Figure 1.1.1 (A) Energy potential of renewable energy sources per year (Source: <https://www.resilience.org/stories>)
(B) Growth of photovoltaic technology since 1992 in terms of power generation
 (Source: https://en.wikipedia.org/wiki/Growth_of_photovoltaics)

Classified as generations of technology, “first generation solar cells” are made from single crystalline Si wafers (c-Si) and a leading technology in the commercial market with a record efficacy of $\sim 25\%$ has been reported for the state-of-the-art single crystalline c-Si device in the year 1998 by Martin Green’s group.¹¹⁻¹³ However, tedious fabrication technique and high manufacturing cost led the researchers to develop more economical thin-film solar cells termed as “second generation solar cells”. Second generation solar cells mostly involves the use of materials such as, amorphous silicon (a-Si), copper indium gallium selenide (CuInGaSe₂), cadmium telluride (CdTe) etc. Although cost-effective, these devices failed to meet the milestone set by the ‘first generation solar cell’ in terms of efficacy and stability.¹⁴⁻¹⁶ With the idea of lesser cost and ease of fabrication procedure, scientists have developed “third generation solar cells” that are based on the nanostructured photoactive materials, which could overcome the theoretical “Shockley and Queisser” upper limit of single junction solar cells.¹⁷⁻¹⁸ This class of solar cells include dye-sensitized solar cell (DSSC), quantum dot-sensitized solar cell (QDSSC), polymer solar cells or bulk-heterojunction (BHJ) solar cell, perovskite solar cell etc.¹⁹ The seminal paper by O’Regan and Grätzel on DSSC, in the year 1991 achieving $\sim 7.1\%$ efficacy utilizing TiO₂ as semiconductor scaffold, ruthenium (Ru) based dye as electron-injecting sensitizer, paved a pathway for researchers to develop new designs for highly efficient DSSCs.²⁰ Since then, researchers have developed various photoanodic architecture, wide visible light absorbing sensitizers and electrolytes over the years and achieved a record power conversion efficiency of $\sim 13\%$ using a Zinc porphyrin dye as sensitizer and a cobalt ^{II/III} complex as redox shuttle.²¹



Figure 1.1.2. (A) Flexible DSSC device fabricated by G24i Ltd., UK and (B, C) its integration to i-PAD keyboard and backpacks (D) Large area DSSC module demonstration from Dyesol., Australia

In contrast to First and Second generation solar cells, DSSCs endows advantages such as lightweight and flexibility, and can be fabricated employing roll-to-roll processing on flexible plastic substrates e.g. PET or thin metal foils making it feasible for usage as portable and wearable

devices on an everyday basis.²²⁻²⁴ It is well established that DSSCs can endure continuous illumination of more than 20000 h, and potential outdoor lifetime beyond 20 years.²⁵⁻²⁷ Aforementioned advantages encouraged companies like G24 Innovations (G24i), Dyesol, Solaronix, 3GSolar, Aisin Seiki, BASF, Bosch, Toyota, Sharp, Sony etc. in development, manufacturing and commercialization of this technology.^{22, 28} Among them G24i became the first company to commercialize DSSC²⁸ in 2009 as well as integrate high efficacy DSSC module into items like camouflaged solar panels for military, bag-packs, and computer accessories etc.²⁹⁻³² as can be seen from figure 1.1.2.

With enormous research and findings by scientific community in DSSCs over the last two decades, a $\sim 10\%$ efficacy for commercial modules has been achieved.³³ However, many challenges lie ahead in technological advancement of DSSCs for widespread practical applications. Usage of cost-effective components, alternative semiconductor/oxide materials, electrolyte and sensitizers is paving a path for rapid development of DSSC technology. Methodologies that are technically sound and economically viable for an enhanced spectral response, better charge transfers still demand enormous advancements to meet the threshold for mass production and commercial applications.

1.2 COMPONENTS AND OPERATIONAL PRINCIPLE OF DSSC

DSSCs are in essence photoelectrochemical devices, comprising of two electrodes, in which one is photoanode or working electrode and other is counter electrode or cathode sandwiched together separated by a $\sim 30\text{-}40\text{ }\mu\text{m}$ thick spacer. An electrolyte commonly known as redox couple is introduced in to the space left-behind between the sandwiched electrodes and works as a conductive medium to complete the device. Complete architecture of a DSSC and working mechanism are schematically depicted in figure 1.2.1 (A) and (B).

The primary configuration and the materials used in a DSSC are discussed as follows:

- (a) Transparent conductive oxide substrate (TCO): Commonly used are Fluorine doped Tin oxide (FTO) or Indium doped Tin oxide (ITO) or FTO coated PET substrate.
- (b) The anode is composed of a wide band-gap nanostructured mesoporous metal oxide (size $\sim 10\text{-}30\text{ nm}$) e.g., ZnO, TiO₂, WO₃, SnO₂, etc. film of $\sim 10\text{-}15\text{ }\mu\text{m}$ thick coated over FTO/ITO etc.

- (c) A light absorbing species or Photosensitizer: Generally used are Ruthenium based metal complexes, phthalocyanines, porphyrins as well as metal-free organic dyes having anchoring groups (-COOH, -H₂PO₃, -SO₃H etc.) with a visible light absorptivity.
- (d) An electrolyte with high chemical stability, visible light transparency, inert to the dye or metal oxide e.g., Iodide/ tri-iodide (I⁻/I₃⁻), cobalt (II/III) metal complexes are usually utilized as redox shuttles in (acetonitrile: Valeronitrile) solvent mixture.
- (e) A cathode or counter electrode: Mostly a very thin layer of Platinum (Pt) deposited on FTO substrate. Other than Pt coated FTO, carbon based materials, cobalt sulfides, organic polymer such as PEDOT: PSS are also used in some cases.

The basic working principle along with the energetics and kinetics for a dye-sensitized solar cell is illustrated schematically in Figure 1.2.1 (B). Primary processes involve i) Light absorption ii) Dye excitation (**Process 1**) iii) Injection of photo-generated electron in to the conduction band (CB) of sensitizer scaffold i.e. metal oxide in femtosecond (10⁻¹⁵s) time scale range (**Process 2**)³⁴ iv) Transmission of electron through interparticle network of mesoporous metal oxide framework in a millisecond (10⁻³ s) time scale range (**Process 3**)³⁵⁻³⁶ v) Extraction of electron at the collecting electrode i.e., FTO and to the external circuit (**Process 4**) vi) Regeneration of oxidized dye by redox shuttle in 10⁻⁸ s (**Process 5**)^{37,38} vii) electron transfer from counter electrode i.e., Pt coated FTO to regenerate the redox mediator and complete the cycle (**Process 6**). These processes in a DSSC are known as forward or favorable processes. Energetically, the Lowest Unoccupied Molecular Orbital (LUMO) of the sensitizer must be more positive than the conduction band of metal oxide semiconductor (CB_{MO}) for an efficient charge injection while, the redox potential of the electrolyte must be more positive than the Highest Occupied Molecular Orbital (HOMO) of the sensitizer for an efficient regeneration of dye.³⁹ Whereas, The maximum output photo-voltage (V_{oc}) from a device is given by the difference between the Fermi level (E_F) of the semiconductor metal oxide and the redox potential of the electrolyte as shown in the figure 1.2.1 (B).²³ Apart from all these forward processes there are competitive detrimental processes simultaneously occurring in the devices which tend to reduce the efficacy of a device. For example, i) Direct recombination of exciton or de-excitation of dye in 10⁻⁷s time scale range (**Process 7**), ii) Recombination of photo-injected electron at MO with oxidized sensitizer (**Process 8**) and iii) also with oxidized species of the redox electrolyte (**Process 9**). Both these backward processes compete with dye

regeneration process but occurs at a slower micro to millisecond (10^{-6} to 10^{-3}) timescale. However, in practical scenario due to the slower transport of photoinduced electrons recombination becomes feasible.⁴⁰⁻⁴¹

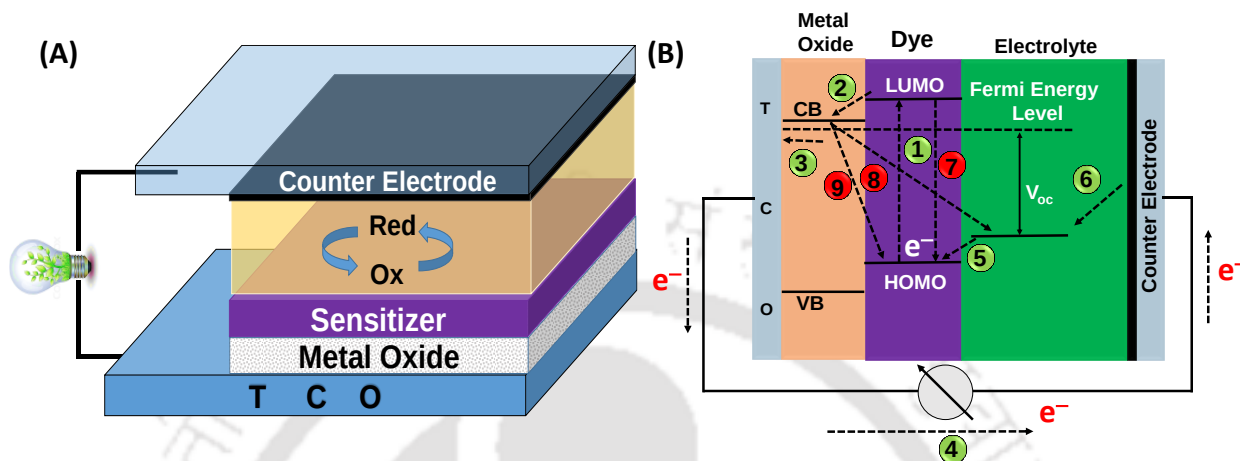


Figure 1.2.1 Schematic shows (A) all segments of a typical DSSC (B) basic working principle of dye-sensitized solar cell with favourable energy levels and various charge transfer processes involved in DSSC. Processes 1,2,3,4,5 and 6 are favorable energy transfer and processes 7, 8, 9 are non-favorable processes respectively

To suppress such detrimental processes different strategies like tuning the redox potential of the electrolyte to lower value,⁴² conduction band modification of the metal oxides,⁴⁴ and involving core-shell structures with a thin layer of shell materials which mainly results in the shift of the conduction band or the existence of an energy barrier,⁴⁵⁻⁴⁶ forming heterojunctions,⁴⁷ introducing materials with high charge carrier mobility⁴⁸ has been adopted. Apart from the recombination issue, one most important concern in DSSCs is the light harvesting efficacy of the device as number of photon absorbed is proportionate to number of exciton generated and it directly reflects the output current generated (J_{sc}). Light harvesting capacity of the photoanode can be enhanced utilizing new dyes with wide visible light absorption property,⁴⁹ co-sensitizing technique,⁵⁰ plasmonic metal nanoparticles,⁵¹ light scattering materials, etc.^{52, 53}

1.3 DEVELOPMENT OF PHOTOANODIC MATERIALS

The light harvesting efficacy and detrimental recombination processes occurring in the devices remain the road block in achieving good efficiencies in DSSCs. To address these issues utilization of semiconductor material with superior opto-electronic properties is a must. Since, the year 1991, as an alternative to TiO_2 , various wide band gap metal oxides such as ZnO ,^{54, 55} SnO_2 ,^{56, 57} Nb_2O_5 ,^{58, 59} Zn_2SnO_4 ,⁶⁰ $SrTiO_3$,⁶¹ etc. have been explored. Among them, ZnO and SnO_2

promises to be the most appealing material owing to unique properties such as, (i) higher electron mobility, ii) comparable band gaps (iii) anisotropic crystal growth.^{62, 63} Table 1.3.1 summarizes a comparative study of basic electronic and optical properties of ZnO, TiO₂, and SnO₂.

Table 1.3.1 Structural and electronic properties of semiconducting metal oxides used in photovoltaic devices

Parameters	ZnO	SnO ₂	TiO ₂	Reference
Crystal Structure	Wurtzite	Rutile	Anatase, Rutile	63–67
Bandgap [eV]	3.2–3.4	3.6–3.8	3.0–3.2	64–68
Electron Mobility [cm ² V ⁻¹ s ⁻¹]	130–200	200–250	0.1–4	63, 70, 71
Conduction Band Minimum [eV]	– 4.36	– 4.88	–4.41	69
Effective Electron Diffusion Coefficient [cm ² .s ⁻¹]	1.1×10 ⁻⁴	7.3×10 ⁻⁵	4.3×10 ⁻⁴	72
Static Dielectric Constant ($\epsilon_{\perp, }$)	9.26, 8.2	14, 9	86, 170	73
Electron Effective Mass	0.26	0.275	9	73–74

As can be seen from the table 1.3.1 both ZnO and SnO₂ have higher electron mobility (SnO₂ ~ 200–250 cm² V⁻¹ s⁻¹, ZnO ~ 130–200 cm² V⁻¹ s⁻¹) which provides faster transport of photo-injected electrons to the collector electrode i.e. fluorine doped tin oxide (FTO) thus reducing the recombination probability. Moreover, SnO₂, with a wider band gap tends to create fewer oxidative holes at the valence band minimizing the dye degradation rate and improves long term stability of DSSCs.⁷⁵ Despite the advantages the light absorption in the nanoparticle based photoanodes remains major bottle neck to achieve good efficacy in DSSCs. Conventional photoanodes utilizing small sized (approximately diameter < 50nm) metal oxide nanoparticles (NPs) of few micrometers (~ 10–15 μ m) thickness ensure a large interfacial surface area for adsorption of dye but suffers a significant optical loss owing to high transparency of the photoanodic film resulting in poorer photovoltaic performance. The dye absorption remains poor especially in the wavelength range λ ~ 600–800 nm.⁷⁶ Increasing the film thickness will provide higher dye adsorption but inhibits the penetration ability of incident light. It is also known that thicker films possess surface trapping/detrapping effects that arise from grain boundaries, inter-particle connections and surface states as well as diffused electrolyte screens the charge transport by easily coupling with the photo-generated electron, resulting in slow transport and a higher probability of recombination of photo-generated electrons.^{77–79} Moreover, higher dye loading hinders light penetration probability to reach the upper surface of the photoanodes as can be seen

in figure 1.3.1. Thus, the thickness of the film should be optimum so as to get the maximum dye loading without compromising on absorption and related optical losses.⁸⁰ Light scattering method has been found to be a simple and convenient way to improve device efficacy by incorporating light scattering materials in DSSC.⁸¹

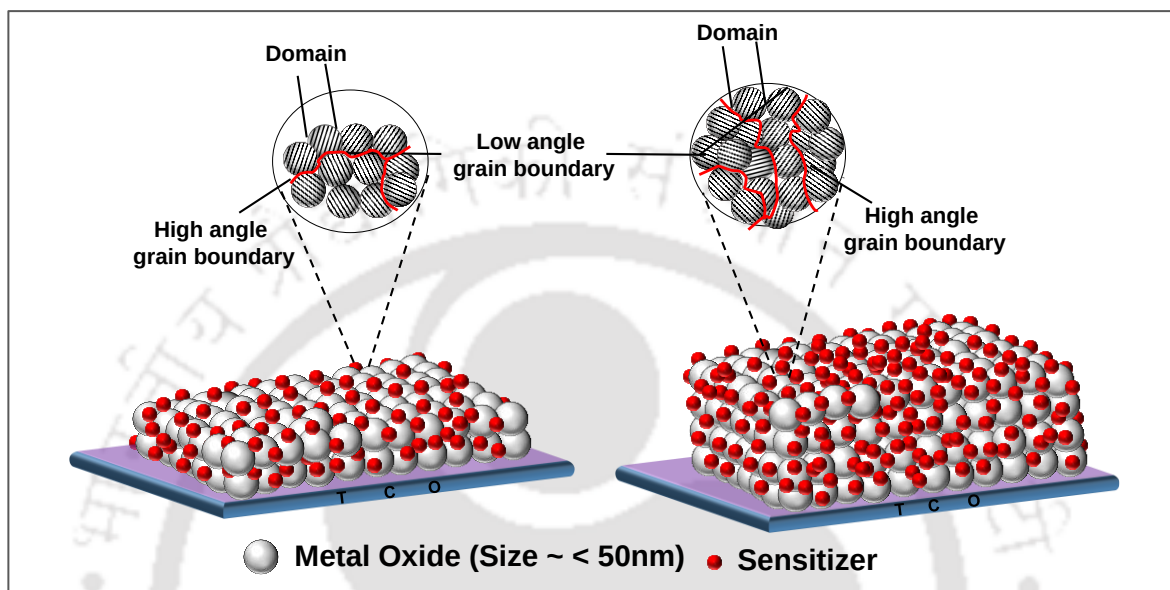


Figure 1.3.1 Schematic representation of photoanodes of different thickness and its effect. Note that there are many crystalline domains present within each nanoparticle film (black and white stripes)

1.3.1 THEORITICAL FRAMEWORK AND APPLICATION OF LIGHT SCATTERING IN DSSC

When light encounters an object of dimension in order of the wavelength of incoming light, it deviates from its normal trajectory governed by the laws of reflection or refraction and spread in all directions giving rise to an optical phenomenon, called light scattering. The object in consideration is known as the light scattering material (LSM) or scattering centers. This is basically the periodic perturbation of electronic environment of the molecules under the influence of incoming radiation which induces a dipole moment to the molecule that acts a source of electro-magnetic (EM) radiation resulting in scattering of light. Among the various theories developed to discuss light scattering, Rayleigh scattering theory and Mie scattering theory are typically applicable for spherical scatterers e.g., particles, droplets, and density fluctuations based upon the wavelength of light and size of the scatterers. Rayleigh scattering theory is specifically applicable for describing the light scattering caused by the scatterers (non-absorbing) with characteristic dimensions much smaller than the wavelength of incident light. The Rayleigh scattering cross-section, $\sigma_{scat, Rayleigh}$ is given as,⁸²

$$\sigma_{scat,Rayleigh} = \frac{2\pi^5 (2\pi)^6}{3 \lambda^4} \left| \frac{m^2 - 1}{m^2 + 2} \right|^2 \dots \dots \dots (1)$$

Where, λ corresponds to the wavelength of the incident photon, and m is the refractive index of the scatterers and defined as $m = n - ik$ (n indicates the refraction of light and the complex term, k , is related to absorption). It can be observed from eq. (1) that Rayleigh scattering cross-sections are inversely proportional to the 4th power of wavelength whereas, directly proportional to the 6th power of particle size. So, Rayleigh's scattering regime is restricted to the scattering of shorter wavelength i.e. blue light of the solar spectrum of the complete solar spectra more efficiently than the longer wavelength red light.

On the other hand, Mie scattering theory applies to the systems where the size of the particles is comparable to the wavelength of the incident light i.e. for the large particles (absorbing or non-absorbing) with no limitations to the particle size. The Mie scattering efficiency, $Q_{scat, Mie}$ is given by,

83-84

$$Q_{scat,Mie} = \frac{\sigma_{scat,Mie}}{\pi r^2}$$

Thus the Mie scattering can be applied to scatterers of variable sizes and can be utilized for scattering of light in the low energy or higher wavelength region of the electromagnetic spectrum. To achieve an efficient light scattering, the size of the scatterers is expected to be comparable to the wavelength of the incident light.⁸⁵⁻⁸⁶ In general, the size of the light scattering materials ranges from several hundreds of nanometers to few micrometers as confirmed by the earlier computer simulations done by Akira Usami and Feber *et.al.* on light scattering and absorption in DSSCs.⁸⁷⁻⁸⁸ In practical DSSC system however there would be a shift in effectual size of the scatterers as refractive index is different for air and the electrolyte that is used in DSSCs.⁸⁹ In fact, such a prediction in theory has been the criterion for determining the size of particles used in the photoelectrode film of DSSCs for the generation of light scattering aimed at improving the optical absorption of the photoelectrode, although the Mie scattering theory is generally applicable to a single scattering or a system including sufficiently separated scatterers, which is not completely the same as practical photoelectrode films typically consisting of particles that are closely packed.^{90, 91}

In DSSCs, light scattering has been established as an effective way to enhance the optical absorption of the cell. The basic principle of the light scattering in DSSCs is to confine the light

propagation and extend the travelling distance of light within the photoanodic film. Optical confinement occurs when light suffers multiple reflections from a large sized particle and gets trapped within the working electrode whereas the scattered light in forward direction increases the path length. Thus interaction events between the sensitizer and incoming light also increases along with the probability of photon absorption by the dye molecules. The light scattering phenomenon increases optical response of the dye at higher wavelength region i.e. $\sim 600\text{--}800\text{ nm}$ where dye adsorbs weakly in nanoparticle based film.⁹¹⁻⁹³ These **LSMs** can be introduced into the photoanode in two ways viz. i) Double-layer structure and ii) Mixture structure as shown in figure 1.3.2.^{88, 94} In the first case, a double-layer structure is created in which the micron/submicron sized particles are placed on the top of the nanocrystalline film, so as to back-reflect/back-scatter the incident light to the film, resulting in improved absorption. While in the second case, a mixture structure is created in which a blend of the **LSMs** and nanoparticles forms the basic absorbing layer of the DSSCs. In case of double layered structure the internal resistance of the solar cells is increased, as a result charge transport within the solar cells gets hindered, whereas in the mixture structure, the large sized particles embedded into the nanocrystalline film unavoidably cause a loss of internal surface area of the photoanodic film.⁹⁵⁻⁹⁶ So, scattering particles having sub-microns or microns size dimension have a narrow concentration window for optimal light harnessing. Moreover, embedded scatterers in mixture structure do not involve further step in the cell fabrication process, which simplifies the fabrication technique as well as reduces the production cost. Therefore, the structure of DSSCs using scattering materials requires a careful design. Several factors, such as morphology, film thickness, and scatterer contents, must be taken into consideration to obtain the optimal synergetic improvement; otherwise, the performance of DSSCs may deteriorate.

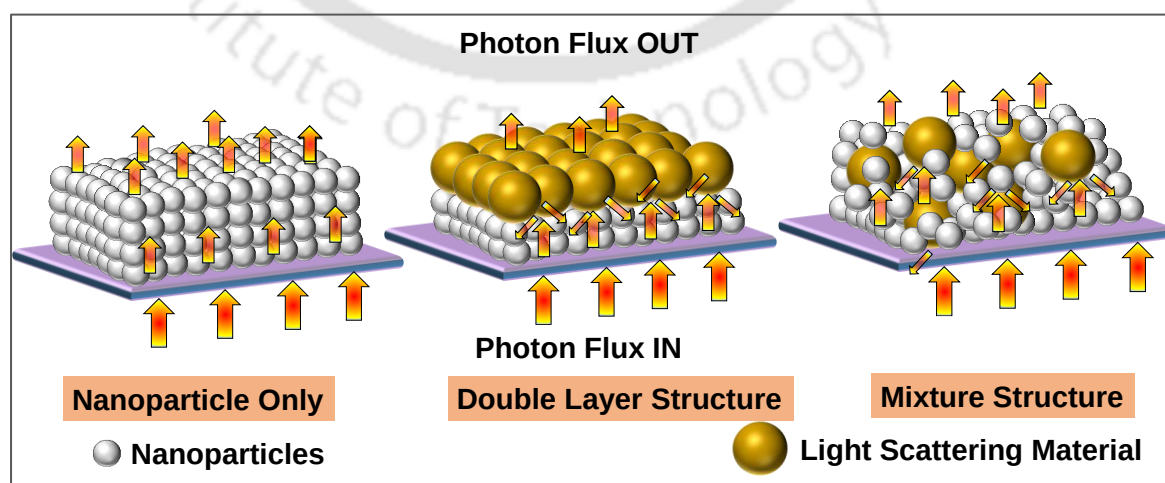


Figure 1.3.2 Schematic representation of photoanodes in DSSCs containing light scattering materials

Based on these optical properties, various structures of **LSMs** like spherical microspheres,⁹⁷ large particles,⁹⁸ nanoflowers,⁹⁹ spherical voids,¹⁰⁰⁻¹⁰¹ nanotetrapods,¹⁰² nanocubes,¹⁰³ octahedra¹⁰⁴ etc. as well as materials with different index of refraction, e.g., SnO₂, SiO₂, Nb₂O₅, SrTiO₃ etc.,¹⁰⁵⁻¹⁰⁸ have been explored in DSSCs to enhance the performance of the devices as depicted in table 1.3.2. Different light propagation pathways in nanocrystalline photoanodic film and film containing light scattering materials is shown in Figure 1.3.3.

Table 1.3.2 Photovoltaic performance of DSSCs utilizing different light scattering materials

Structures of Photoanodes	Primary Material (Reference)	Secondary Material	η of reference device (%)	η after improvement (%)	Ref.
Double layer	TiO ₂ nanoparticles	TiO ₂ microspheres	6.8	9.37	109
Double layer	P25	TiO ₂ microbeads	6.19	8.84	110
Double layer	P25	TiO ₂ octahedra & microspheres	5.76	8.76	111
Double layer	P25	SnO ₂ microspheres	7.29	9.53	105
Double layer	TiO ₂ nanoparticle	Hierarchical TiO ₂	6.6	10.3	112
Double layer	P25	CeO ₂ Nanocube	7.3	8.6	103
Double layer	P25	CeO ₂ octahedra	7.33	7.92	104
Double layer	P25	submicrometer Al ₂ O ₃ Particles	6.5	7.3	113
Mixture Structure	TiO ₂ nanoparticles	TiO ₂ nanowires	6.7	8.6	114
Mixture Structure	TiO ₂ nanoparticles	SiO ₂ /TiO ₂ Core/Shell spheres	6.5	7.9	115
Mixture structure	TiO ₂ nanopartilce	TiO ₂ nanospheres	5.3	6.7	96
Mixture structure	P25	SiO ₂ powder	4.6	6.8	106
Mixture structure	TiO ₂ nanoparticle	TiO ₂ rutile/ZrO ₂	4.7	6.8	116
Mixture Structure	Anatase TiO ₂	TiO ₂ Urchin	3.73	6.92	117
Mixture Structure	ZnO nanoparticle	ZnO nanoburger	3.07	4.03	118
Mixture structure	SnO ₂ nanoparticle	ZnO nanotetrapods	2	6.31	102
Mixture Structure	TiO ₂ nanoparticle	ZnO treated TiO ₂ nanofiber	3.87	6.54	119
Mixture Structure	TiO ₂ nanoparticle	TiO ₂ nanohelix	7.91	8.4	120
Nano architecture + LSMs	TiO ₂ nanoaparticle	SiO ₂ hierarchical spheres	7.32	9.53	121
Nano architecture + LSMs	SnO ₂ nanoparticle	ZnO Microstructure	1.2	4.96	122

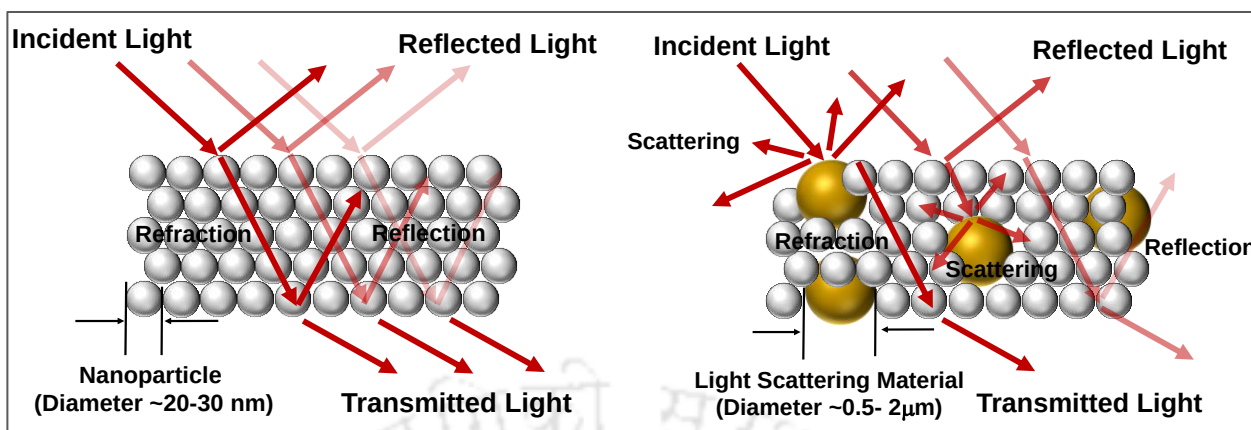


Figure 1.3.3 Light propagation pathways in (A) Nanocrystalline film (B) Mixture film containing LSMs

However, recent advances in the rational design of large-sized scattering materials led researchers to synthesize hierarchical structures that can improve the light-harnessing efficacy of the photoanodes without sacrificing the specific surface area of the photoanodic films. A micrometer- or sub-micrometer-sized structure formed by assembly of nanoparticles satisfy dual requirements i.e. can ensure a high specific surface area, whereas the larger-sized spherical assemblies can boost the light-harnessing efficacy via the effective scattering from a single moiety as well as from the scatterers blend.¹²³⁻¹²⁵ Optical confinement of incoming photons inside the photoanodic film upsurges the probability of light absorption by the sensitizer, thereby increasing the number of photoinduced electrons and thus improving the device performance. Chou *et al.* has first introduced these nanocrystallite aggregates of ZnO, in the year 2007.¹²⁶ They synthesized ZnO aggregates via polyol assisted hydrolysis of zinc salt and DSSC showed an enhancement of $\sim 83\%$ in PCE. After that researchers developed different strategies to synthesize hierarchical microstructures and applied in photoanodic section of DSSCs and observed enormous enhancement in the device efficacy. For example, TiO₂ microbeads formed from TiO₂ nanocrystallite furnished very high a surface area of $\sim 89 \text{ m}^2 \text{ g}^{-1}$ with a diameter of $\sim 830 \text{ nm}$ and DSSC device showed a PCE of $\sim 9.1\%$ which is much higher than the reference P25 (commercially available TiO₂ nanoparticle) film owing to better light scattering effect.¹²⁷ Hierarchical solid microstructure particles, although possess a good scattering capacity and surface area, unfortunately inhibit diffusion of electrolyte, which is essential for better performance of DSSC in terms of dye regeneration (**Process 5, Section 1.2**). On the contrary, hollow spheres (HSs) can effectively increase light harvesting via light trapping within the cavity and scattering from the ensemble as well as provide accessible pores that assist the penetration of the liquid electrolyte to

regenerate the sensitizer as can be seen in figure 1.3.4.¹²⁸⁻¹²⁹ Hierarchical hollow microstructures along with the cavity, due stacking of the bigger assemblies provide a multi-scale porous structure, with the bigger mesopores as well as small micropores formed by the stacking of primary nanocrystallites. These type of porous structures are quite advantageous for effective electrolyte infiltration, especially for viscous electrolytes such as ionic liquids, gel electrolytes and solid state electrolytes.¹³⁰ Recent advancements in design and development of hierarchical and hollow microstructure for enhanced photovoltaic performance of DSSCs are summarized in Table 1.3.3. Figure 1.3.5 shows some examples of different photoanodic architectures with hierarchical superstructures and hollow architectures utilized in DSSC.

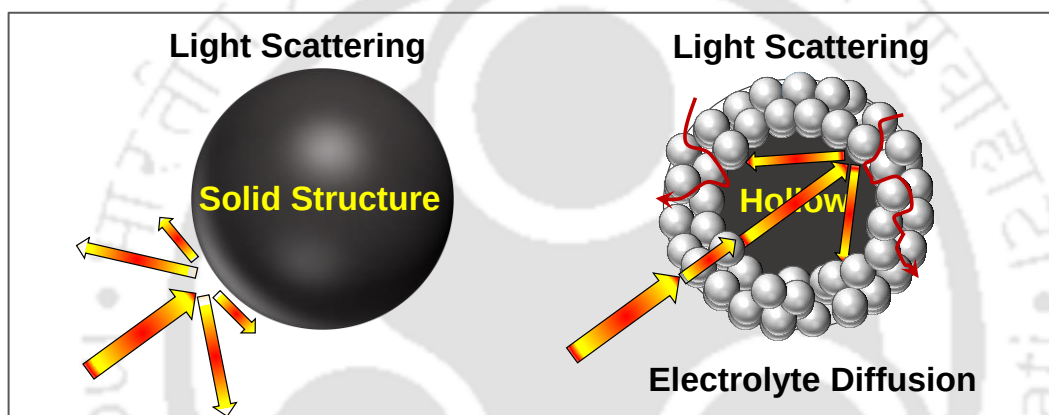


Figure 1.3.4 Light scattering and electrolyte diffusion pathways in different morphological structures

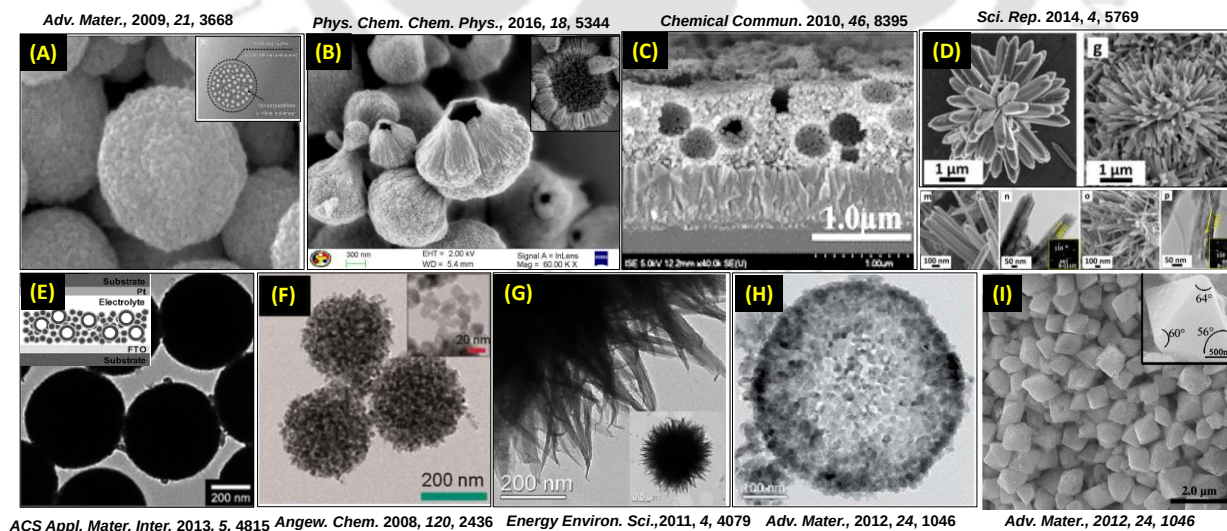


Figure 1.3.5 Examples of morphological features of different semiconductor/oxide utilized as light scattering materials in DSSCs [(A, B, H) is for ZnO, C is for Spherical voids, (D, G, F) is for TiO₂ (I) is for SnO₂]

Table 1.3.3 Photovoltaic performance of different hierarchical structure based DSSCs

Structure of photoanode	Reference sample	Material For improvement	η of ref. device (%)	η after improvement (%)	Ref
Nanoarchitecture	P25	TiO ₂ hierarchical bead	5.66	7.20	131
Nanoarchitecture	P25	TiO ₂ hierarchical spheres	4.01	6.70	132
Nanoarchitecture	ZnO nanoparticle	ZnO hierarchical spheres	2.4	5.4	133
Nanoarchitecture	ZnO nanoparticle	ZnO hierarchical film	6.58	7.5	134
Nanoarchitecture & composite	TiO ₂ nanoparticles	TiO ₂ nanosheets on SnO ₂ hollow spheres	4	8.2	135
Nanoarchitecture & scattering layer	TiO ₂ hollow spheres	TiO ₂ hierarchical nanotubes & hollow spheres	5.55	8.38	136
Nanoarchitecture	P25	Nano embossed TiO ₂ Hollow spheres	7.79	10.34	137
Nanoarchitecture & post-treatment	SnO ₂ nanoparticle	Mesoporous SnO ₂ microstructure	1.61	6.23	138
Nanoarchitecture + post- treatment	P25	Mesoporous TiO ₂ beads	8.5	10.6	139
Nanoarchitecture + scattering layer	P25	TiO ₂ Microflower	2.1	5.3	140
Nanoarchitecture	ZnO nanoparticle	Hierarchical ZnO hollow sphere	3.12	4.33	141
Nanoarchitecture	SnO ₂ nanoparticle	TiO ₂ coated SnO ₂ hollow spheres	1.0	5.65	142
Nanoarchitecture	SnO ₂ nanoparticle	Hierarchical SnO ₂ nanooctahedra	5.21	6.40	143
Nanoarchitecture	P25	Hierarchical yolk-shell TiO ₂ micro bead	7.56	9.05	144

1.4 CONCLUSIONS AND OUTLOOK

With great efforts in rational design of photoanodic architecture utilizing submicron or micron sized semiconductor/oxides of various morphologies as well as with different optical properties, power conversion efficiency (PCE, η) of nanoparticle based DSSCs significantly enhanced. Hierarchical microstructures supplied a great deal of interest to develop photoanodes with better light harvesting efficacy without sacrificing dye adsorption. However, further development ZnO/SnO₂ nanoparticle based photovoltaic devices is necessary to meet the requirements for their practical feasibility. Coupling of ZnO/SnO₂ with light scattering materials is a convenient approach to enhance light harnessing ability of the photoanodes. Moreover, materials with well-matched band positions enhance charge separation and minimize the electron losses in devices. By forming heterojunction, using high electron mobility materials or using an energy barrier, reverse tunneling probability of photo-injected electron can be screened. All these strategies allow the development of highly efficient multifunctional photoanodic materials for

better device performance. Even though, it remains challenging to the scientific community to optimize various key parameters in a single photoanode to enhance the light harvesting ability and reduce the recombination in the devices. So, approaches for design and development of new cost effective photoanodic architecture is highly desirable to bring a new hope for this field of research.

1.5 MOTIVATION AND OBJECTIVES OF THE PRESENT WORK

ZnO and SnO₂ furnishes superb bulk electron mobility as well as anisotropic crystal growth for diverse morphologies, establishing them as promising photoanodic materials to be used in DSSCs. ZnO/SnO₂ has well-matched band positions with most of the other semiconductors to be coupled to form hetero-junctions for a better charge separation as well as reduced recombination. However, wide band gap semiconductor nanoparticle based devices suffers internal optical loss due to transparency in the visible region. Materials with submicron or micron sized with high index of refraction can be coupled in a blend structure with primary nanoparticle based device to enhance the optical response. Hence, further improvement in the device architecture is highly sought after. Based on these properties, we have envisioned to further improve the light harvesting ability as well as electron transport properties of the ZnO/SnO₂ based dye-sensitize solar cell devices. The primary objectives of the present work are as follows:

- Design and development of photoanodic architecture with a nano-micro combination having ZnO/SnO₂ nanoparticles as reference platform and other semiconductor/oxide as light scattering materials/ material with proper band alignments with ZnO and dye
- Understanding the synergistic effect of foreign material used in conjunction with ZnO or SnO₂ primary nanoparticle with the secondary materials in terms of light harvesting as well as charge transfer processes
- Optimization of the concentration of foreign material for achieving best device performance
- Coupling of ZnO/SnO₂ with suitable semiconductor materials based on band alignments for efficient charge separation
- Evaluation of photovoltaic properties of as fabricated photoanode in DSSCs
- Understanding the photovoltaic performances of the as-designed and fabricated photoanodic architectures

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CHAPTER 2

Experimental

This chapter briefs basic instrumentation techniques and procedures utilized for material characterization and basic device fabrication. Devices characterization using standard solar simulator 1Sun, AM 1.5G (Newport Sol3A) connected to a Keithley 2400 sourcemeter and incident photon-to-current analyzer (IQE 200) have been included. A short outline to photovoltaic performance parameters and electrochemical impedance spectroscopy (EIS) and its application to dye-sensitized solar cell is also provided.

Material Synthesis



Characterization

2.1 INTRODUCTION

Light scattering phenomenon is a simple and convenient strategy to enhance light harnessing efficacy in nanoparticle based DSSC. Semiconductor/Oxide materials with size in the submicron or micron range are excellent scatterer of incident light having wavelength equivalent to the size of the scatterer.¹⁻² ZnO and SnO₂ nanoparticle based devices provides excellent electron mobility but suffers a huge optical losses due to its smaller size dimension.³⁻⁴ Design and synthesis of different morphological features of semiconductor/oxide materials with dimension in Mie scattering size requires various chemicals as precursors as well as structure directing agents in various reaction conditions. This Chapter lists all the materials utilized at different phases along with their basic characterization. Detailed fabrication procedure dye-sensitized solar cell (DSSC) are also counted in. Further, device characterization techniques are also discussed in detail.

2.2 EXPERIMENTAL METHODS

2.2.1 MATERIALS AND CHEMICALS USED

Zinc acetate dihydrate (Aldrich), ethanolamine (Himedia), 2-methoxyethanol (Aldrich), zinc chloride (Merck), sodium hydroxide (Aldrich), silver nitrate (Merck), hexachloroplatinic acid (H₂PtCl₆, Aldrich), 4-tert-butylpyridine (Aldrich), di-tetrabutylammonium cis-bis-(isothiocyanato)bis(2,20-bipyridyl-4,40-dicarboxylato)ruthenium(II) (Dyesol, Australia), acetonitrile (HPLC grade, Merck), valeronitrile (Aldrich), absolute ethanol (TMEDA), *tert*-butanol, Tetraethylorthosilicate (TEOS, Merck), 0.2 μ m PTFE filter paper (Axiva/ Rankem, India), thermoplastic sealant (Dyesol, Australia), ethanolamine (Merck), PEG-PPG-PEG (Sigma Aldrich), Ethocel (Himedia), hexadecyltrimethylammonium bromide (Rankem), zinc chloride (Merck), sodium hydroxide (Himedia), ammonium hydroxide (Merck), SnCl₂·2H₂O powder (Merck), SnCl₄·5H₂O (Aldrich), Zn(NO₃)₂·6H₂O (Aldrich), PEG 200 (Merck), acetylacetone (Merck), α -terpineol (Himedia), chloroplatinic acid (Sigma-Aldrich), butanol (Merck), methanol (Merck), urea (Sigma-Aldrich), SrCl₂·2H₂O (Merck), HNO₃ (Merck), titanium isopropoxide Ti(iOPr)₄, Ce (NO₃)₂·6H₂O (Merck), Graphite powder (99%), Sodium Nitrate (Merck), hydrazine hydrate (Merck, 80%), hydrochloric acid (Merck), KMnO₄ (Merck), H₂O₂ (Merck), 2-propanol (Merck), acetone (Merck), lithium iodide (Sigma Aldrich), iodine (Merck), 4-tert-butylpyridine (Himedia), 1-butyl 3-methyl imidazolium iodide (Sigma Aldrich), polymeric spacer, guanidium

thiocyanate (Aldrich), FTO (sheet resistance $8\text{--}12\ \Omega\ \text{cm}^{-2}$, Aldrich) are purchased and used without further purification. High grade Milli-Q water ($18.2\ \text{M}\Omega\cdot\text{cm}$) was used for all the experiments.

2.2.2 CHARACTERIZATION TECHNIQUES

The as-synthesized materials and fabricated devices are characterized using a number of instrumental techniques. The instrumental techniques/tools used include:

- (1) Powder X-ray diffraction (PXRD) is recorded using Rigaku RINT 2500 TTRAX-III with X-ray source Cu-K $_{\alpha}$ ($\lambda = 1.54\ \text{\AA}$) and Bruker D2 PHASER X-ray diffractometer with Cu-K $_{\alpha}$ X-ray generator ($\lambda = 1.54\ \text{\AA}$).
- (2) UV-Visible Diffuse reflectance spectra (DRS) using LAMBDA 750 UV/ Vis/ NIR Spectrophotometer and JASCO Model V-650 spectrophotometer with 150 mm integrating sphere and BaSO $_4$ internal standard.
- (3) Photoluminescence (PL) measurements are carried out using a Horiba-Jobin Yvon Fluoromax 4C spectrofluorimeter and LifeSpec II Edinburgh with Nd: YAG lasers of different excitation wavelengths.
- (4) Brunauer-Emmett-Teller (BET) measurements are carried out using Beckman-Coulter SA 3100 N $_2$ adsorption apparatus maintained at liquid nitrogen temperature.
- (5) Field emission scanning electron microscope (FESEM) and Energy-dispersive X-ray spectroscopy (EDS) are carried out using a FESEM Zeiss (Model: Sigma 300), FESEM Zeiss (Model: Sigma); (for FESEM, operating voltage $\sim 2\text{--}5\ \text{kV}$ and for energy-dispersive X-ray (EDX), $\sim 20\ \text{kV}$).
- (6) The transmission electron microscopy (TEM) measurements using a JEOL JEM 2100 microscope and JEOL JEM 2100F (operating voltage of $200\ \text{kV}$).
- (7) Laser micro Raman spectroscopic analysis are carried out in a Horiba LabRAM HR spectrometer equipped with a He-Ne laser with an excitation wavelength of $488\ \text{nm}$.
- (8) Spin Coating using SPS SPIN-150 spin coater.
- (9) Thickness of individual films are measured using a Veeco Dektak 150 surface profilometer.

- (10) Current density–voltage (J–V) measurements were carried out under 1 sun illumination (AM 1.5, 100 mW/cm²) with a Newport ORIEL Sol3A solar simulator and a Keithley 2400 source meter equipped with a calibrated Si reference cell.
- (11) Incident photon-to-current conversion efficiency (IPCE) measurements were performed in a Newport Oriel IQE-200 (250 W quartz tungsten halogen, QTH) lamp as the light source)
- (12) Electrochemical impedance spectroscopic (EIS) and Open Circuit Voltage decay (OCVD) measurements are carried out using CH instruments Inc., Austin, TX CHI660E.

2.2.3 STEP-WISE FABRICATION PROCESSES OF DSSC

- (1) Transparent conductive oxide i.e. FTO is first cut into specific dimension [(1.5×1.5) cm²]. FTO substrates are then cleaned using soap solution, acetone, 2 –propanol, dried under N₂ flow and subjected to UV-Ozone treatment. Device area is fixed to 0.16 cm² using scotch tape mask as shown in image (4), figure 2.2.1. [digital image (4)]
- (2) To prepare the sensitizer scaffold, firstly, semiconductor materials or composites are dispersed in ethanol for a period of ½hr to 1hr to minimize agglomerations. Then the homogeneous pastes of the semiconductor oxides (e.g., ZnO/SnO₂) or their composites are prepared using Ethocel/ PEG-PPG-PEG as binder and terpineol to make it viscous. The steps are shown pictorially in figure 2.2.1, [digital image (1), (2), and (3)].
- (3) After removing the masks, the semiconductor oxide scaffold films are dried at 100-120 °C in a hot air oven followed by calcination at 450-500 °C temperatures in a temperature programmed muffle furnace to get the final film as shown in image (5), figure 2.2.1.
- (4) As-prepared film are then sensitized with Dye using dip coating method for a period of 8h-10h (depending upon the nature of semiconductor film). After sensitization process films are washed with solvent and dried (digital image 6).

- (5) Counter electrode is prepared by spin coating solution of chloroplatinic acid in isopropanol onto pre cleaned FTO substrates and calcining it 450°C for $\frac{1}{2}\text{hr}$ in a temperature programmed muffle furnace (digital picture 7).
- (6) Finally, photoanode and counter electrode are sandwiched together using a low-temperature thermoplastic sealant/ plastic spacer ($30\mu\text{m}$) and electrolyte is inserted into the space left behind between the electrodes to complete the cycle (digital picture 8).

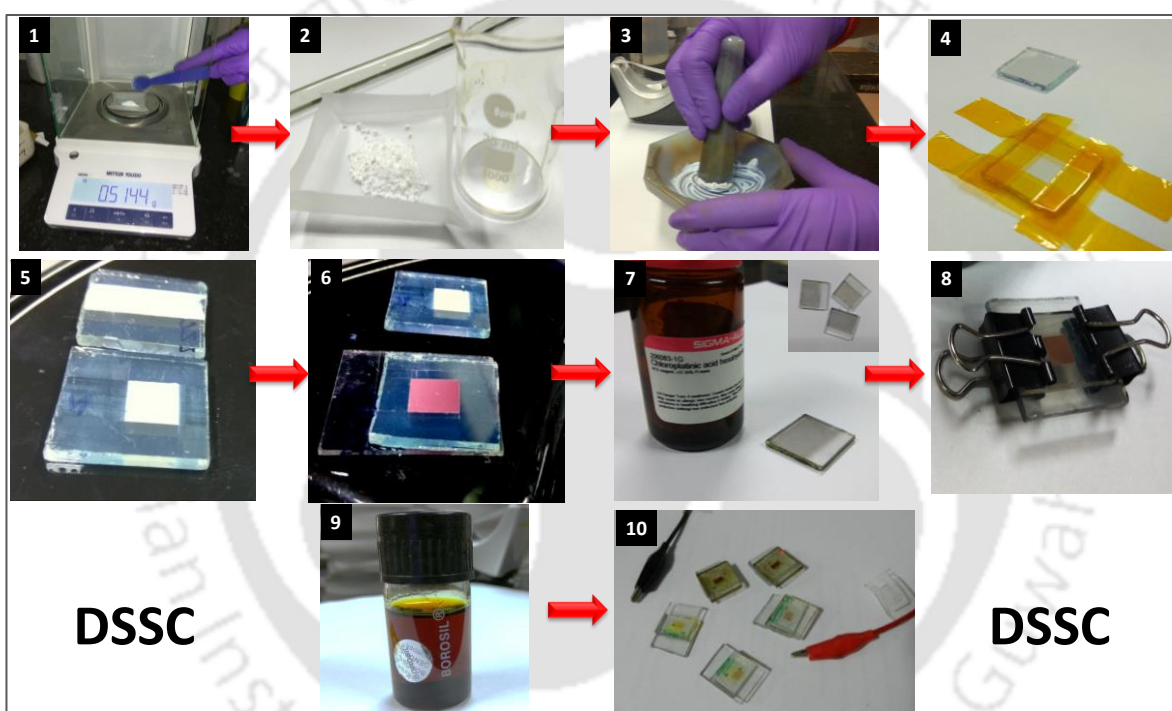


Figure 2.2.1. Pictorial representation of step-wise fabrication of DSSC

2.2.4 EVALUATION OF DSSC PERFORMANCE

- (1) The as-fabricated devices are connected to Keithley 2400 Sourcemeter.
- (2) Current vs. Voltage ($I-V$) characteristics under dark condition are measured sweeping the voltage from -1 V to $+1\text{ V}$.
- (3) Then the device is illuminated with solar light of 1 Sun and AM 1.5G and step 2 is repeated. To check precision, process 3 is repeated for 5 times.

- (4) Current vs. Voltage (I - V) graphs are plotted by taking current values as abscissa and voltage as ordinate.
- (5) Values of various photovoltaic parameters e.g. short circuit current (I_{sc}), open circuit potential (V_{oc}), Fill Factor (FF), Power Conversion Efficiency (PCE, η) are obtained and calculated from the (I - V) plot. To remove the dependence of the solar cell area, it is more common to list the short-circuit current density (J_{sc} in mA/cm^2) rather than the short-circuit current (I_{sc}) as given below,

$$J_{sc} = \frac{I_{sc}}{\text{Active area}}$$

2.2.5 SOLAR CELL PERFORMANCE PARAMETERS

The performance of any solar cell can be defined by the following physical parameters.

1. Short-circuit current density (J_{sc})
2. Open-circuit voltage (V_{oc})
3. Fill factor (FF)
4. Efficiency (η)
5. Incident photon to current conversion efficiency (IPCE).

Current–Voltage (I - V) curve of a solar cell provides information of device behavior under light irradiation. J_{sc} , V_{oc} and maximum power (P_{max}) of the solar cell can be obtained from the I - V curve. The pictorial presentation of the effect of light on the current–voltage characteristics of a solar cell is depicted in figure 2.2.2.

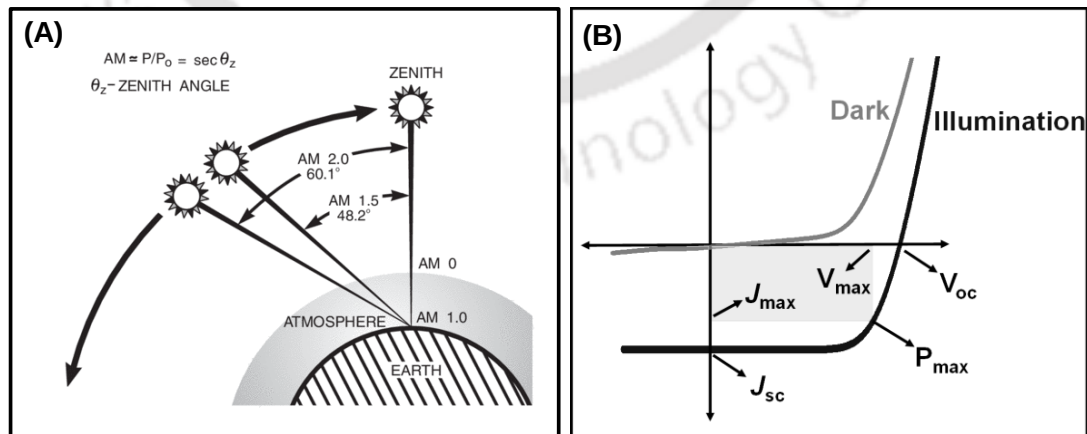


Figure 2.2.2 (A) Path length of solar irradiation in air mass (AM) unit showing the zenith angle (ϕ); (source: <https://www.newport.com>) **(B)** Schematic of typical current–voltage (J - V) curve of a solar cell in dark condition and under AM 1.5 G simulated solar irradiation

The solar cell characteristics are evaluated at a standard simulated 1 Sun with AM 1.5 G (air mass) which corresponds to a Zenith angle (ϕ) 48.2° as shown in figure 2.2.2 (B).

The short-circuit current (I_{sc}) is the current passing through the solar cell when voltage across the circuit is zero and hence it is due to the collection of light-generated carriers. The value I_{sc} increases with increase in light intensity. Higher the photon flux more will be the excited electrons and hence current. Short circuit current I_{sc} is also proportional to the area of the solar cell and expressed as J_{sc} . The V_{oc} is the maximum voltage available from a solar cell obtained at zero current. The open-circuit voltage corresponds to the amount of forward bias on the solar cell. Hence it is a measure of the amount of recombination in the devices. The fill factor (FF) determines the maximum power from a solar cell. It is the ratio of the maximum power from the solar cell to the product of output current (J_{sc}) and voltage (V_{oc}). The largest rectangle that fit in the I - V curve represents the FF of the devices graphically, as shown in Figure 2.2.2 (A). The FF can be expressed as,

$$FF = \frac{P_{max}}{J_{sc} \times V_{oc}}$$

Where, P_{max} is the maximum power of the solar cell. It is obtained as the product of the photocurrent and photovoltage at the voltage where the power output of the cell is maximum. The overall power conversion efficiency (η) of a solar cell is given by,

$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}}$$

Another important parameter of the performance of a solar cell is the incident photon to current conversion efficiency (IPCE). The IPCE value corresponds to the photocurrent density produced in the external circuit under monochromatic illumination of the cell divided by the photon flux that strikes the cell. It can be expressed as,

$$IPCE = 1240 \times \frac{J_{sc}(\lambda)}{\lambda \times P_{in}(\lambda)}$$

2.2.6 ELECTROCHEMICAL IMPEDENCE SPECTROSCOPY (EIS) ANALYSIS

In the DSSC devices electrons travels along various hetero-interfaces i.e. semiconductor/electrolyte, counter electrode/electrolyte etc. So, to gain insight on transport and recombination kinetics of photo-injected electrons at the heterojunctions in DSSC devices, electrochemical impedance spectroscopy (EIS) analyses are performed. The schematic representation of a DSSC cross-section is depicted in figure 2.2.3 (A) which illustrates hetero-junctions, i.e., working electrode (WE)/electrolyte and counter electrode (CE)/electrolyte interfaces. EIS measurements are performed at an external bias equivalent to the open circuit voltage i.e. V_{oc} , in a frequency range of 0.1 Hz to 100 kHz under the dark conditions. Nyquist plots and Bode phase plots are the characteristic plots for EIS analysis as shown in figure 2.2.4. Nyquist plot elucidates the characteristic interfacial charge transfer and recombination processes happening within the devices at different frequency regions, viz., high-frequency region corresponds to processes occurring at the counter electrode and electrolyte interface (10^0 – 10^2 kHz), the mid-frequency region corresponds to processes occurring at the semiconductor/ sensitizer/electrolyte interface (10^{-1} – 10^0 kHz), and the low-frequency region corresponds to that of the diffusion of electrolyte (10^{-1} – 10^{-2} kHz).⁵ Figure 2.2.3 (B) shows an equivalent circuit to fit the Nyquist plot derived from EIS analysis according to Transmission Line Model. In the equivalent circuit, resistance R_s is the sheet resistance related to the resistance of the TCO, CE material, is the resistance of electrolyte; R_{CT1} is the charge-transfer resistance of the counter electrode; $CPE1$ is the constant-phase element of the counter electrode; R_{CT2} is the charge-transfer resistance of the working electrode; and $CPE2$ is the constant-phase element of the working electrode. In the typical Nyquist plot, the semicircle in the mid-frequency region reveals the charge recombination resistance, which is attributed to the charge transfer resistance (R_{CT2}) at the metal oxide/sensitizer/electrolyte interface.⁶

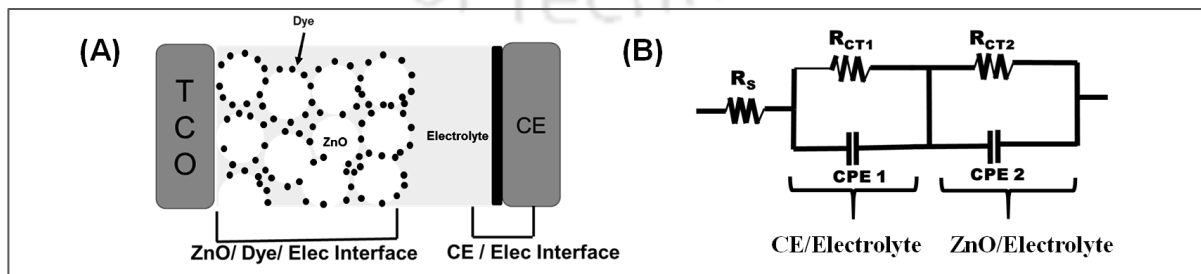


Figure 2.2.3 (A) Schematic of cross-sectional view of a DSSC **(B)** Equivalent circuit diagram according to Transmission line model

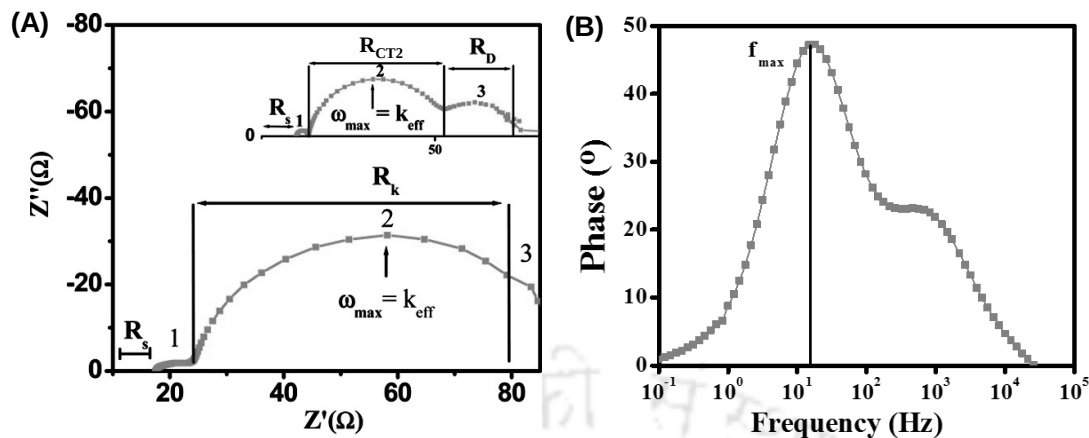


Figure 2.2.4 Schematic of (A) Nyquist plot with all the three semicircles, i.e., (1) electrochemical process at CE/Electrolyte interface (2) electrochemical process at Semiconductor/Electrolyte interface and (3) Nernst diffusion of the electrolyte (Figure taken from reference No. 4) (B) Typical Bode phase plot showing f_{max} at mid-frequency region

On the other hand, Bode phase plots also furnishes the photo-induced electron lifetime (τ_e) in the DSSC devices using the following equation.⁷

$$\tau_e = \frac{1}{2\pi f_{max}}$$

Where, f_{max} is the maximum peak value at mid-frequency region. Higher the τ_e value, longer will be the photo-injected electron stay in the semiconductor before get extracted at the collector electrode/recombined.

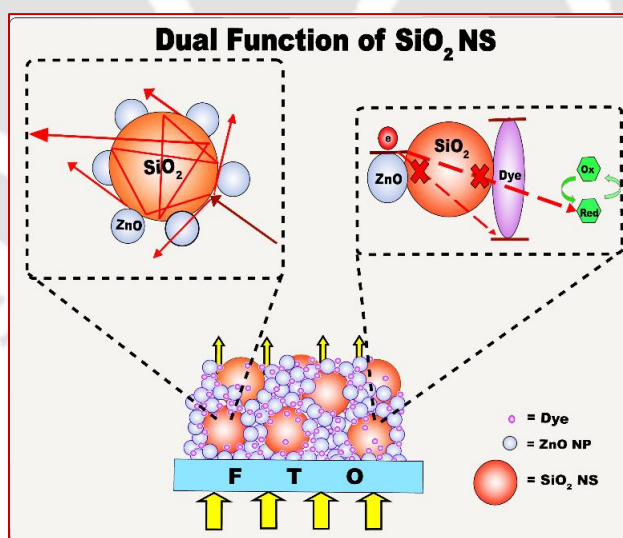
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CHAPTER 3

Dual Function of silica nanospheres in enhancing the photovoltaic performance in ZnO nanoparticle based dye-sensitized solar cells

This chapter presents design and developments of a binary hybrid photoanode utilizing a sub-micrometer sized insulating oxide silica nanosphere (SiO_2 NS) in conjunction with small sized ZnO nanoparticle ($\sim 20\text{-}50\text{ nm}$). The salient features of the binary hybrid photoanodes in enhancing the photovoltaic performance are– (i) Superb light scattering properties of silica nanospheres for repetitive excitation of photo sensitizer molecule, (ii) Impeded back transfer of photo-injected electron offered by insulating silica nanospheres at the working electrode/electrolyte interface (iii) mesoporous nature of SiO_2 NS for better penetration of liquid electrolyte species.

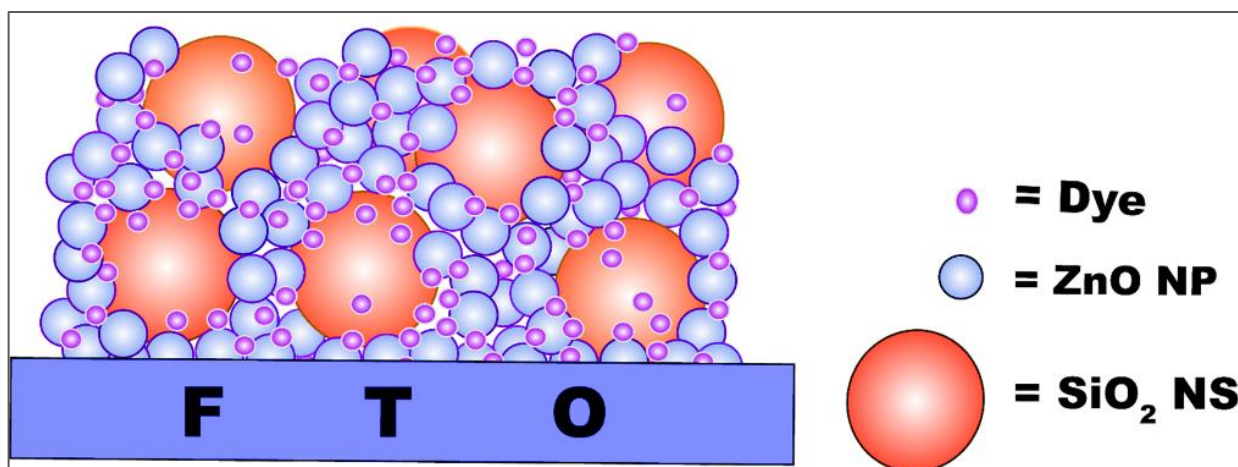


3.1 INTRODUCTION

Conventional photoanodic films fabricated utilizing small sized (approximately diameter $\sim$ 20-50 nm) ZnO nanoparticles (ZnO NPs) suffers a significant optical loss owing to high visible light transparency resulting in an inferior photon-to-electricity conversion efficiency.¹⁻² Zinc oxide, despite having several advantages e.g. high electron mobility ($130\text{--}200\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$),³ larger diffusion length ($\sim 10^3\text{ nm}$),⁴ suffers severe photo-injected electron back recombination at the ZnO/dye/electrolyte interface.⁵ A cost-effective and robust approach of utilizing materials of submicron/micron size commonly known as light scattering materials in a blend with smaller sized nanoparticle has emerged out to be potential in enhancing the light harvesting efficacy in turn the solar-to-electricity generations in a dye-sensitized solar cell.⁶⁻⁸

Silicon dioxide (SiO_2), an insulator material, only absorbs shortwave ultraviolet light ($<300\text{ nm}$) and has found application in photocatalytic reactions,⁹ metathesis of propene,¹⁰ oxidation of CO,¹¹ epoxidation of propene¹² only under UV light illumination and as a partial energy barrier for inhibiting the back transfer of electron in solar cells.¹³⁻¹⁴ SiO_2 has high thermal stability, excellent mechanical strength and helps to create new catalytic active sites due to interaction between different metal oxide semiconductors.¹⁵⁻¹⁶ In a report, selective deposition of insulating and transparent silica onto TiO_2 enhanced the power conversion efficiency by $\sim 36\%$ due to the reduction of photo-injected electron loss at hetero-interface.¹⁷ On another report $\text{TiO}_2/\text{SiO}_2$ core/shell nanoparticles of different sizes has shown enhancement in power conversion efficiency for an optimum shell thickness and size dimension owing to energy barrier and light scattering properties of silica.¹⁸ Recently, SiO_2 incorporated TiO_2 crystallites improved the efficiency of the solar cell owing to elevated dye-excitation, suppressed back recombination of electron with redox shuttle, and enhanced dye photostability.¹⁹

In this chapter, we propose the utilization of SiO_2 nanosphere as a binary hybrid composite of ZnO nanoparticle and SiO_2 nanosphere (**ZS_x**) in the photoanodic segment as shown in scheme 3.1.1. Optimized amount of SiO_2 NS in composite photoanode displayed a $\sim 22\%$ enhancement in device performance over pristine ZnO nanoparticle based photoanode owing to dual function of SiO_2 nanosphere as an efficient scatterers and partial energy barrier in the photovoltaic devices.



Scheme 3.1.1 Schematic cross-sectional representation of the binary hybrid photoanode

3.2 EXPERIMENTAL METHODS

3.2.1 SYNTHESIS OF ZnO NANOPARTICLES

ZnO nanoparticles (ZnO NPs) were synthesized following a previously reported protocol.²⁰ In the typical synthesis, ZnCl_2 (1.10 g, 8mmol) was dissolved in 40 mL of distilled water at 90 °C under vigorous stirring, followed by a slow addition of 3.2 mL of aqueous NaOH (5.0 M) solution. The reaction mixture was allowed to stir further for 30 min at 90 °C, cool down to room temperature and stand for 30 min to settle down the precipitate. The supernatant liquid was decanted and the solid product was washed with plenty of distilled water to remove the traces of NaCl (confirmed by AgNO_3 test). To resist agglomeration, particles were then dispersed in 10 mL iso-propanol under ultrasonic treatment for 10 min. The solid product was then isolated by centrifugation and calcined at 450 °C for 2 h in a muffle furnace to obtain the ZnO NPs.

3.2.2 SYNTHESIS OF SILICA NANOSPHERES (SiO_2 NS)

The synthesis of the silica nanospheres was carried out following a reported protocol.²¹ Briefly, 6 ml of tetraethoxysilane (TEOS) added dropwise into a 10 mL of 4.5 M ammonia solution in 100 mL ethanol and 5ml of water under vigorous stirring for 8 h to hydrolyse TEOS. Then the resultant product was obtained by centrifugation and the precipitate was washed thrice with ethanol and dried at 70 °C in a hot air oven. Finally, the product was calcination at 550 °C for 4 h to obtain SiO_2 nanospheres.

3.2.3 PREPARATION OF ZnO NP-SiO₂ NS COMPOSITES (ZS_x, X=1, 5, 10)

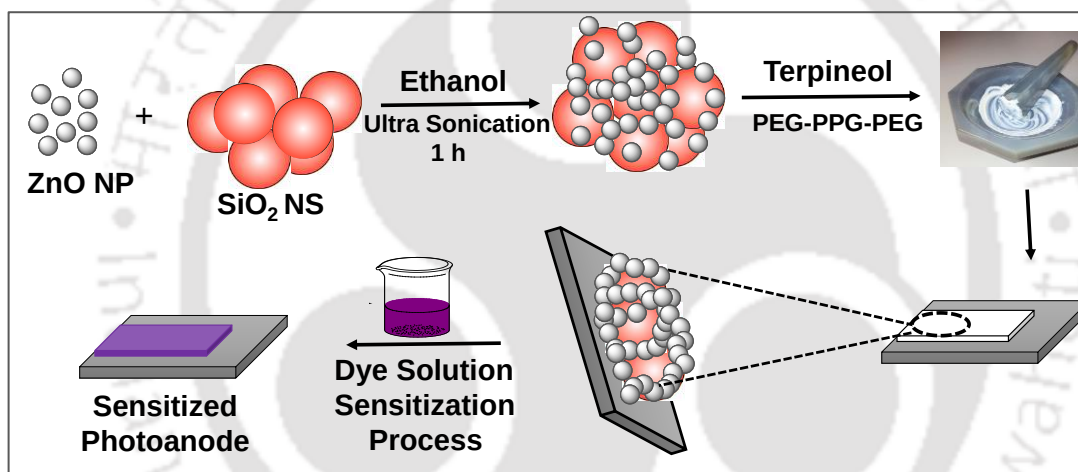
The ZnO NP- SiO₂ NS composites were prepared by ultra-sonication treatment of desired amount of SiO₂ NS and ZnO NP. In detail, an appropriate amount (according to weight ratio) of as synthesized SiO₂ NS was dispersed in iso-propanol under ultrasonic treatment for 45 min. 1g of as synthesized ZnO NPs was added into each dispersed solution and the ultrasonic treatment was continued for another 45 min. Finally, the solution was placed inside a hot air oven to evaporate the solvent to obtain the composite products, named hereafter as **ZS₁** (ZnO NP -1 wt. %SiO₂ NS), **ZS₅** (ZnO NP-5 wt. % SiO₂ NS) or **ZS₁₀** (ZnO- 10 wt. % SiO₂ NS).

3.2.4 DEVICE FABRICATION

All the photoanodes were fabricated by making a homogenous paste of ZnO NP and ZnO NP-SiO₂ NS composite viz. **ZS₁**, **ZS₅**, **ZS₁₀** containing 1wt%, 5wt% and 10wt% of SiO₂ NS. First, a ZnO seed solution was prepared by dissolving 0.30 g of zinc acetate and 0.084 mL of ethanolamine in 4.50 mL of 2-methoxyethanol under vigorous stirring for 6 h. As-prepared ZnO seed solution was filtered through a 0.2 µm membrane filter (Axiva Sicheem, India). FTO coated glass substrates were cleaned with soap solution and washed with Milli-Q water. After that the washed FTO substrates subjected to ultrasonic treatment for 15 min each in acetone and 2-propanol and then dried by blowing argon. The cleaned FTO substrates underwent an ozone treatment for 30 min using Novascan UV-ozone chamber. The filtered ZnO seed solution was spin coated on the FTO substrates followed by heating at ~175 °C for 10 min. The process was repeated for once more to obtain the uniform ZnO layer film on FTO substrates.²² For the preparation of homogeneous pastes, 0.1 g of ZnO nanoparticle powder or ZnO-SiO₂ (**ZS_x**) composites were ground with a mixture of terpineol and triblock copolymer (PEG-PPG-PEG) in an agate mortar. This homogenous paste was coated on ZnO seed layered FTO using doctor blade technique and the films were dried in air, followed by calcination at 450 °C for 30 min to remove the polymer.

Scheme 3.2.2 depicts pictorial presentation of the step-by-step photoanode fabrication processes. The thickness of the photoanode layers were measured by surface profilometer and found to be in the range of 13–15 µm. These substrates were then immersed into N719 dye solution in acetonitrile: *tert*-butanol (7:3) (3×10⁻⁴ M) for 6 h. The sensitized photoanodes were then removed from dye solution, washed with acetonitrile and dried under hot air blow. The

photovoltaic devices were fabricated by sandwiching the photoanodes and counter electrodes. Pt counter electrode was fabricated by spin coating a solution of chloroplatinic acid (5 mM in isopropanol) on a pre-cleaned ozonized FTO substrate followed by calcination at 450 °C for (heating ramp of 5 °C /min) 30 min in a muffle furnace and cooled down to room temperature naturally. Then electrolyte solution was added after the sealing (using low-temperature thermoplastic sealant, thickness ~50 µm) to complete the device. The I^-/I_3^- electrolyte solution was prepared by dissolving 0.5 M LiI, 0.05 M I_2 , 0.1 M guanidium thiocyanate, and 0.5 M 4-tert-butylpyridine in a solvent mixture of acetonitrile: valeronitrile (85:15, v/v). The active area for all fabricated devices were fixed and it was found to be 0.16 cm². All devices were kept for 24 h under dark conditions prior device measurements.



Scheme 3.2.2 Step-by-Step photoanode fabrication process showing probable charge transfer pathways

3.3 RESULTS AND DISCUSSIONS

3.3.1 POWDER X-RAY DIFFRACTION ANALYSIS

Powder X-ray diffraction (PXRD) patterns of as-synthesized pristine materials and composite photoanodes are displayed in figure 3.3.1. All the diffraction peaks from lattice planes (100), (002), (101), (102), (110), (103), (112) and (201) were indexed to the formation of hexagonal wurtzite phase (JCPDS File Card No. 36-1451) of ZnO NP with a $P6_3mc$ space group symmetry and calculated lattice constants of $a = 0.3248$ nm and $c = 0.5205$ nm with no traceable impurity peaks. The PXRD spectrum of SiO_2 NS display a broad band centered at $2\theta = 22.0^\circ$ from

lattice plane (100), implied to the amorphous nature of SiO_2 (JCPDS No. 29-0085). Notably, recorded PXRD pattern for composites **ZS₁**, **ZS₅** and **ZS₁₀** shows the diffraction peaks assignable to ZnO, while the diffraction peaks for SiO_2 NS remained silent in the composite. This may be due to the low crystallinity and low loading percentage of SiO_2 NS.

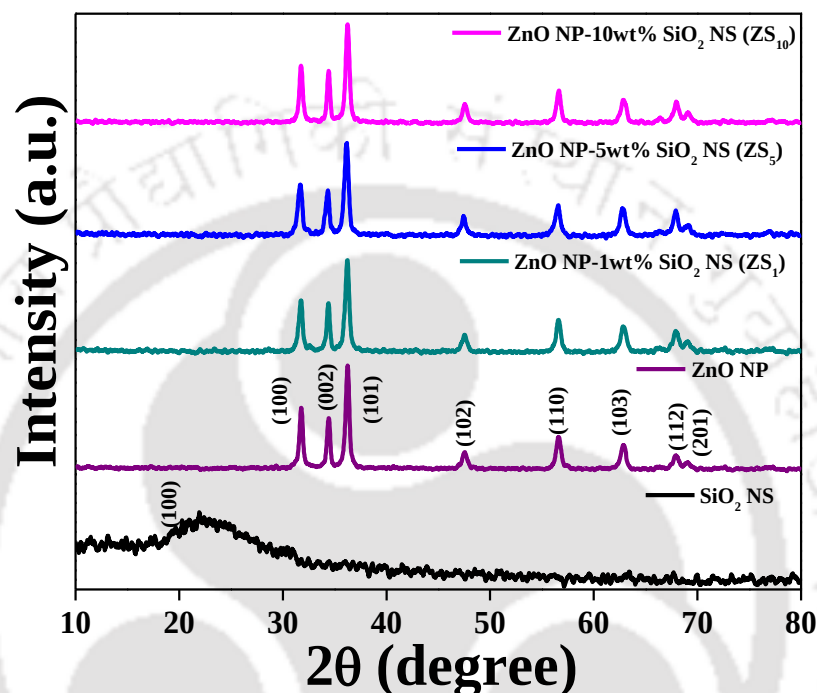


Figure 3.3.1 Powder XRD patterns for SiO_2 nanosphere (black line), ZnO nanoparticle (purple line) ZnO- SiO_2 composites viz. ZnO- 1wt% SiO_2 (**ZS₁**, dark cyan line), ZnO-5wt% SiO_2 (**ZS₅**, blue line) and ZnO-10wt% SiO_2 (**ZS₁₀**, magenta line) films on glass

To examine any change in average crystallite size of ZnO NP upon SiO_2 NS loading the average crystallite sizes of bare ZnO NP and composites **ZS₁**, **ZS₅**, **ZS₁₀** were calculated using the Debye–Scherrer relation²³ monitoring (101) lattice plane of ZnO NP. However, it was observed that with 1%, 5% and 10% loading of SiO_2 NS did not alter the crystallite size of ZnO NP significantly (ZnO NP ~ 20.77 nm, **ZS₁** ~ 19.46 nm, **ZS₅** ~ 19.12nm, **ZS₁₀** ~ 20.74 nm) which is indicative of the retention of the crystallinity of ZnO NP even after loading of SiO_2 NS.

3.3.2 RAMAN ANALYSIS

Vibrational characteristics of materials recorded by Raman spectroscopy and provides information regarding crystallization, structural disorder, material defects and optical properties as shown in figure 3.3.2. For all samples a sharp and dominant peak observed at 439 cm^{-1} is assigned

to E_2 (high) mode of wurtzite hexagonal ZnO lattice. This mode is a fingerprint of the degree of crystallinity of the wurtzite ZnO nanoparticles associated with oxygen displacement.²⁴ A suppressed peak appeared at 581cm^{-1} is attributed to A_1 (LO) mode which probably may have occurred due to oxygen vacancy.²⁵ The peak observed 333cm^{-1} is assigned to multiphonon second order scattering process of (E_2 (high)- E_2 (low)) occurred due to overtones of first order modes.²⁶

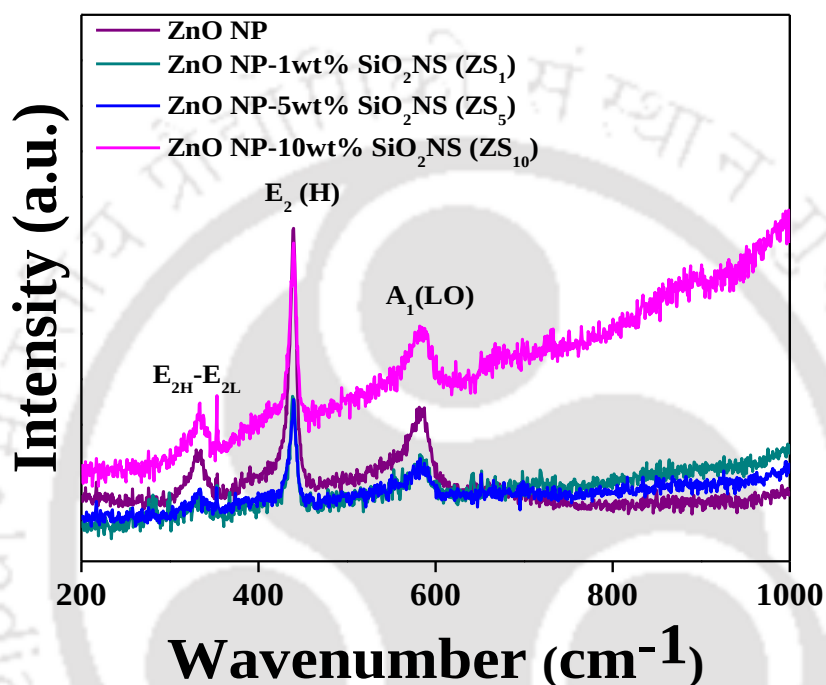


Figure 3.3.2 Room temperature Raman spectra of ZnO NP film (purple line), ZnO-1wt % SiO₂ (ZS₁, dark cyan), ZnO-5wt % SiO₂ (ZS₅, blue line) and ZnO-10wt % SiO₂ (ZS₁₀, magenta line) all on glass substrates

It was observed that upon SiO₂ NS loading there is no shift in peak positions of wurtzite hexagonal ZnO lattice inferring presence of amorphous SiO₂ and the results are in good agreement with XRD results.

3.3.3 UV-VISIBLE DIFFUSED REFLECTANCE AND ENERGY DISPERSIVE X-RAY ANALYSIS

Diffused reflectance measurements carried out for photoanode films of comparable thickness based on bare ZnO NP film (magenta line), ZnO-1wt % SiO₂ (ZS₁, purple cyan line), ZnO-5wt % SiO₂ (ZS₅, dark cyan line) and ZnO-10wt % SiO₂ (ZS₁₀, black line) deposited on glass substrates prior to dye sensitization and depicted in figure 3.3.3.

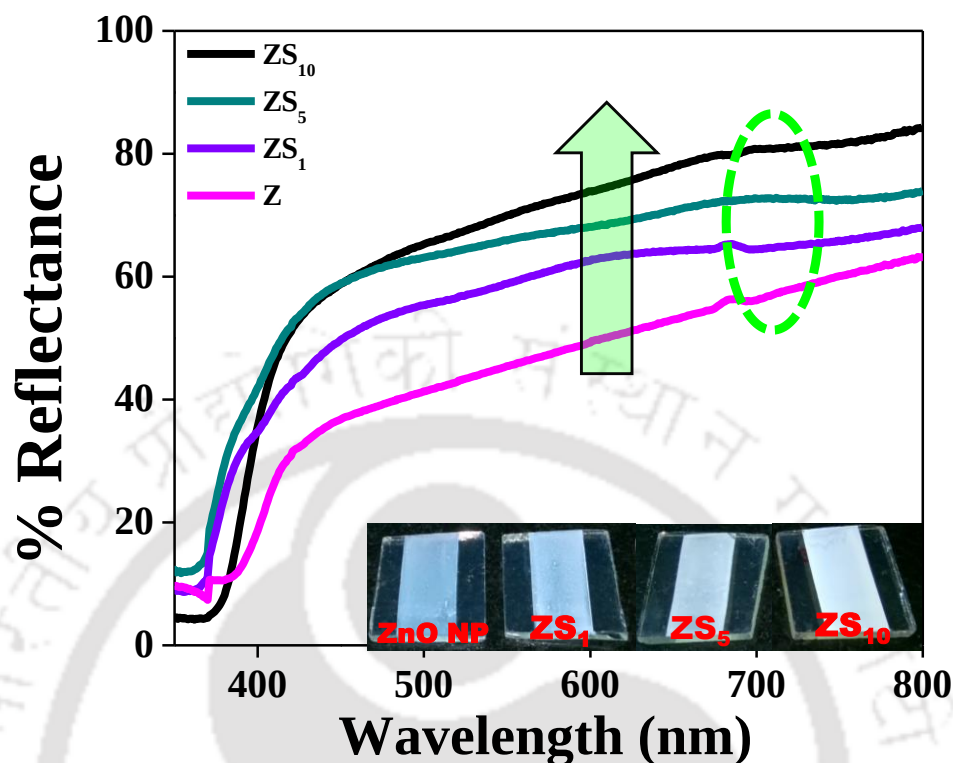


Figure 3.3.3 UV-Vis diffused reflectance spectra of photoanodes ZnO NP film (magenta line), ZnO-1wt % SiO₂ (ZS₁, purple cyan line), ZnO-5wt % SiO₂ (ZS₅, dark cyan line) and ZnO-10wt % SiO₂ (ZS₁₀, black line) all on FTO coated glass substrates. Inset shows the digital images of fabricated photoanode with ZnO NP and composites ZS₁, ZS₅, ZS₁₀

The composite photoanodic film containing 1wt% SiO₂ NS shows higher diffused reflectance than the pristine ZnO NP film owing to the scattering by individual submicron sized SiO₂ NS as well as enhanced scattering from the ensemble.²⁷ Further increasing the SiO₂ content, the diffused reflectance increases and composite with 10wt% SiO₂ NS (ZS₁₀) exhibits highest reflectance among all the composites in the wavelength range 600–800 nm.

It is seen from elemental mapping (EDX), figure 3.3.4, that the distribution of SiO₂ NS are homogeneous throughout the sample, contributing to the effective light trapping and scattering effects. Superior light harvesting through confinement of light propagation extends the optical path length of incident light by multiple reflections within the photoanodic film entailing SiO₂ NS, resulting in a reduced loss of incident light. Scheme 3.3.1 depicts pictorial presentation showing the light scattering pathways in the composite photoanode fabricated with various amounts of SiO₂ NS and ZnO NP resulting in a better light harvesting capacity as compared to pristine ZnO NP photoanode.

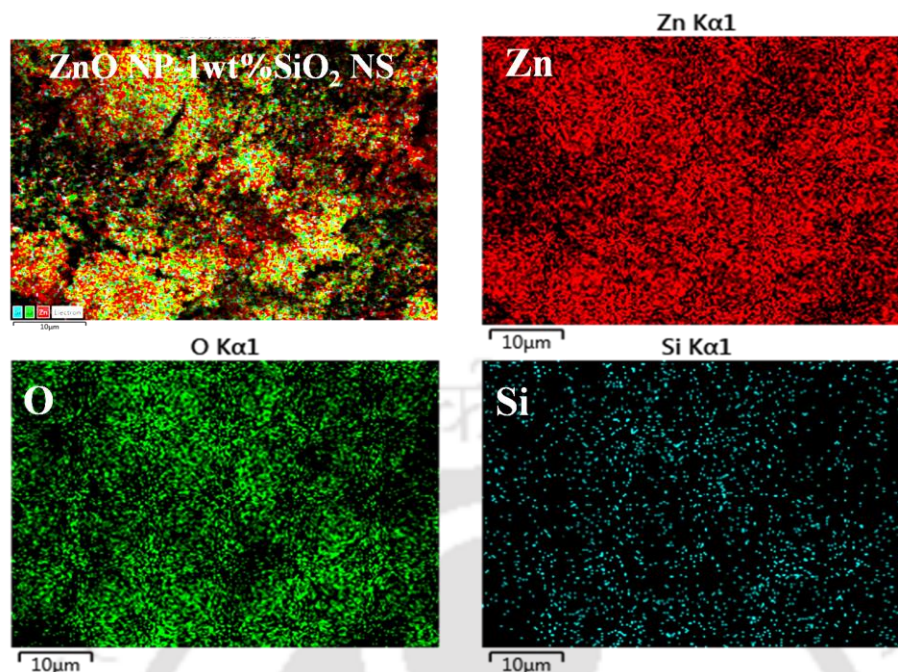
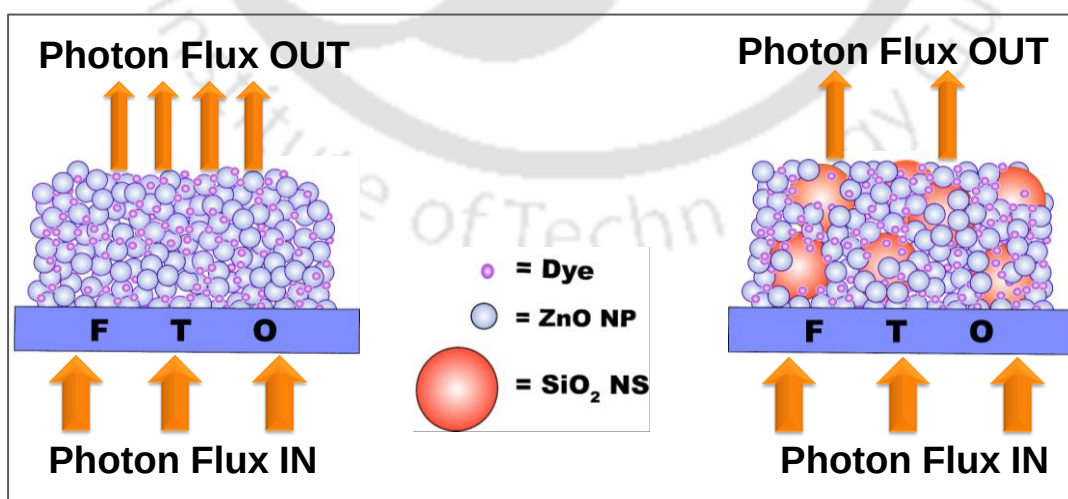


Figure. 3.3.4 Energy-dispersive X-ray spectroscopy (EDS) mapping of best performed photoanode i.e. ZnO-1wt% SiO₂ (ZS₁)

Though it is observed that the light scattering effect is maximum in case of 10wt % SiO₂ NS loading, the opaqueness of the films increases with increase in SiO₂ NS content resulting in a decrement of penetration ability of the incoming photon flux (inset to figure 3.3.3) i.e., reducing the light absorption thereby the harvesting ability, causing adverse effect on the device performances.²⁸



Scheme 3.3.1 Schematic showing incident and outgoing photon flux in case of only nanoparticle and hybrid photoanode based device

3.3.4 BET SURFACE AREA AND CHEMISORPTION ANALYSIS

Figure 3.3.5 depicts the N_2 - physisorption curve of SiO_2 NS. The BET surface area provided by SiO_2 NS is ($13.5 \text{ m}^2\text{g}^{-1}$). According to the Brunauer–Deming–Deming–Teller (BDDT) classification, the physisorption isotherms can be grouped into six types. As can be seen, the BET plot exhibits type IV isotherm and H3 hysteresis loops indicating the mesoporous nature of SiO_2 NS.²⁹

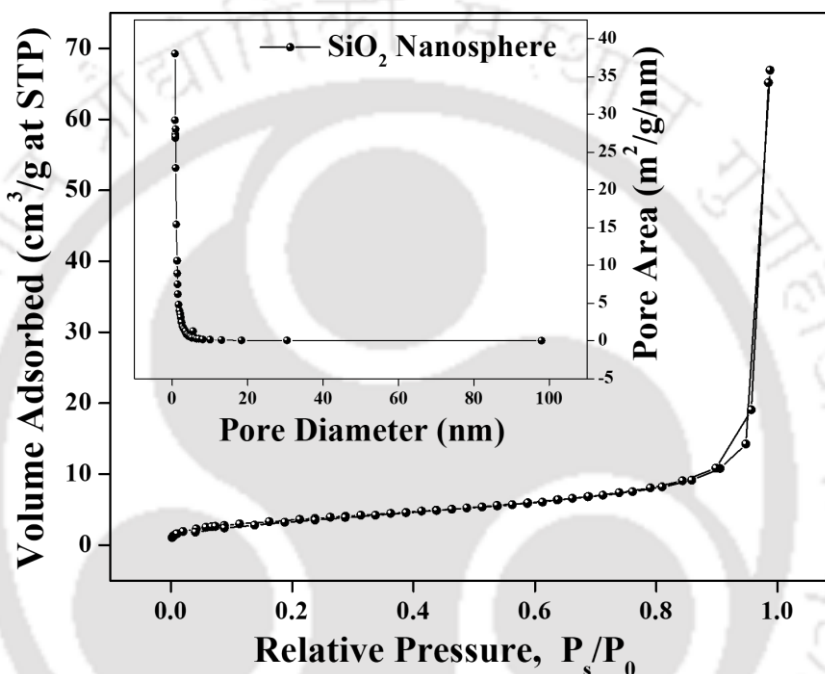


Figure 3.3.5 Nitrogen adsorption–desorption isotherms and Barrett–Joyner–Halenda (BJH) pore size distribution plot(Inset) for SiO_2 NS

The Barrett–Joyner–Halenda (BJH) pore size distribution curve (inset) indicates the high degree of uniformity of pores in the range of 3–5 nm. [$BET_{ZnO} \sim 49.2 \text{ m}^2\cdot\text{g}^{-1}$, $BET_{Zs1} \sim 41.3 \text{ m}^2\cdot\text{g}^{-1}$, $BET_{Zs5} \sim 37.2 \text{ m}^2\cdot\text{g}^{-1}$] The porous nature of SiO_2 NS facilitates the trapping of light by individual molecule as well as facilitates the electrolyte diffusion for better regeneration of Dye molecules. Quantity of dye chemisorbed onto the fabricated photoanodes was evaluated by employing a dye adsorption-desorption process using a $1 \times 10^{-4} \text{ M}$ NaOH solution in ethanol/water (1:1, v/v).³⁰ Briefly, each of the dye sensitized photoanodes were immersed in a $1 \times 10^{-4} \text{ M}$ NaOH solution in 1:1 ethanol: water mixture. Then the photoanodes were removed from the solution after complete desorption of dye and the UV-Vis absorbance was recorded. The concentration of the desorbed dye per cm^2 area was then calculated using Beer's law. It was observed that the photoanodes have

shown an optimum quantity of dye loading with values for ZnO NP $\approx 9.49 \times 10^{-7}$ mol cm $^{-2}$, for **ZS₁** $\approx 9.05 \times 10^{-7}$ mol cm $^{-2}$, for **ZS₅** $\approx 8.85 \times 10^{-7}$ mol cm $^{-2}$ and for **ZS₁₀** $\approx 8.53 \times 10^{-7}$ mol cm $^{-2}$. The decrease in the adsorption of dye is ascribed to the lower BET surface area (13.5 m 2 g $^{-1}$) provided by SiO $_2$ NS in the composite photoanode.

3.3.5 PHOTOVOLTAIC PERFORMANCES OF THE FABRICATED DEVICES

Photovoltaic performances of the fabricated DSSCs evaluated against Pt counter electrode employing I $^-$ /I $_3^-$ redox shuttles under AM 1.5G with a standard sunlight illumination intensity of 100 mW.cm $^{-2}$ is depicted in figure 3.3.6 (A). The overall photovoltaic performances of all the DSSCs employing I $^-$ /I $_3^-$ redox shuttles are summarized in table 3.3.1. From table 3.3.1, we have seen that a short-circuit current density (J_{sc}) of ~ 8.61 mA/cm 2 , an open circuit voltage (V_{oc}) of ~ 616 mV and a fill factor (FF) of $\sim 47.5\%$ affording a PCE of $\sim 2.53\%$ exhibited by the cell with pristine ZnO NP. Interestingly, in the case of 1wt% SiO $_2$ NS loaded ZnO NP device (**ZS₁**), we observed an increment of $\sim 22\%$ in the efficacy value as compared to pristine ZnO NP based device, affording a PCE of $\sim 3.08\%$ with $J_{sc} \sim 9.31$ mA/cm 2 , a $V_{oc} \sim 625$ mV, a FF $\sim 53.6\%$. Devices loaded with 5wt% and 10wt% SiO $_2$ NS i.e. **ZS₅** and **ZS₁₀** showed lower performances yielding a $J_{sc} \sim 8.40$ mA/cm 2 , a $V_{oc} \sim 609$ mV, a FF $\sim 42.1\%$ and a PCE $\sim 2.15\%$, for **ZS₅** and a $J_{sc} \sim 6.87$ mA/cm 2 , a $V_{oc} \sim 596$ mV, a FF $\sim 41.8\%$, a PCE $\sim 1.71\%$ for **ZS₁₀** device.

Table 3.3.1 Short-Circuit Photocurrent Density (J_{sc}),^a Open-Circuit Voltage (V_{oc}),^a Fill Factor (FF),^a Power Conversion Efficiency (PCE, η), Maximum Incident Photon-to-Current Conversion Efficiency (IPCE $_{max}$) and photo-induced electron lifetime (τ_{el})^b for the Fabricated DSSCs Composed of ZnO NP and ZnO NP-SiO $_2$ NS Composite Based Photoanodes Employing I $^-$ /I $_3^-$ Redox couple

DSSC photoanode	J_{sc} (mA/cm 2)	V_{oc} (mV)	FF (%)	PCE (η , %)	IPCE $_{max}$ (%)	τ_{el} (ms)
ZnO NP	8.61	616	47.5	2.53	38	7.3
ZnONP-1wt% SiO $_2$ NS	9.31	625	53.6	3.08	43	9.3
ZnO NP-5wt% SiO $_2$ NS	8.40	609	42.1	2.15	32	5.7
ZnO NP-10wt% SiO $_2$ NS	6.87	596	41.8	1.71	30	4.4

^a Data reported are the results of the best performing device out of five devices for each configuration.

^b Electron lifetime measurements are performed only for the best performed devices.

Increase in short-circuit current density is credited to several factors viz., (i) utilization of photoanodes having microstructures of SiO $_2$ NS with superior light scattering ability for enhanced

light harvesting (ii) reduced recombination of photo generated electrons and (iii) exploitation of photosensitizers with higher molar extinction coefficient. Increase in overall efficacy of the device **ZS₁** as compared to pristine ZnO NP device can be attributed to the efficient light scattering ability and reduced recombination (back electron transfers) of photo generated electrons using SiO₂ NS.

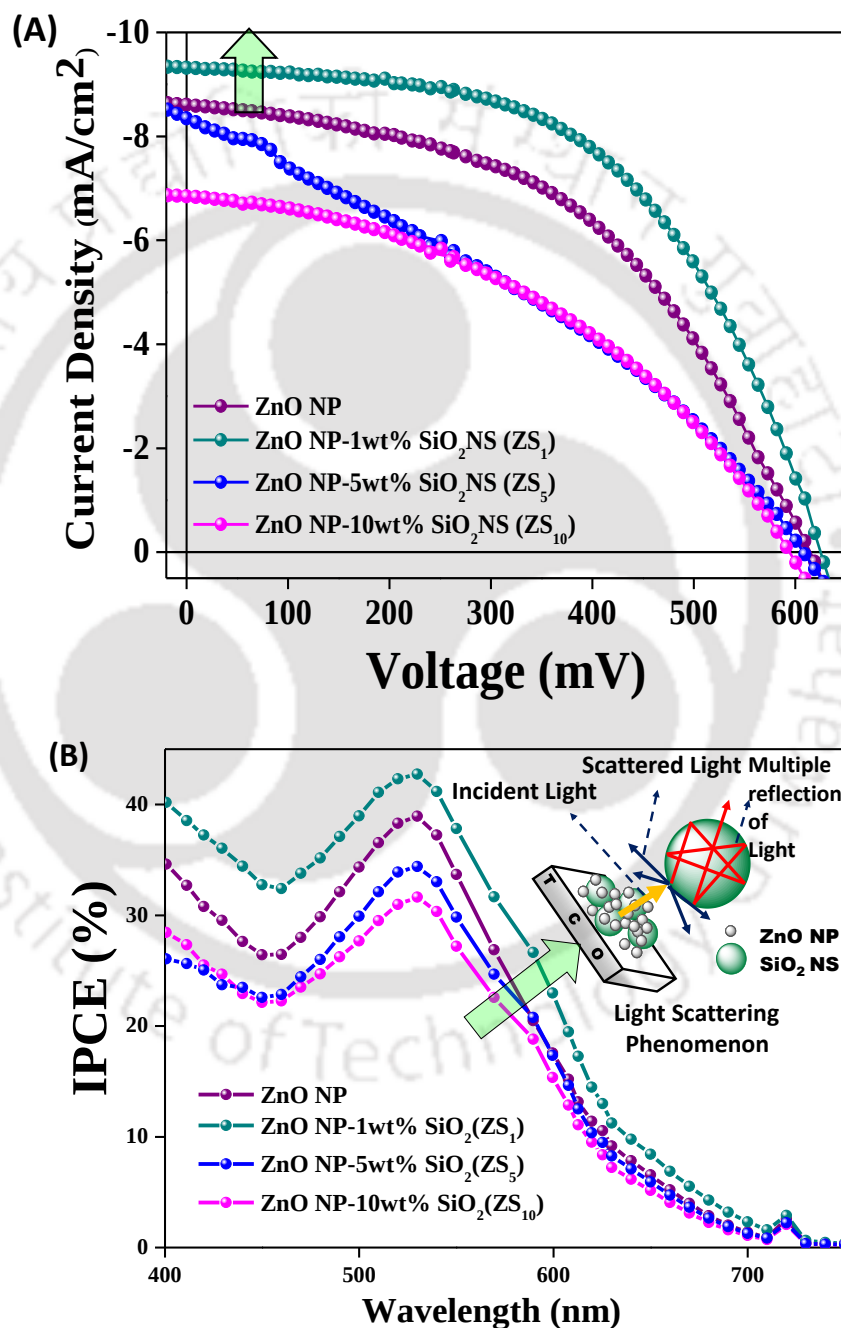


Figure 3.3.6 (A) Current density–voltage ($J-V$) curves for the photovoltaic devices ZnO NP (purple line), ZnO-1wt % SiO₂ (**ZS₁**, dark cyan line), ZnO-5wt % SiO₂ (**ZS₅**, blue line) and ZnO-10wt % SiO₂ (**ZS₁₀**, magenta line) and (B) IPCE plots for the respective devices employing I^-/I_3^- redox shuttles

Due to the enhanced light scattering ability of the composite photoanode entailing submicron sized SiO₂ NS, the path length of the incident light increases owing to multiple internal reflections and hence light spends more time within the photoanode. This in turn generates a high number of photoexcited electrons in the CB level of semiconductor which can be extracted at the collecting electrode, i.e. transparent conductive oxide glass substrate (TCO). Increase in the charge collection efficiency of the device results in increase in the current density value and device performance. SiO₂ NS owing to its higher CB position (~ 0.9 eV Vs E_{vacuum}) and insulating nature also functions as a partial energy barrier, thus reducing the back transfer of electrons from conduction band of ZnO to that the dye/ electrolyte interface, enhancing the collection efficacy at the electrode. SiO₂ NS containing devices (**ZS₁**) also exhibit an improved fill factor of around $\sim 54\%$ compared to pristine ZnO containing device, which shows a fill factor of around $\sim 48\%$, indicative of a better electron transport characteristics. Although the scattering ability of photoanodes **ZS₅** and **ZS₁₀** is more as compared to the **ZS₁**, the submicron sized SiO₂ NS provides lesser specific surface area in photoanodic segment for dye adsorption, resulting in decreased dye loading as can be seen from chemisorption analysis section 3.3.4. Reduced dye loading effects the absorption of incoming light, providing lesser number of photo-generated electron in the CB of semiconductor resulting in poor charge collection. On the contrary, increase in SiO₂ content from optimal concentration causes the FF to decrease due to the insulating nature of SiO₂ NS. This phenomenon is further explained in EIS analysis, where in recombination resistance plays a major role in determining the efficacy of the devices.

The photocurrent characteristics of the fabricated DSSCs depicted in figure 3.3.6 (B) depicts a prominent photosensitization throughout the visible region achieved by the dye with maximum IPCE values of $\sim 38\%$, $\sim 42\%$, $\sim 33\%$ and $\sim 30\%$ at 525 nm for ZnO NP, **ZS₁**, **ZS₅** and **ZS₁₀** based photovoltaic cells respectively. The higher IPCE values observed at longer wavelength in the IPCE spectra in case of **ZS₁**, **ZS₅** and **ZS₁₀** signifies the enhanced light scattering ability of submicron sized SiO₂ NS. The increase in overall IPCE value in **ZS₁** device as compared to pristine ZnO NP device is due to higher flux of photo-generated electrons owing to the optimal dye loading and light scattering effect with 1wt% SiO₂ NS. Further increase in SiO₂ content, the charge collection efficiency at the TCO decreases due to low dye loading capacity of the photoanode resulting in a lower IPCE value.

3.3.6 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPIC ANALYSIS

To corroborate the effect of SiO₂ NS loading on kinetics and interfacial energetics of electron transport and recombination properties in fabricated DSSCs, electrochemical impedance spectroscopy (EIS) measurements were carried out for the best-performing devices under the dark conditions at an external bias equivalent to open circuit voltage (V_{oc}) in the frequency range of 0.1 Hz to 100 KHz as shown in figure 3.3.7 (A) and 3.3.7 (B).

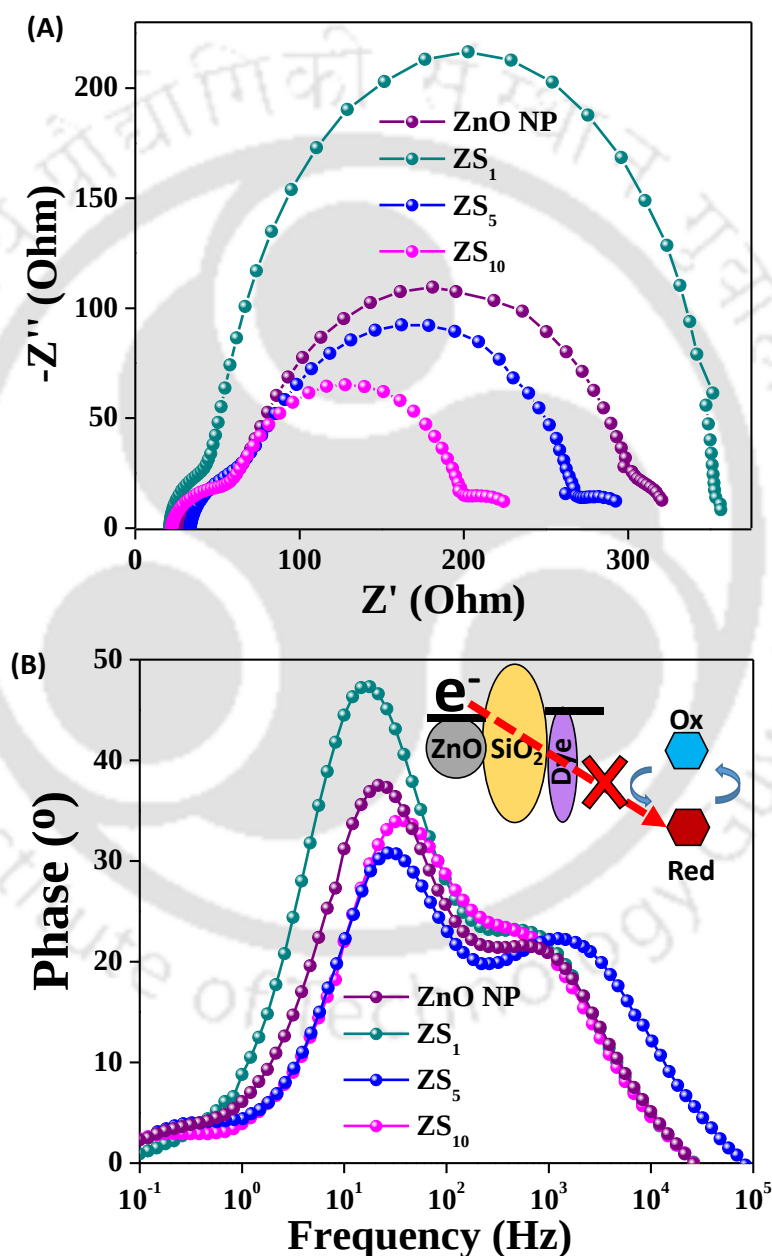


Figure 3.3.7 (A) Nyquist plots and (B) Bode phase plots for the fabricated DSSCs composed of ZnO NP (purple line), ZnO-1wt % SiO₂ (ZS₁, dark cyan line), ZnO-5wt % SiO₂ (ZS₅, blue line) and ZnO-10wt % SiO₂ (ZS₁₀, magenta line) based photoanodes. Inset shows schematic representation of inhibited electron interception at ZnO/dye/electrolyte interface

EIS analysis for the DSSCs typically explicates the characteristics of interfacial charge transfer and recombination processes taking place in the device, viz. at the interface of counter electrode and electrolyte (1–100 KHz, high-frequency region), the semiconductor/dye/electrolyte interface (0.1–1 KHz, mid-frequency region), and the diffusion of electrolyte (0.1–0.01 KHz, low-frequency region).³¹ As can be seen from corresponding Nyquist plot i.e. figure 3.3.7 (A), the diameter of the semicircle in the mid frequency region for device with 1wt% SiO₂ NS loading is larger as compared to the bare ZnO NP based device that endorses a greater charge recombination resistance (R_{ct}) in case of ZnO NP-1wt% SiO₂ NS device relative to that of ZnO NP based device. Large value of R_{ct} for ZnO NP-1wt% SiO₂ NS based device implies retarded backward reaction of dye injected electron at the semiconductor/dye/electrolyte interface or lesser interfacial charge recombination with holes of the electrolyte in the device. Incorporation of SiO₂ NS serves as an energy barrier layer that hinders the back electron recombination as shown in inset to fig. 3.3.7 (B). It has been found that further increase in SiO₂ content the R_{ct} decreases which is attributed to the greater resistance posed by insulating SiO₂ and a similar trend is noticed in fill factors (FF) of the devices. FF can be related to V_{oc} using following equation:³²

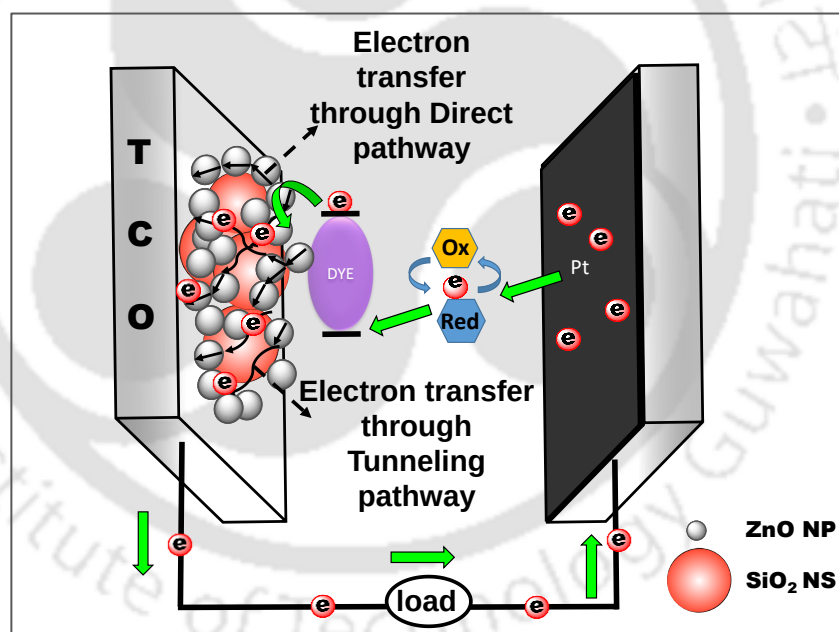
$$FF = \frac{V_r - \ln(V_r + 0.72)}{V_r + 1}$$

Where, V_r is the reduced voltage and given by $V_r = \beta q V_{oc} / k_B T$, β is the recombination exponent.

Since, there is no significant change in V_{oc} , FF can now be considered as a function of β only. So increase in recombination resistance (R_{ct}) will enhance the FF which is seen in the device **ZS₁** (ZnO NP-1wt% SiO₂ NS) with highest fill factor of ~ 54 %. Further increase in SiO₂ NS content as in **ZS₅**, **ZS₁₀**, there is a decrease in recombination resistance owing to the insulating nature of SiO₂ results in a decreased fill factor of the corresponding devices.

Figure 3.3.7 (B) portrayed the corresponding Bode phase plots for the fabricated DSSCs. The two observed distinct peaks at the mid- and high-frequency regions confirms the two diode interfaces present in the devices. The phase angle peak, at the intermediate-frequency region are located at ~ 21.7 Hz, ~ 16.4 Hz, ~ 27.7 Hz, ~ 35.4Hz for ZnO NPs, ZnO NP- 1wt% SiO₂ NS, ZnO NP- 5wt% SiO₂ NS and ZnO NP- 10wt% SiO₂ NS device respectively. The values of photo-induced electron life time τ_e in conduction band of photoanode based cells can be estimated from

the Bode phase plot using the relation $\tau_e = (2\pi f_p)^{-1}$, where f_p is the observed maximum peak frequency in the mid-frequency region.³³ The calculated τ_e for different photoanodes are 7.3ms, 9.7ms, 5.7ms, 4.4ms for ZnO NPs, **ZS1**, **ZS5** and **ZS10** devices as shown in table 3.3.1. The increase in the photo-induced electron lifetime also validates the hindrance created by 1wt% SiO₂ NS incorporation in the photoanode which acts as a partial barrier for electrons to undergo recombination with the oxidized electrolyte. Further increase in SiO₂ NS content decreases τ_e which is indicative of impeded photo-generated electron injection from dye to semiconductor. On increase in the SiO₂ NS the tunnelling possibility of far less photo-induced electrons from dye to ZnO across the SiO₂ NS barrier gets reduced when the optimal concentration is crossed resulting in a poor charge collection efficiency. From the understanding of photovoltaic and electrochemical impedance analysis, we are proposing a schematic of electron transfer occurring in DSSCs as shown in scheme 3.3.2.



Scheme 3.3.2 Schematic showing electron transfer mechanism occurring in DSSC

The photogenerated electron tunnels through the insulating SiO₂ NS to ZnO NP and then collected at FTO. In other way photo-generated electron can also transfer from sensitizer to ZnO NP through a direct pathway and finally to the collector electrode i.e. FTO. The electrons travel through the external circuit, reach at counter electrode and oxidized sensitizer molecules are regenerated by using I⁻/I₃⁻ redox shuttle.

In order to check the stability of the best performed device, dependence of photovoltaic parameters such as short circuit current density (J_{sc}), open circuit voltage (V_{oc}), Fill factor (FF) and the power conversion efficiency (η) on time durations (over 48 h) are shown in figure 3.3.8.

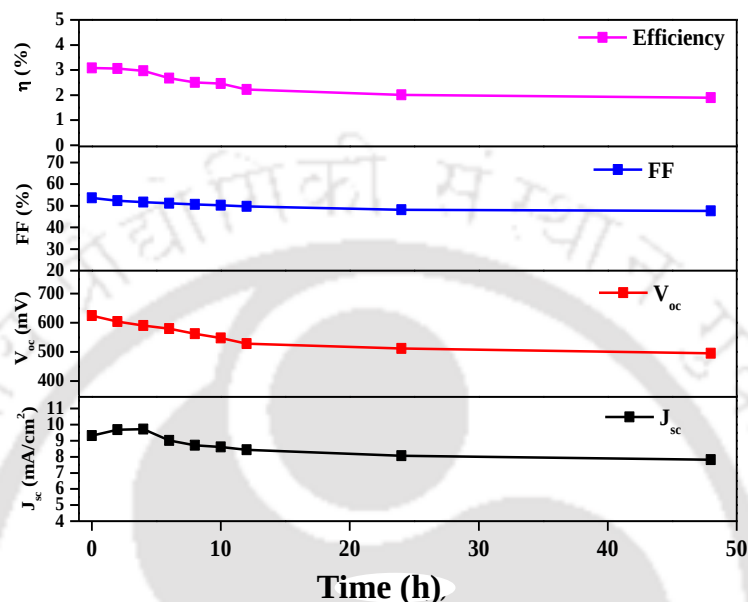


Figure 3.3.8 Stability test for the best performing solar cell

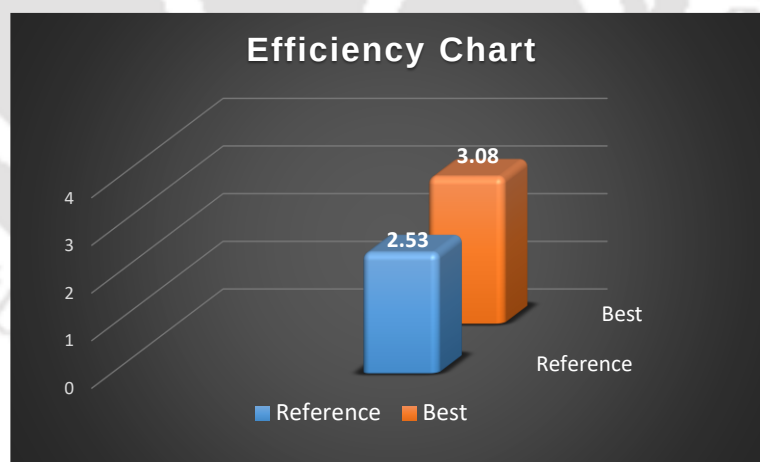
In order to check the stability of the devices, dependence of photovoltaic parameters such as short circuit current density (J_{sc}), open circuit voltage (V_{oc}), Fill factor (FF) and the power conversion efficiency (η) on time durations (over 48 h) are shown in figure 3.3.8. The photovoltaic characteristics are collected at an interval of 2h for 12h and then up to 48h in air and examinations show that a ~30% reduction of efficacy is observed after 48h duration. Therefore, it indicates that the devices are quite stable initially but shows slow decrease in performance with increased time.

3.4. CONCLUSIONS

In summary, a facile approach for enhanced light harvesting and reduced recombination of photo-generated electrons in ZnO based DSSC is demonstrated by introducing a low cost, easily synthesizable SiO₂ NS. SiO₂ NS owing to its optimal size can effectively scatter incident light and can increase the light propagation path by multiple reflections within the photoanode. SiO₂ NS can also function as a partial energy barrier for back transfer of photo-generated electrons at the

working electrode/electrolyte interface, and lifts the photovoltaic efficacy. We have performed photovoltaic studies by varying the amount of SiO₂ NS with reference to ZnO NP viz. 1wt%, 5wt% and 10wt% among which ZnO NP-1wt% SiO₂ photoanode shows ~ 22% increase in PCE as compared to bare ZnO NP based photoanode. In essence, SiO₂ NS plays a vital role in increasing the light harnessing capability of the photoanode and acts as an energy barrier preventing the back electron transfer processes, leading to an enhanced efficacy of the solar cell. A few highlighted points of the current work are as follows,

- ✚ A ~22% **improvement** in power conversion efficiency (PCE, η) is observed for a device fabricated with the binary hybrid composite of 1 wt% SiO₂ NS and zinc oxide nanoparticle (ZnO NP), i.e., (**ZS₁**) over the pristine ZnO NP device.
- ✚ Enhanced light absorption by multiple scattering of the incident light within the photoanode entailing SiO₂ NS.
- ✚ A higher Fill Factor (~ **12% increase**) furnished by **ZS₁** as compared to reference device is attributed to minimum photo induced electron interception at Semiconductor/dye/electrolyte interface.



3.5 REFERENCES

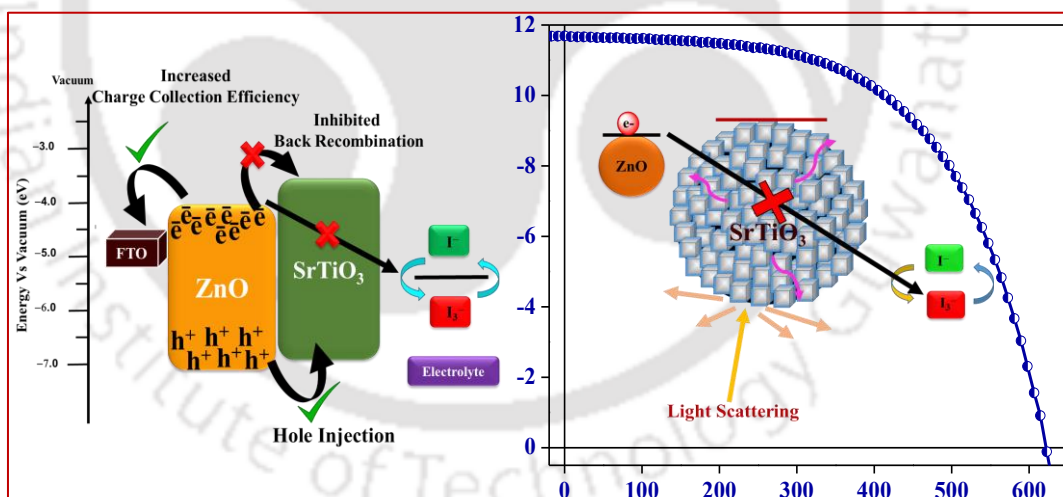
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CHAPTER 4

Nanocube assembled SrTiO_3 in enhancing the photovoltaic properties through its energy barrier and light scattering effects

This chapter presents utilization of an easily synthesizable and cost-effective nanocube assembled micron-sized SrTiO_3 (STO NCMS) in ZnO nanoparticle based photovoltaics. An effective photoinduced charge separation achieved with a uniquely aligned band structure, resulted in enhanced charge collection efficiency in devices. Moreover, improved photovoltaic performance of photoanode with composite scaffold can be accredited to the boosted optical response in conjunction with impeded reverse tunneling probability of STO NCMS containing photoanode.



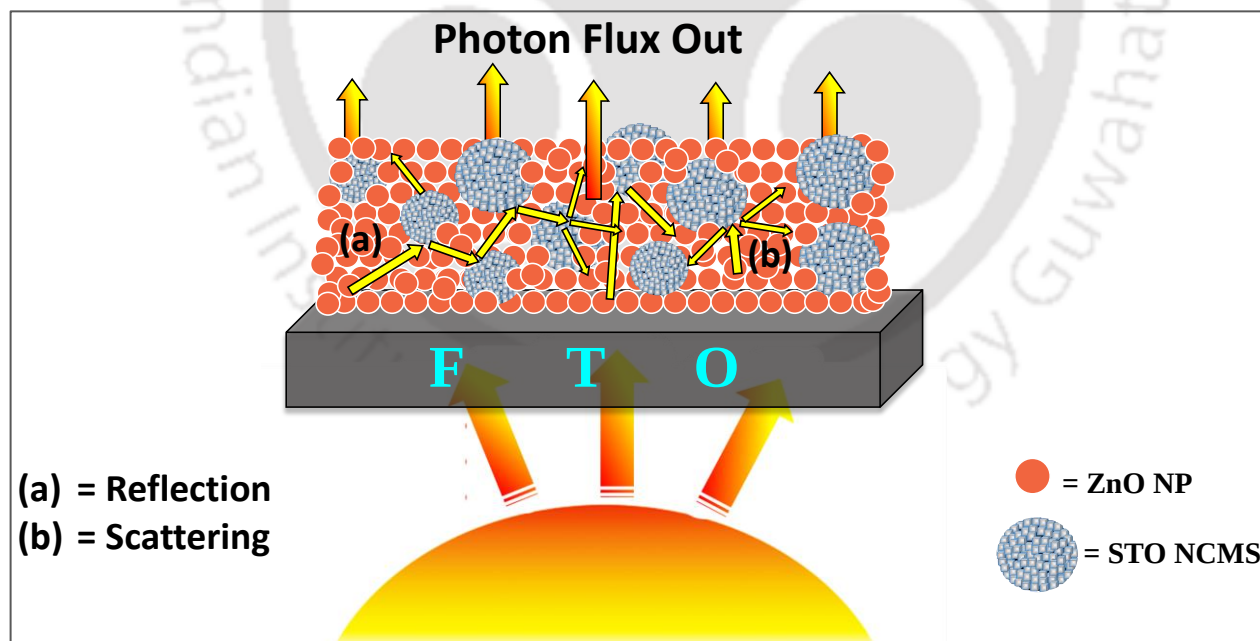
4.1 INTRODUCTION

Performance of nanoparticle based devices has been largely hindered by inadequate utilization of the low-energy photons and difficulties in efficiently collecting photoinduced electrons due to competing and thermodynamically favorable back transfer reactions between the photoinduced electrons and oxidized species present in the system.¹⁻² Zinc oxide (ZnO), a II-VI semiconductor, despite having advantages like higher electron mobility³ and diffusion length⁴ suffers a low power conversion efficiency due to the aforementioned reasons. Numerous approaches have been developed to facilitate the light harvesting in dye-sensitized solar cell throughout the visible range of the electromagnetic spectrum viz. utilization of new sensitizer molecules,⁵⁻⁶ co-sensitization with quantum dots,⁷ utilizing plasmonic nanoparticles,⁸ formation of a light-scattering layer in the working electrode.⁹ Among these, a cost effective and easily processed way to enhance the light harvesting ability of the photoanode is to utilize light scattering materials. Basic principle of light scattering is defined as the confinement of incident light within the photoanode by multiple light scattering from the large microparticles present in the ensemble, extending the path-length of incident light within the photoanodic film, thus increases the probability of photon absorption by the dye molecules.¹⁰⁻¹² On the other hand, in the DSSC, intrinsically complex and competitive interfacial processes exist, viz. semiconductor/redox couple interface, sensitizer/ redox couple interface and FTO/redox couple interface, where charge carriers in separate phases come across each other following physical interactions. Hence, a series of thermodynamically driven back transfer of charge carriers which are detrimental to device performance, competing with the forward transfers.¹³ These processes of photoinduced electron generation, separation of charges and charge recombination occur predominantly at hetero-interfaces. The proximity of photoinduced charges, and the lack of energy barrier between them lead to charge carrier's annihilation.¹⁴ Certainly, the efficiency of the device largely depends upon interfacial physical and photoelectrochemical processes.

SrTiO₃, an important n-type perovskite multimetal oxide with an indirect band gap varying from 3.2 to 3.4 eV, has been widely investigated and has many potential applications in various microelectronic heterostructures,¹⁵ oxygen sensors,¹⁶ solar cells,¹⁷ and batteries,¹⁸ due to its superior photocorrosion resistibility, excellent dielectric, photoelectric, optical and catalytic properties and ease of doping to control the electrical properties.¹⁹⁻²¹ SrTiO₃, offers a conduction

band offset of 0.2 eV closer to the vacuum level than that of traditionally used TiO_2 and has much higher mobility $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ which would be favorable for reducing recombination losses and faster electron transport.²² This makes SrTiO_3 , a good candidate for coupling with ZnO to improve photovoltaic performance. The negative shift of the conduction band in SrTiO_3 can significantly reduce charge recombination at hetero-interface by acting as partial energy barrier for back-transfer of photo-injected electron from ZnO . Moreover, a heterojunction formed by suitable band alignments of SrTiO_3 with ZnO can enhance charge separation.

This chapter demonstrates synthesis of a nanocube assembled SrTiO_3 microstructures (**STO NCMS**) through hydrothermal process and utilized as a light scattering material in a composite with ZnO nanoparticle for dye-sensitized solar cell. Systematic study on the effects of **STO NCMS** on photovoltaic properties showed a ~ 2 -fold increase in power conversion efficiency as compared to reference cell owing to better light scattering properties (shown in scheme 4.1.1) as well as inhibited reverse tunneling of photo-injected electron. Furthermore, formation of heterojunction with well-matched band positions resulted in an efficient charge collection.



Scheme 4.1.1 Schematic representation showing various light scattering and reflections occurring in composite based photoanode

4.2 EXPERIMENTAL METHODS

4.2.1 SYNTHESIS OF NANOCUBE ASSEMBLED SrTiO_3 MICROSTRUCTURES (STO NCMS):

SrTiO_3 NCMS were synthesized following a reported protocol with slight modifications.²³ In the synthetic procedure, 1 ml titanium iso-propoxide was added dropwise in 50 ml anhydrous acetone and heated at 200 °C for 10hrs in a Teflon lined stainless steel autoclave in a hot air oven. The precipitate was recovered by centrifugation and washed with de-ionized (DI) H_2O and acetone for several times and dried at 60 °C in an oven (named as A). In the next step, 20 mg of A was dispersed ultrasonically in aqueous NaOH of pH=12, followed by an addition of 0.2 mmol CTAB and 2 mmol $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ under constant stirring and then heated to 150 °C in a Teflon lined stainless steel autoclave for 12h. Finally, product was obtained by centrifugation, washed with dilute HNO_3 (to remove SrCO_3 impurity) DI water, and ethanol several times and dried at 60 °C in a vacuum oven.

4.2.2 SYNTHESIS OF ZnO NANOPARTICLES (ZnO NPs)

ZnO NPs were synthesized following a reported protocol.²⁴ Briefly, anhydrous ZnCl_2 (16 mmol) was dissolved in 80mL of DI H_2O under vigorous stirring at 90 °C followed by dropwise addition of 3.2 mL of aq. NaOH (5M) solution. After stirring about half an hour further at 90 °C and cooled down to 25 °C. The solid precipitate was washed with DI water to remove the traces of any inorganic salt. Further, particles were dispersed in isopropanol under ultrasonic treatment to restrict agglomeration of nanoparticles. The solid product was obtained calcined at 450 °C for 2 h in a muffle furnace.

4.2.3 DEVICE FABRICATION

Firstly, composite powders were prepared by taking desired amount of **STO NCMS** and the rest amount (e.g. 10mg of **STO** and 990mg ZnO for **ZSTO₁**) and dispersed in ethanol by ultrasonic treatment for an hour. Finally, composite product was obtained by evaporating solvent. Rest of the composites have been made following similar procedure taking 20mg, 30mg, 40mg, 50mg of **STO NCMS** and rest ZnO NP and named hereafter **ZSTO_x** (**x** = 2-5). To fabricate the

devices firstly a homogenous paste of pristine material i.e. ZnO NPs and its composites **ZSTO_x** viz. **ZSTO₁**, **ZSTO₂**, **ZSTO₃**, **ZSTO₄**, **ZSTO₅** were prepared. FTO coated glass substrates were cleaned by soap solution, Milli-Q water, then sonicated in acetone and 2-propanol stepwise and then dried by blowing argon. Cleaned FTO substrates were then ozone treated for 30 min using Novascan UV-ozone chamber. A compact layer of ZnO was deposited onto the pre-cleaned ozonized FTO by spin coating a solution containing mixture of zinc acetate (0.30g), ethanolamine (84μL) in 2-methoxyethanol (4.50 mL) followed by calcination at 300 °C.²⁵ Homogenous paste of ZnO NP or **ZSTO_x** composites were prepared by grinding 0.5 g of respective samples with a mixture of terpeneol and ethyl cellulose in an agate mortar and applied on ZnO compact layer coated FTO using doctor blade technique and the films were dried at 120 °C, followed by calcination at 500 °C for 30 min. The thickness of the photoanode layers were found to be ~ 13–15 μm, measured by surface profilometer. These substrates were then immersed for 8 h into N719 dye solution in acetonitrile: *tert*-butanol (7:3) (0.3 mM). After removing from dye solution, sensitized photoanodes were washed with acetonitrile and dried under N₂ blow. Platinum used as the counter electrode, was fabricated by spin coating a 5 mM solution of H₂PtCl₆ (in isopropanol) onto a ozonized FTO and calcined at 450 °C for 45 minutes in a temperature programmed muffle furnace and allowed to cool down to 25 °C. The photoanodes and counter electrodes are sandwiched together using polymeric tape as a spacer between the electrodes and adding redox shuttle to complete the device. The I⁻/I₃⁻ redox shuttle was prepared by dissolving I₂ (0.05 M), LiI (0.5 M), 4-*tert*-butylpyridine (0.5 M) and guanidium thiocyanate (0.1 M) in a solvent mixture of acetonitrile: valeronitrile (8.5:1.5, v/v). The active area for all fabricated devices were 0.16 cm².

4.3 RESULTS AND DISCUSSIONS

4.3.1 POWDER X-RAY DIFFRACTION ANALYSIS

The crystal structures and phase purity of as synthesized ZnO NP, SrTiO₃ **NCMS**, and composites were confirmed by Powder X-ray diffraction (PXRD) patterns. In figure 4.3.1, diffraction peaks from lattice planes (100), (002), (101), (102), (110), (103), (200), (112) and (201) were perfectly indexed to the formation of hexagonal wurtzite phase (JCPDS File Card No. 36-1451) of ZnO NP with a space group symmetry P6₃mc. Whereas, SrTiO₃ **NCMS** exhibits a cubic phase perovskite structure with lattice planes (100), (110), (111), (200), (211), (220) similar to the

standard XRD pattern of SrTiO_3 , JCPDS File Card No. 40-1500. Notably, the recorded PXRD pattern for composites ZSTO_1 , ZSTO_2 , ZSTO_3 , ZSTO_4 , and ZSTO_5 predominantly showed the diffraction peaks for ZnO NP, while well-distinct diffraction peaks for **STO NCMS** remained silent at low loading (e.g. ZSTO_1 , ZSTO_2). With increase in SrTiO_3 content from ZSTO_3 to ZSTO_5 the peaks correspond to SrTiO_3 also became assignable.

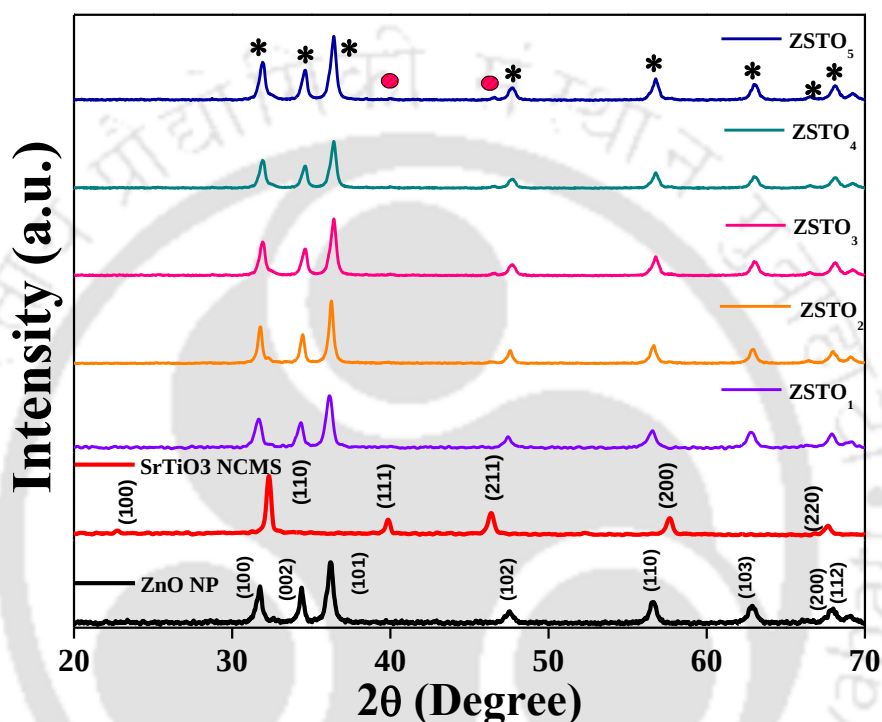


Figure 4.3.1 Powder XRD patterns for ZnO nanoparticles (black line), SrTiO_3 NCMS (red line), ZnO NP_1% STO NCMS (ZSTO_1 , violet line), ZnO NP_2% STO NCMS (ZSTO_2 , orange line), ZnO NP_3% STO NCMS (ZSTO_3 , pink line), ZnO NP_4% STO NCMS (ZSTO_4 , dark cyan line) and ZnO NP_5% STO NCMS (ZSTO_5 , blue line) films on glass substrates

4.3.2 MATERIAL MORPHOLOGY

To investigate the morphological and microstructural features of the as-synthesized SrTiO_3 we have carried out FESEM analysis. Figure 4.3.2 (A) shows FESEM image of as synthesized SrTiO_3 hollow spheres. It has been observed that SrTiO_3 have an average size dimension of ~ 0.7 - $1.5 \mu\text{m}$ which is well within the range of Mie scattering that helps in enhancing the light harvesting efficiency of photoanode by increasing the optical path length of incident light through multiple reflections as well as scattering. High magnification FESEM image Figure 4.3.2 (B) reveal that these microspheres are formed by assembly of regular SrTiO_3 nanocubes of size ranging from $\sim$

50-70 nm as primary blocks. These primary SrTiO_3 nanocubes self-organizes and self-assembled in Ostwald-ripening mechanism to produce the microstructures.

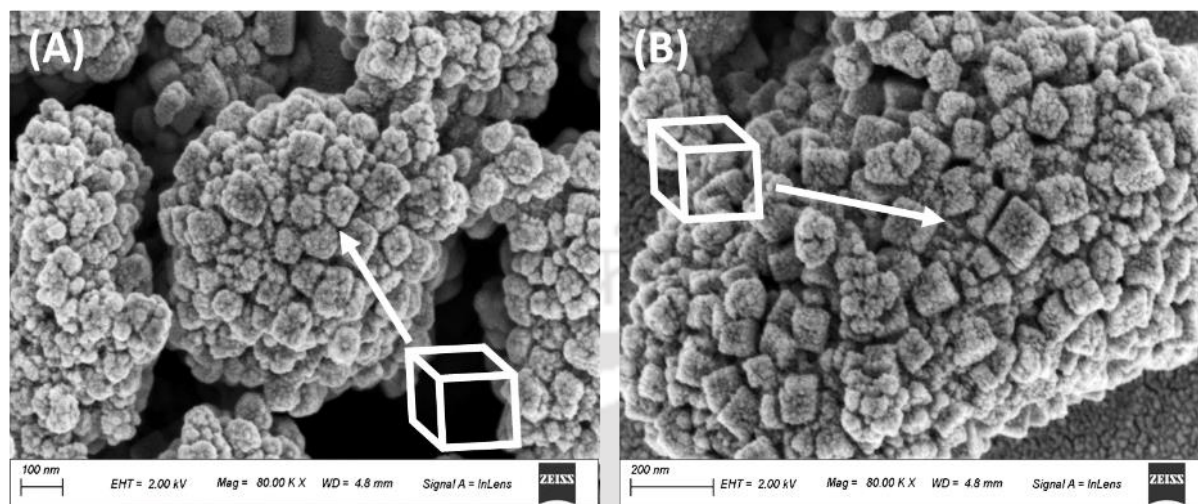


Figure 4.3.2 (A) Field Emission Scanning Electron Microscopic (FESEM) and (B) magnified FESEM image of as synthesized SrTiO_3 NCMS

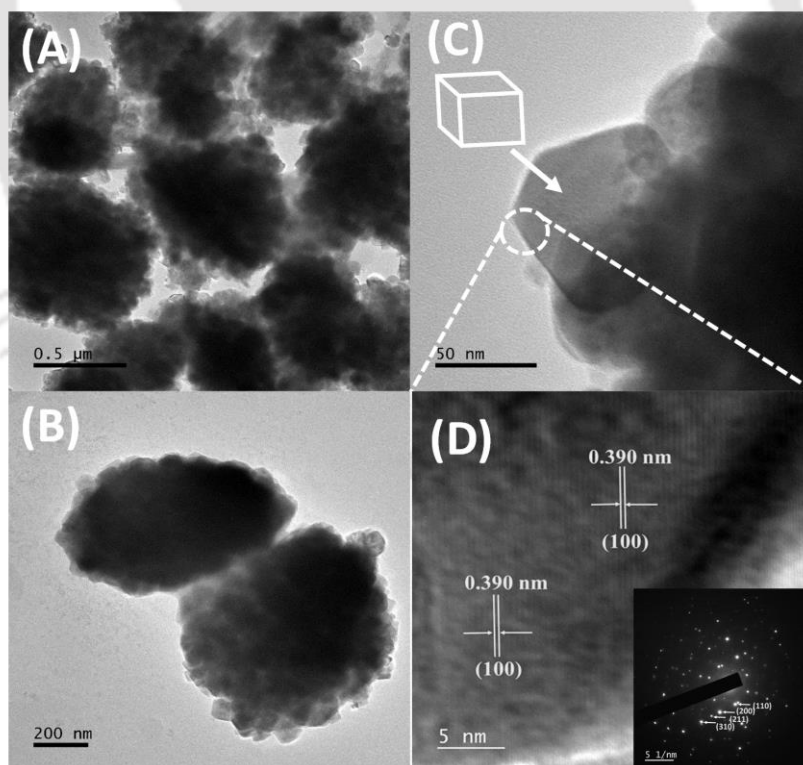


Figure 4.3.3 (A-C) Transmission Electron Microscope (TEM) image and magnified TEM images of as synthesized SrTiO_3 NCMS. Trace (D) represents the HRTEM image of building block of SrTiO_3 NCMS depicting the growth along (100) plane. Inset to figure (D) represents the corresponding SAED pattern

Furthermore, TEM analysis has been carried out to confirm the morphological features of SrTiO_3 as shown in **Figure 4.3.3**. From figure 4.3.3 (A-C), it can be seen that **STO NCMS** are formed by self-assembly of nanocubes. High magnification image at the edges [**Figure 4.3.3 C**] depicts the nanocube structures. The high-resolution TEM (HRTEM) image (**Fig. 4.3.3 D**) of a single SrTiO_3 nanocubes depicts a well-resolved lattice pattern, indicative of its crystalline nature that facilitates photoinjected charge migration. The spacing of the lattice fringes is 0.39 nm as shown in the HRTEM image (**Figure 4.3.3 D**), which is associated with the (100) lattice plane of the Cubic SrTiO_3 . It has been demonstrated theoretically and experimentally that for perovskite, the (100) planes have the lowest surface energy, and thus the cube bound by the (100) facets should be thermodynamically stable morphology of a particle.²⁶ The SAED pattern depicts a crystalline nature of the as synthesized **STO NCMS** describing the cubic crystalline structure consistent with the PXRD analysis.

4.3.3 BET SURFACE AREA ANALYSIS

Porosity and surface area are two essentials for a photoanodic material in DSSCs. Porous structure promotes electrolyte diffusion while the later relates to the dye adsorption.²⁷ Brunauer-Emmett-Teller (BET) measurements have been carried out for **STO NCMS** to evaluate the pore size distribution as well as surface area.

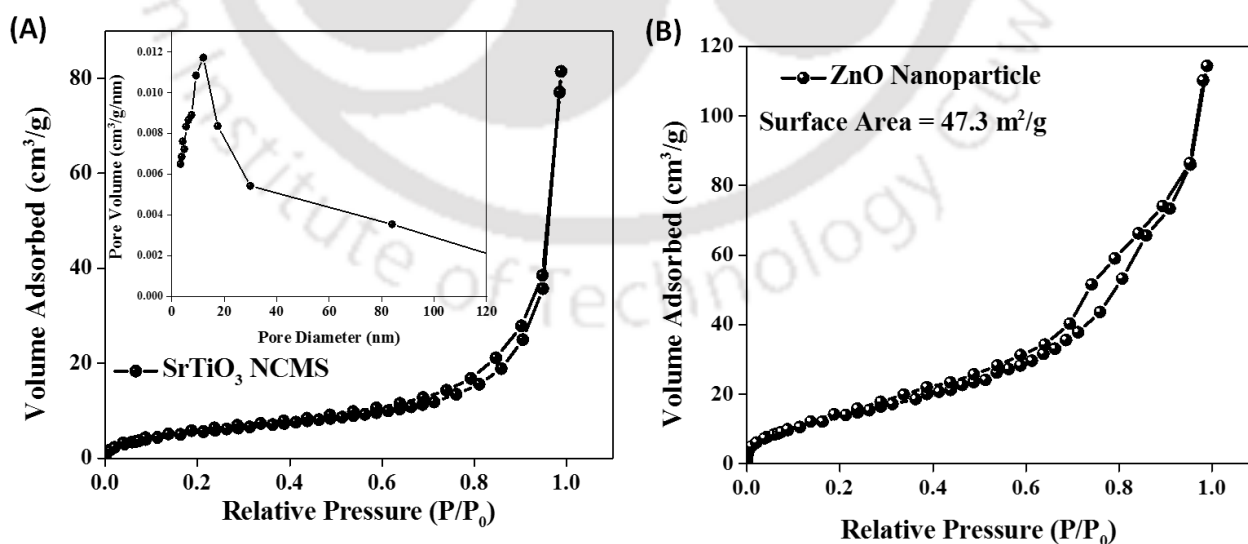


Figure 4.3.4 Nitrogen (N_2) adsorption-desorption isotherms for (A) SrTiO_3 NCMS (B) ZnO nanoparticle. Inset to figure 4 (A) shows BJH pore size distribution plot for SrTiO_3 NCMS

N_2 - physisorption isotherm shown in Figure 4.3.4, displays the typical type IV isotherm and H3 hysteresis loops according to the Brunauer–Deming–Deming–Teller (BDDT) classification, confirming the characteristic mesoporous nature of $SrTiO_3$ NCMS, an essential parameter for photovoltaic performance.²⁸ The surface area of the **STO NCMS** was found to be $\sim 21.3 \text{ m}^2\text{g}^{-1}$. A uniformly distributed pores in the range of $\sim 16 \text{ nm}$ has been depicted in Barrett–Joyner–Halenda (BJH) pore size distribution curve (Inset to figure 4.3.4). Due to the mesoporous nature, $SrTiO_3$ NCMS facilitates diffusion of electrolyte through the pores to regenerate the oxidized sensitizer for a better functioning of the devices. The surface area of ZnO NP was found to be $\sim 47.3 \text{ m}^2\text{g}^{-1}$.

4.3.4 UV-VISIBLE DIFFUSED REFLECTANCE ANALYSIS:

Light scattering phenomenon boosts light absorption of a photoanode via multiple reflection as well as scattering and induces an increased path length of the incident light, thereby increasing the photon absorption probability by the sensitizer molecule.

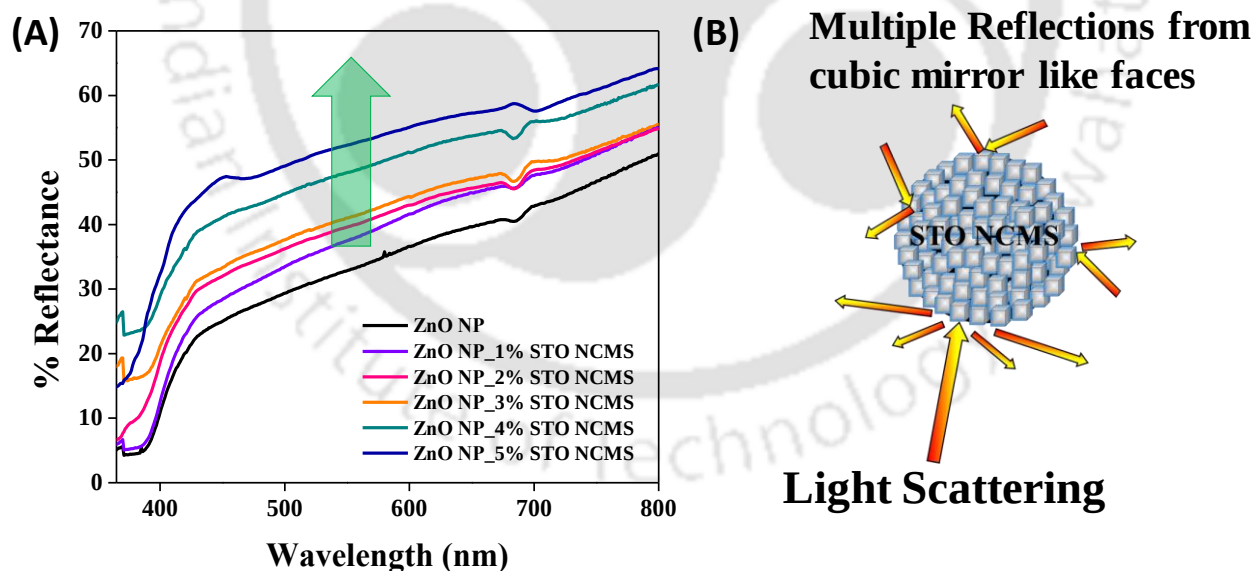


Figure 4.3.5 (A) Ultraviolet-visible diffused reflectance spectra of photoanodes ZnO nanoparticles (black line), ZnO NP_ 1% **STO NCMS** (**ZSTO₁**, violet line), ZnO NP_ 2% **STO NCMS** (**ZSTO₂**, pink line), ZnO NP_ 3% **STO NCMS** (**ZSTO₃**, orange line), ZnO NP_ 4 % **STO NCMS** (**ZSTO₄**, dark cyan line) and ZnO NP_ 5 % **STO NCMS** (**ZSTO₅**, blue line) films on glass substrates **(B)** Schematic showing light reflections and scattering phenomenon by individual **STO NCMS**

UV-Vis diffuse reflectance spectroscopic (DRS) analysis of various photoanodic films of comparable thickness was carried out to investigate the light scattering ability of micron sized SrTiO_3 NCMS. Figure 4.3.5 depicts the diffused reflectance measurements carried out for photoanode films based on pristine ZnO NP film, ZSTO_1 , ZSTO_2 , ZSTO_3 , ZSTO_4 and ZSTO_5 on FTO. UV-Vis diffused reflectance spectra show that the hybrid photoanodic films shows a higher diffused reflectance that increases progressively with the increase in STO NCMS loading owing to the multiple reflections of the incident light from the mirror like facets of STO NCMS nanocubes as well as multiple scattering offered by micron sized STO NCMS.

4.3.5 STEADY STATE AND TIME RESOLVED PHOTOLUMINESCENCE ANALYSES

To probe the excited state dynamics and recombination processes in the photoactive materials, steady-state and dynamic photo-luminescence (PL) studies were carried out. Fig. 4.3.6 (A) depicts the PL spectra for N719 dye and sensitized photoanodes. It has been observed that N719 shows an emission peak around 740nm as a consequence of emission from the triplet MLCT excited state, which displays a gradual static quenching of PL intensity when anchored to ZnO NP and ZSTO_x ($x=1-5\%$) photoelectrode.

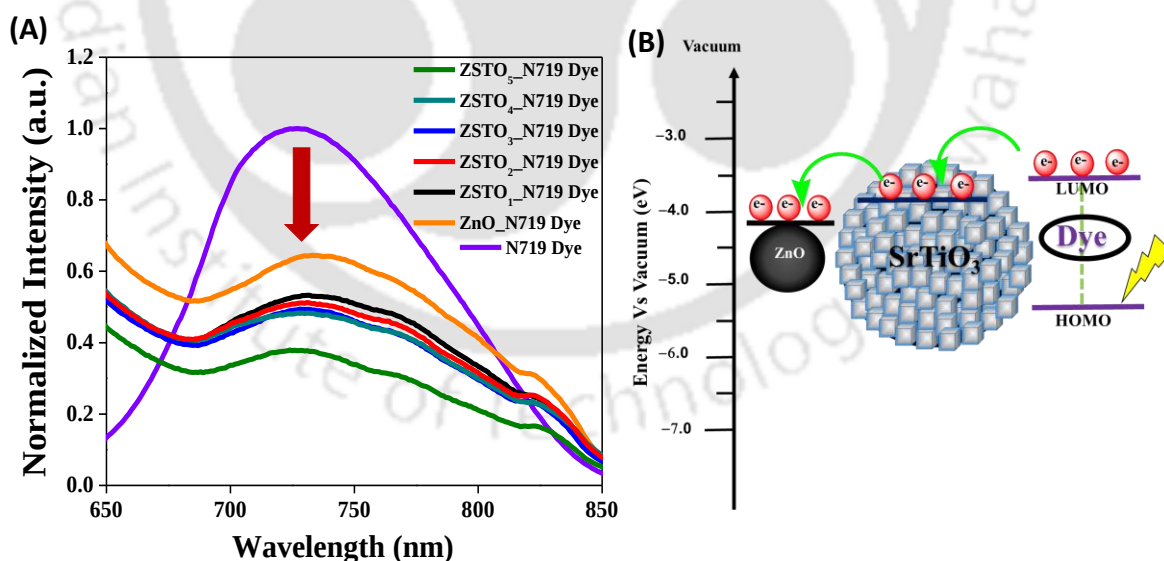


Figure 4.3.6 (A) Steady-state photoluminescence spectra of dye; N719 (violet line), ZnO NPs-N719 (orange line), ZnO NPs_1% SrTiO_3 -N719 (black line), ZnO NPs_2% SrTiO_3 -N719 (red line), ZnO NPs_3% SrTiO_3 -N719 (blue line), ZnO NPs_4% SrTiO_3 -N719 (cyan line) and ZnO NPs_5% SrTiO_3 -N719 (olive line) excited at 520 nm. **(B)** Schematics showing photo generated charge transfer from Dye to semiconductor through proper band alignment

This signifies an inhibited recombination of ($e^- - h^+$) pairs, possibly due to better charge separation and transfer with a well matched band alignment between the conduction band (CB) edges of semiconductors and lowest unoccupied molecular orbital (LUMO) of dye [as shown in Fig 4.3.6 (B)].⁶ A slight shift of 10-15 nm is also seen in the PL emission profile for the sensitized photoanodes which ascribed to a strong electronic interaction between dye and semiconductor electrodes viz. ZnO NP and **ZSTO_x**.

In order to get further idea in synergistic effects between dye and ZnO NP and ZnO NP_x% **STO NCMS** ($x=1-5\%$) hybrid composites and the electron injection dynamics from the dye to semiconductor we have carried out TRPL analysis for sensitized photoanode and dye, measured at emission peak with 475 nm wavelength diode laser excitation source as shown in Fig. 4.3.7. The average exciton lifetime, $\langle \tau \rangle$ values have been evaluated by fitting the time-decay patterns with a bi-exponential function (summarized in Table 4.3.1) by the equation (1).²⁹

$$\langle \tau \rangle = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2} \quad (1)$$

The kinetic curves shown in Figure 4.3.7 indicate much faster decay patterns for Dye when adsorbed onto ZnO NP and ZnO NP_X% **STO NCMS** ($X=$, indicative of efficient charge injection -%) from LUMO of dye to CB of ZnO and ZnO NP_X% **STO NCMS**.

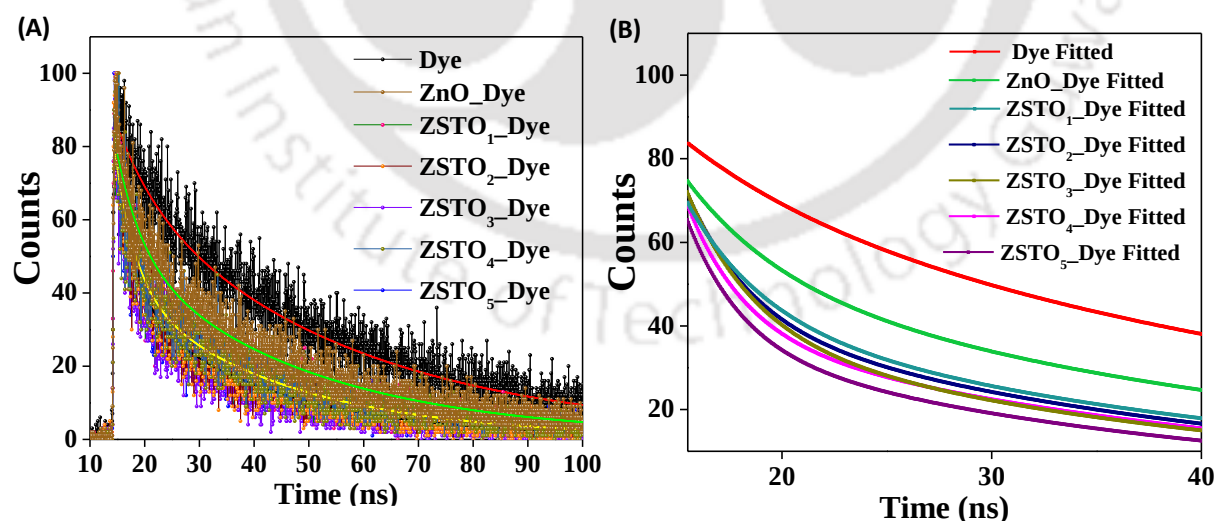


Figure 4.3.7 (A) Time-resolved photoluminescence spectra of dye film on FTO (black symbol), dye-ZnO NP film on FTO (dark yellow symbol), dye-(ZnO NP₃% **STO NCMS**, Olive symbol), dye-(ZnO NP₃% **STO NCMS**, Brown Symbol), dye-(ZnO NP₃% **STO NCMS**, Violet symbol), dye-(ZnO NP₄% **STO NCMS**, Cyan symbol), dye-(ZnO NP₅% **STO NCMS**, Blue symbol) film on FTO with their fitting curves excited at 475 nm **(B)** All the fitted curves of respective dye sensitized photoanodes

It can be seen from Table 4.3.1 that there is a significant decrease in the corresponding lifetime values for dye decrease from ~ 7.00 ns (τ_1) and ~ 41.086 ns (τ_2) to ~ 4.723 and ~ 33.742 ns for ZnO _ Dye and to ~ 2.988 and ~ 26.136 ns for **ZSTO₃_Dye**. Consequently, calculated average exciton lifetime values, $\langle \tau \rangle$ for dye; N719 has been found to decrease from ~ 40.81 ns to ~ 33.381 ns (ZnO_Dye) and 25.764 ns (**ZSTO₃_Dye**), advocate improved interfacial charge transfer in the composite photoanodic film through proper band alignments as shown in Figure 4.3.6 (B). Considering electron transfer as the sole pathway for the deactivation of photoexcited dye, the rate constants for the electron injection (k_{inj}) from dye to ZnO and ZnONP_3% **STO NCMS** composite is calculated from equation (2) and listed in Table 1: ²⁹

$$k_{\text{inj}} = \frac{1}{\langle \tau \rangle_{\text{composite}}} - \frac{1}{\langle \tau \rangle_{\text{dye}}} \quad (2)$$

The higher value of k_{inj} for **ZSTO₃_Dye** composite ($\sim 1.40 \times 10^8 \text{ s}^{-1}$) as compared to ZnO_Dye ($\sim 0.05 \times 10^8 \text{ s}^{-1}$) corroborating a faster charge transfer dynamics in **STO NCMS** loaded hybrid photoanode that resulted in a decreased recombination processes favoring the improved performance of hybrid composite based DSSCs.

Table 4. 3. 1: Fitting parameter (χ^2), exciton lifetimes (τ_1 , τ_2), pre-exponential factors (α_1 , α_2), average exciton lifetimes ($\langle \tau \rangle$) and injection rate (k_{inj}) for as fabricated photoanodes

Samples	χ^2	τ_1 (ns)	τ_2 (ns)	α_1 (%)	α_2 (%)	$\langle \tau \rangle$ (ns)
Dye	1.11	7.00	41.086	4.431	95.569	40.81
ZnO NP - Dye	0.99	4.723	33.742	8.146	91.854	33.38
ZnO NP_1%STONCMS-Dye	0.99	3.724	28.746	11.905	88.095	28.31
ZnO NP_2%STONCMS-Dye	0.99	2.729	26.596	12.883	87.117	26.24
ZnO NP_3%STONCMS-Dye	0.99	2.988	26.136	12.474	87.526	25.76
ZnO NP_4%STONCMS-Dye	1.01	3.211	25.835	15.277	84.723	25.34
ZnO NP_5%STONCMS-Dye	1.01	2.605	23.237	14.403	85.597	22.85

4.3.7 PHOTOVOLTAIC CHARACTERISTICS OF THE SOLAR CELLS

To examine the effect of **STO NCMS** in light harvesting and charge transfer, photovoltaic characteristics of the fabricated ZnO NP, **ZSTO₁**, **ZSTO₂**, **ZSTO₃**, **ZSTO₄** and

ZSTO₅ film based DSSCs were evaluated against Pt counter electrode employing I^-/I_3^- redox electrolyte under AM 1.5 with illumination intensity of 100 mW cm^{-2} , as illustrated in **figure 4.3.8. (A)**.

Photovoltaic device based on ZnO NP exhibited a PCE of $\sim 1.97\%$ with a short-circuit current density (J_{sc}) of $\sim 8.67 \text{ mA/cm}^2$, an open circuit voltage (V_{oc}) of $\sim 548 \text{ mV}$ and a fill factor (FF) of $\sim 41.4\%$. **STO NCMS** incorporated device, **ZSTO₁**, afforded a PCE of $\sim 3.10\%$ with $J_{sc} \sim 10.61 \text{ mA/cm}^2$, a $V_{oc} \sim 576 \text{ mV}$, a FF $\sim 50.7\%$ indicating that 1% **STO** loading greatly enhance the photovoltaic performance. On further increase in **STO NCMS** concentration devices up to **ZSTO₃** i.e. ZnO NP_ 3% **STO NCMS** displayed a gradual increase in the photovoltaic performances followed by a decrease in **ZSTO₄** and **ZSTO₅** photoanode based devices. **ZSTO₂** afforded a PCE of $\sim 3.29\%$ with $J_{sc} \sim 10.91 \text{ mA/cm}^2$, a $V_{oc} \sim 609 \text{ mV}$, a FF $\sim 51.5\%$ whereas device with 3% **STO**, **ZSTO₃** showed best performance yielding a $J_{sc} \sim 11.65 \text{ mA/cm}^2$, a $V_{oc} \sim 622 \text{ mV}$, a FF $\sim 54.7\%$ and a PCE $\sim 3.97\%$. All the photovoltaic parameters are depicted in **Table 4.3.2**.

In general, superior photovoltaic performance of a device depends upon better light harvesting capability as well as charge transport properties through interfaces of the photoanodes. The increase in efficiency in case of composite photoanode can be mainly attributed to increase in the photocurrent density, open circuit potential as well as fill factor. From **Table 4.3.2** it is seen that J_{sc} increases on loading of **STO NCMS** progressively up to **ZSTO₃** and then decreased in **ZSTO₄** and **ZSTO₅** photoanode based devices. The superior photo current density in case of composite photoanodes is accredited to better light harvesting capability by photoanodes incorporated with large sized **STO NCMS** corroborated by the UV-Vis diffused reflectance spectra [as can be seen in **Fig. 4.3.5**]. **STO NCMS** due to its larger size increases the light harvesting efficiency of the hybrid photoanode by trapping the incident light within the photoanode thereby increasing the path length of incident light by scattering. In case of **ZSTO₄** device, we have encountered a decrease in J_{sc} value which further decreases upon increase in **STO NCMS** concentration to 5%.

To investigate the present scenario we carried out dye desorption analysis. As the capacity of dye intake exerts a profound impact on the photocurrent density for DSSCs, the amount of adsorbed N719 dyes is estimated by measuring eluted dye molecules from sensitized photoanodes

ZSTO_x/ZnO heterostructures using a 0.1 mM NaOH in ethanol/water (1:1, v/v). The concentration of the dye desorbed per cm² area was then evaluated using Beer's law.³⁰

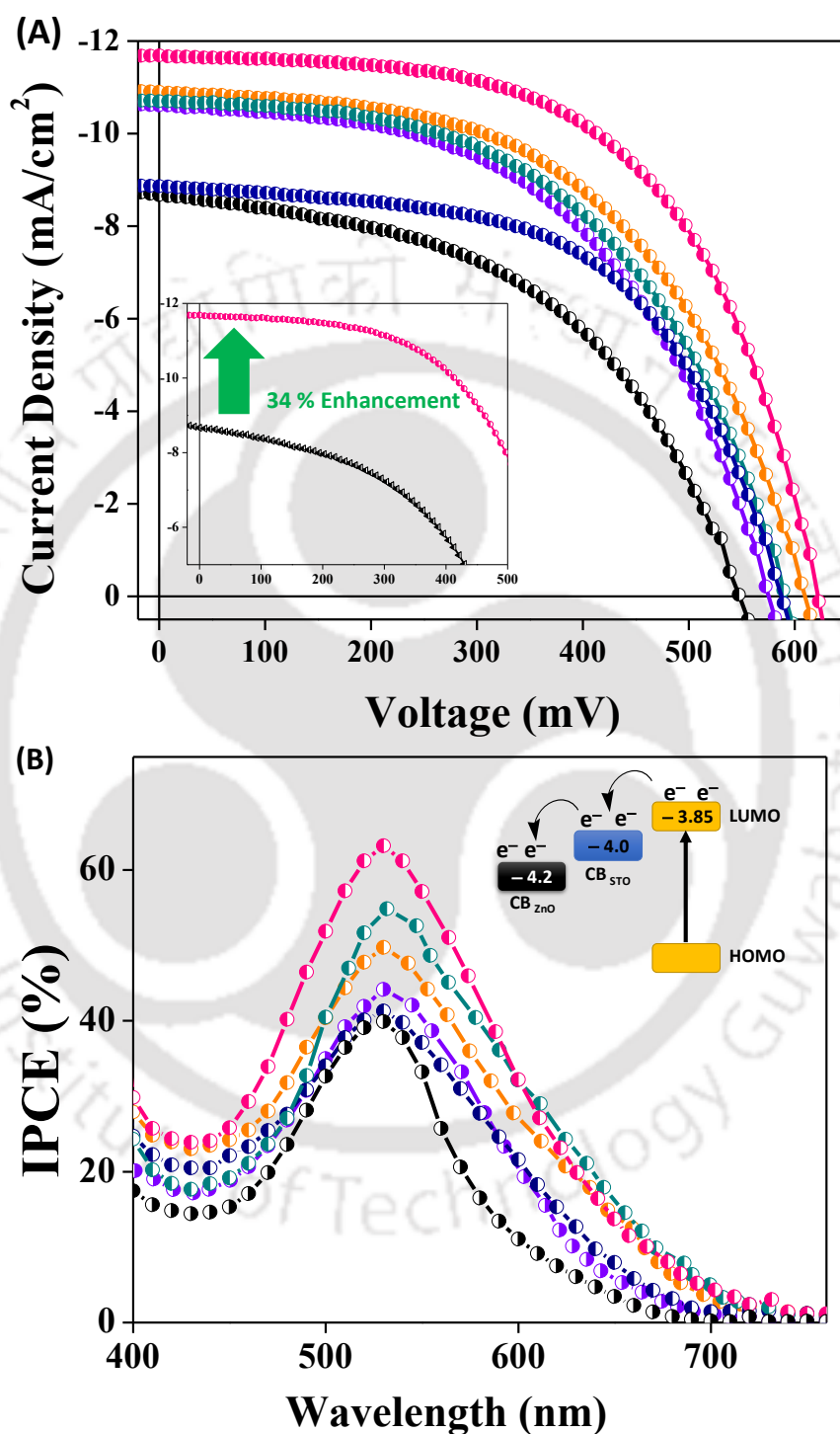


Figure 4.3.8 (A) Short circuit current density–voltage (J–V) (B) IPCE plots for devices with ZnO NP film (black line), ZnO NP_1% STO NCMS (ZSTO₁, violet line), ZnO NP_2% STO NCMS (ZSTO₂, orange line), ZnO NP_3% STO NCMS (ZSTO₃, pink line), ZnO NP_4% STO NCMS (ZSTO₄, dark cyan line) and ZnO NP_5%STO NCMS (ZSTO₅, blue line) photoanodes

The optimum quantity of dye loading per photoanodes was observed with values for ZnO NP $\sim 3.94 \times 10^{-7}$ mol.cm⁻², for **ZSTO₁** $\sim 3.67 \times 10^{-7}$ mol. cm⁻², for **ZSTO₂** $\sim 3.44 \times 10^{-7}$ mol.cm⁻², **ZSTO₃** $\sim 3.17 \times 10^{-7}$ mol.cm⁻², **ZSTO₄** $\sim 2.97 \times 10^{-7}$ mol.cm⁻² and for **ZSTO₅** $\sim 2.81 \times 10^{-7}$ mol.cm⁻². The decrease in adsorption of the dye in case of composite photoanodes can be attributed to incorporation of **STO NCMS** which furnishes lower effective specific surface area for dye adsorption. Hence it can be concluded that the light harvesting in case of composite photoanode is solely due to the higher light scattering properties of **STO NCMS** which increases the optical path of incident light through multiple scattering from individual entity as well as the ensemble resulting in an increase in photon absorption by sensitizer molecule. Higher number of photons absorbed in turn gives higher number of photo-generated electrons resulting in an increased short-circuit current density, J_{sc} in the devices. In addition, the closely packed nanocube building blocks form a good transport pathway for the injected electrons resulting in a higher J_{sc} . In case of devices with lower loading of **STO NCMS** the lower dye adsorption is compensated/ counter balanced by the trapping of light by enhanced scattering from ensemble. Moreover, amount of back scattered light at the FTO junction may increase with the increase in **STO NCMS** content which may hinder the light penetration probability in the composite photoanode resulting in a loss of incident light. So the lower photovoltaic performance in case of **ZSTO₄** and **ZSTO₅** photoanode based DSSC can be accredited to a decrease in the absorbing unit i.e. dye from optimal concentration as well as radiation loss at the FTO interface.³¹⁻³² Moreover from Table 4.3.2 it can be seen that in case of composite **ZSTO_x** (x= 1–5%) photoanodes, we observed an increase in open circuit potential or V_{oc} . Open circuit voltage or V_{oc} of a dye sensitized solar cell can be defined as the potential difference between the Fermi level of the metal oxide semiconductor and the redox potential of the electrolyte. Increase in the V_{oc} for composite photoanodes can be accredited to the higher conduction band edge of **STO NCMS**, which is ~ 200 meV more negative compared to ZnO as well as reduced back recombination of photoinjected electrons from the CB of ZnO. On the other hand, it can be seen that all the hybrid photoanode based devices have shown a higher fill factor than the pristine ZnO NP based device. Fill factor of a device indicates a well-behaved diode characteristic, where in the voltage and current displays a proportional relationship obtaining the maximum power output from the device. Increase in FF can be attributed to a lower recombination of photo-generated electrons leading to a better charge separation, facilitated by the enhanced

diffusion of electrolyte through pores of mesoporous **STO NCMS** to regenerate the oxidized species in the respective layers by the redox couple.³³

IPCE measurements were carried out to study the conversion of photon to electron under the monochromatic light. In principle, the IPCE of a solar cell is dependent on the light harvesting efficiency of a photoanode, the quantum yield of charge injection from the excited state of dye to the semiconductor and charge collection efficiency.³⁴ Figure 4.3.8 (B) portrays the sensitization achieved by the dye throughout the visible region with maximum IPCE values of ~ 39%, ~ 43%, ~ 53%, ~ 62%, ~ 49% and ~ 41% at 525 nm for the ZnO NP, **ZSTO₁**, **ZSTO₂**, **ZSTO₃**, **ZSTO₄** and **ZSTO₅** based photovoltaic cells, respectively. The higher IPCE values observed in red region of the IPCE spectra for devices loaded with **STO NCMS** signify an efficient light confinement within the ensemble of hybrid photoanodes owing to the enhanced light scattering ability of larger sized **STO NCMS** as well as multiple reflections from the mirror like facets of **STO NCMS**.³⁵ Increase in the overall IPCE values on going from pristine ZnO NP based device to **ZSTO₃** devices is due to the higher flux of photo-generated electrons because of the optimal dye loading and light scattering effect on incorporation of 3% **STO NCMS**.

Table 4.3.2. Short-Circuit Photocurrent Density (J_{sc})^a, Open-Circuit Voltage (V_{oc})^a, Fill Factor (FF)^a, Power Conversion Efficiency (PCE, η), Maximum Incident Photon-to-Current Conversion Efficiency (IPCE_{max}), for the fabricated DSSCs Employing I⁻/I₃⁻ Redox couple

DSSC photoanode	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	PCE (η , %)	IPCE _{max} (%)
ZnO NP Bare	8.64	548	41.4	1.97	39
ZnONP_1wt% STO	10.61	576	50.7	3.10	43
ZnONP_2wt% STO	10.91	609	51.5	3.29	53
ZnONP_3wt% STO	11.65	622	54.7	3.97	62
ZnONP_4wt% STO	10.67	605	49.6	3.20	49
ZnONP_5wt% STO	8.87	600	50.5	2.68	41

^a Data reported here are the results of the best performed devices out of five devices for each configuration

Furthermore, heterostructures formed between SrTiO₃ and ZnO with a uniquely matched conduction band edge with proper band gap energy structure helps in separation of photogenerated charge carriers in an efficient way. In this regard, a suitable band alignment of SrTiO₃ with ZnO creates thermodynamic driving force and improves electron transfer ability from the LUMO of dye to CB of SrTiO₃ to that of ZnO (inset to IPCE figure) which increases charge injection

efficiency from excited state of dye. On the other hand, photogenerated holes get impregnated from the valence band of ZnO to that of SrTiO₃ as shown in scheme 4.3.1 in the following section. This reduces the probability of recombination thereby increasing photogenerated charge collection efficiency of the devices. While moving from 3% to 4% we observed a lower photon to electron conversion efficiency which is due to low dye loading capacity of the photoanode as corroborating the lower J_{sc} value, where light scattering ability is overridden by dye intake by corresponding photoanodes.

4.3.8 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPIC (EIS) ANALYSIS

Electron transport dynamics and recombination kinetics are the key factors that governs the overall efficiency of dye-sensitized solar cell. To better understand the kinetics and energetics of charge transport and interfacial recombination properties, EIS measurements were carried out at an external bias equivalent to V_{oc} in a frequency range of 0.1 Hz to 100 KHz under the dark conditions as shown in figure 4.3.9 (A) and (B). EIS elucidates the characteristic interfacial charge transfer and recombination processes happening within the devices at different frequency regions, viz. high-frequency region corresponds to processes occurring at the counter electrode and electrolyte interface (10^0 – 10^2 KHz), mid-frequency region corresponds to processes occurring at the semiconductor/sensitizer/electrolyte interface (10^{-1} – 10^0 KHz), and low-frequency region corresponds to that of the diffusion of electrolyte (10^{-1} – 10^{-2} KHz). Inset to figure 4.3.9 (A) represents the equivalent circuit diagram according to transmission line model and fitted values are represented in Table 4.3.3. Under dark conditions, the DSSC behaves as a leaky capacitor and on forward bias condition, electrons are transported through the mesoscopic semiconductor and react with oxidized species of electrolyte i.e. I_3^- . Simultaneously, I^- is oxidized to I_3^- at the counter electrode. The dark reaction impedance due to back electron transfer from the CB of the semiconductor film to oxidized species of electrolyte is represented by the semicircle at the intermediate frequency regime in the Nyquist plots. This semicircle in equivalent circuit model correspond to R_{ct2} , commonly known as recombination resistance (R_{rec}). The bigger the middle frequency semicircle in the Nyquist plots is, the lesser the electron recombination at the semiconductor/sensitizer/electrolyte interface.³⁶ From the Nyquist plot it can be seen that the diameter of the semicircle at the mid frequency region increases with loading of **STO NCMS**.

Also from Table 4.3.3, it can be seen that the value of R_{rec} increases gradually with loading of **STO NCMS**. The increased value of R_{rec} signifies a higher recombination resistance at the ZnO-STO/sensitizer/electrolyte interface than the pristine ZnO device.

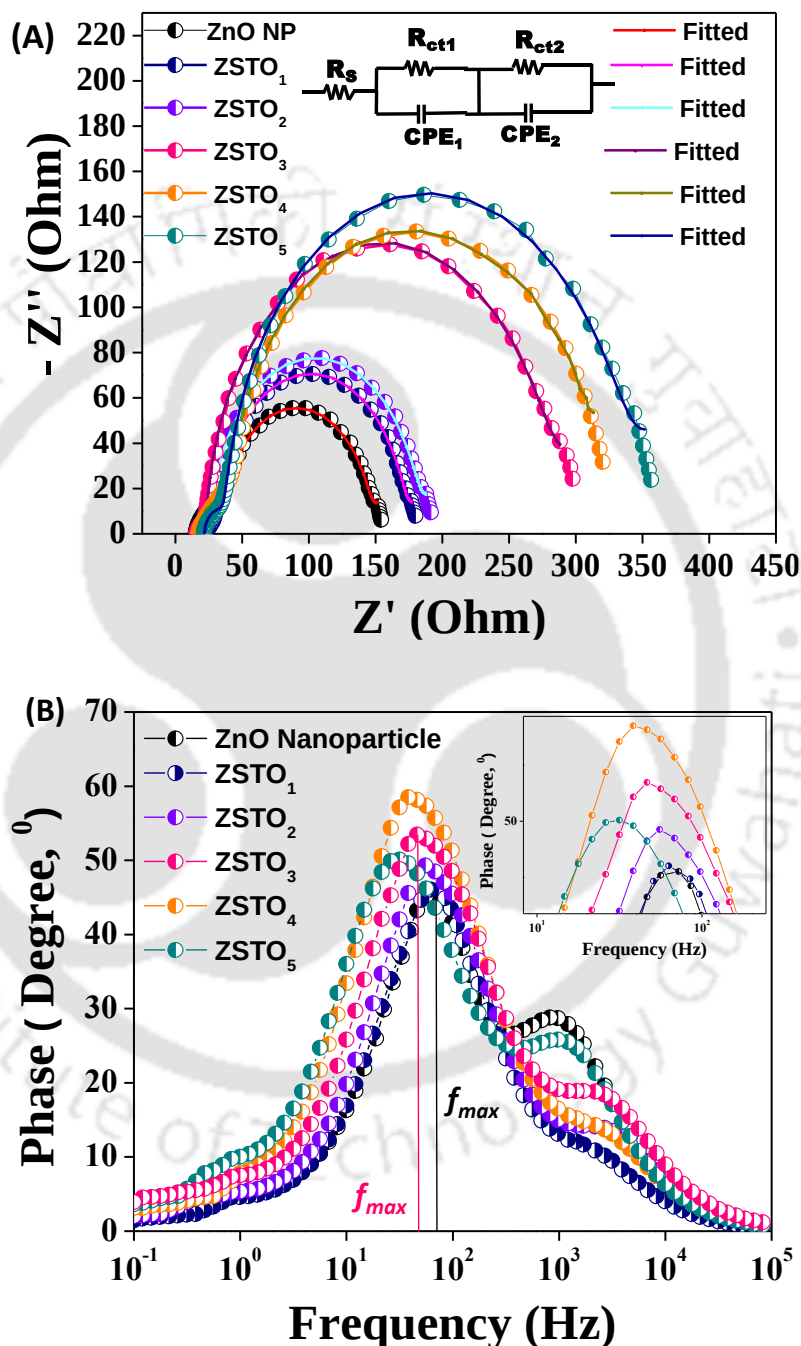
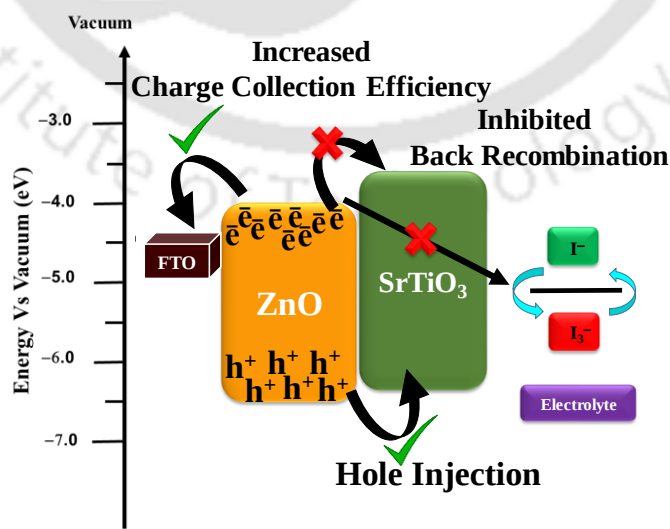


Figure 4.3.9. (A) Nyquist plots and (B) Bode plots for the devices composed of ZnO NP film (black line), ZnO NP film (black line), ZnO NP_ 1% **STO NCMS** (ZSTO₁, navy line), ZnO NP_ 2% **STO NCMS** (ZSTO₂, violet line), ZnO NP_ 3% **STO NCMS** (ZSTO₃, pink line), ZnO NP_ 4 % **STO NCMS** (ZSTO₄, orange line) and ZnO NP_ 5 %**STO NCMS** (ZSTO₅, dark cyan line) based photoanodes. Inset to (A) shows equivalent circuit diagram and Inset to (B) shows enlarged spectra

The higher recombination resistance indicates that the recombination of electrons at the ZnO-STO/sensitizer/electrolyte interface is impeded indicative that the loss of the photo injected electrons at the hetero-interface is decreased resulted in an increased V_{oc} for the **STO NCMS** based devices. Although devices with higher loading of **STO NCMS** showed a higher R_{rec} but due to the lesser flux of photogenerated electrons the device performance is inferior. Further it is believed that a low values of R_{ct1} signifies a favorable charge-transfer process for the reduction of oxidized species of electrolyte i.e. I_3^- at the Pt counter electrode/electrolyte interface thereby increasing the fill factor. It can be seen that **ZSTO₃** device has the lowest value for R_{ct1} as compared to the other devices which corroborate the improved performance of **ZSTO₃** device. On the other hand, it has been observed in the corresponding Bode plot that the characteristic recombination peak of the DSSC based on the hybrid ZnO-STO NCMS photoanodes shifts to a lower frequency (from 71.7 to 31.3 Hz). The photo-induced electron life time τ_e in CBs of different photoanode can be estimated using the relation $\tau_e = (2\pi f_{max})^{-1}$, where f_{max} is the maximum peak frequency in the intermediate frequency region³⁷ and listed in **Table 4.3.3**. The gradual increase in the τ_e in case of hybrid photoanode based devices validates the interference created on addition of **STO NCMS** in the photoanode that acts as a partial barrier for photogenerated electrons to undergo recombination with the oxidized species available at semiconductor/sensitizer/electrolyte interface. A well matched band alignment between ZnO and **STO NCMS** allows migration of holes to **STO** which also decreases the electron hole recombination thus increasing the τ_e as shown in scheme 4.3.1.



Scheme 4.3.1 Schematic representation of various charge transfer processes occurring in the device

Table 4.3.3. Series resistance (R_s), Charge recombination resistance (R_{ct}), Maximum peak frequency (f_{max}), Electron life time (τ_e) values for the fabricated devices composed of ZnO NP film, **ZSTO₁**, **ZSTO₂**, **ZSTO₃**, **ZSTO₄** and **ZSTO₅** based photoanodes as obtained from Nyquist^a and Bode plot^b

DSSC photoanode	R_s^a (Ohm)	R_{rec}^a (Ohm)	f_{max}^b (Hz)	τ_e^b (ms)
ZnO NP Bare	17.74	107.8	70.8	2.2
ZnONP_1wt% STO	18.66	137.8	63.8	2.4
ZnONP_2wt% STO	18.01	151.2	56.3	2.8
ZnONP_3wt% STO	15.46	242.8	46.9	3.3
ZnONP_4wt% STO	18.05	246.6	38.6	4.1
ZnONP_5wt% STO	18.65	286.2	31.3	5.0

Moreover, **STO NCMS** due to its mesoporous nature facilitates the electrolyte diffusion for efficient regeneration of oxidized sensitizer molecule thus preventing recombination of photo-generated electron with oxidized sensitizer therefore increasing the FF of the hybrid photoanode based devices. Moreover, dark-current measurement of DSSCs has been considered as a qualitative technique to describe the extent of the back electron transfer. Dark current arises mainly from recombination of injected electrons with tri-iodide ions (I_3^-) on a semiconductor.³⁸

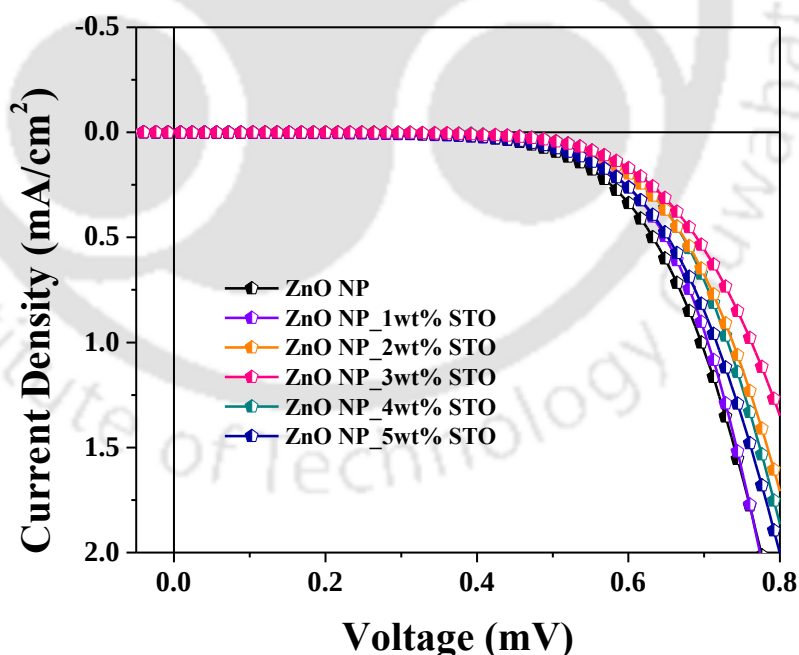


Figure 4.3.10. Current density–voltage (J–V) plots for the fabricated photovoltaic cells composed of ZnO NP film (black line), ZnO NP film (black line), ZnO NP_ 1% **STO NCMS** (**ZSTO₁**, violet line), ZnO NP_ 2% **STO NCMS** (**ZSTO₂**, orange line), ZnO NP_ 3% **STO NCMS** (**ZSTO₃**, pink line), ZnO NP_ 4 % **STO NCMS** (**ZSTO₄**, dark cyan line) and ZnO NP_ 5 %**STO NCMS** (**ZSTO₅**, blue line) photoanodes under dark condition

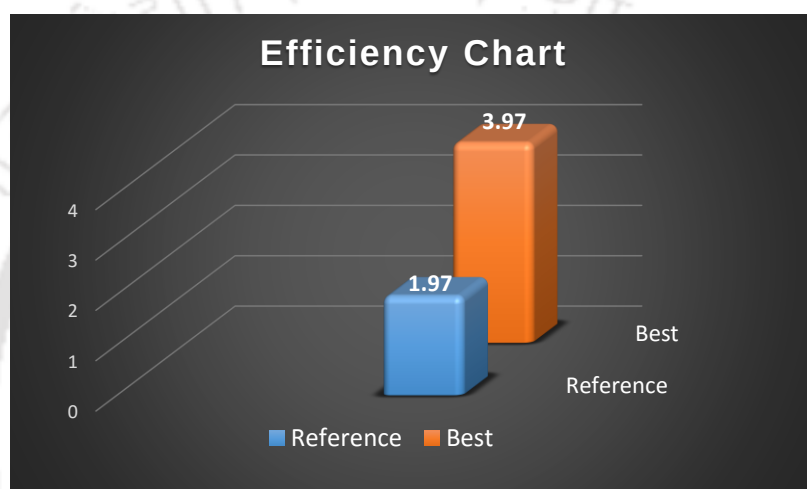
The dark current characteristics for the fabricated devices have been shown in Figure 4.3.10. Dark current charge recombination occurring at the semiconductor/ I_3^- redox and substrate/electrolyte hetero- interfaces plays a significant role in lowering the V_{oc} and thus overall performance of DSSCs. The reduction of the dark current indicates that loading of **STO NCMS** successfully hinders the back transfer of electron thus resulted in an increase of V_{oc} .

4.4 CONCLUSIONS

In summary, a simplistic and convenient approach for better light harvesting and reduced back recombination of photo-generated electrons in ZnO nanoparticle based DSSC was established by introducing an easily synthesizable and cost effective **STO NCMS**. Effective scattering as well as multiple reflections of incident light by **STO NCMS** in the ensemble upsurge the probability of harvesting light, eventually absorbed by the dye molecule, thus boosting the device efficacy. An effective photoinduced charge separation with a uniquely aligned band structure between ZnO and **STO NCMS** resulted in an increased charge collection efficiency of the devices. Moreover, **STO NCMS** owing to its higher conduction band edge position, acts as a partial energy barrier for reverse tunneling of photo-injected electrons at semiconductor/dye/electrolyte hetero-interface. In essence, **STO NCMS** plays a pivotal role in enhancing the device performance by increasing light harnessing capability as well as preventing the detrimental back electron transfer processes occurring in DSSC. A few highlighted points of the current work are as follows,

- ✚ A ~ **2-fold** increase in the power conversion efficiency (PCE, η) is displayed by ZnO NP_STO NCMS [for an optimized 3% **STO NCMS**] composite photoanode device compared to pristine ZnO NP device
- ✚ STO NCMS provides better light scattering probability owing to its size in micron range as well as multiple reflections from edges and facets of nanocubes.
- ✚ An effective photoinduced charge separation with a uniquely aligned band structure between ZnO, **STO NCMS** resulted in an increased charge injection kinetics ($k_{inj} \sim 1.40 \times 10^8 \text{ s}^{-1}$ for **ZSTO**₃, $0.05 \times 10^8 \text{ s}^{-1}$ for reference device) of the devices.

- ✚ Increased Recombination resistance value, R_{rec} ($R_{\text{rec}} \sim 151.2$ ohm for **ZSTO₃** as compared to reference device $R_{\text{rec}} \sim 107.8$ ohm) corroborate the energy barrier property of **STO NCMS** in hybrid device.
- ✚ A higher lifetime of photo-injected electron has been found for STO NCMS based devices.



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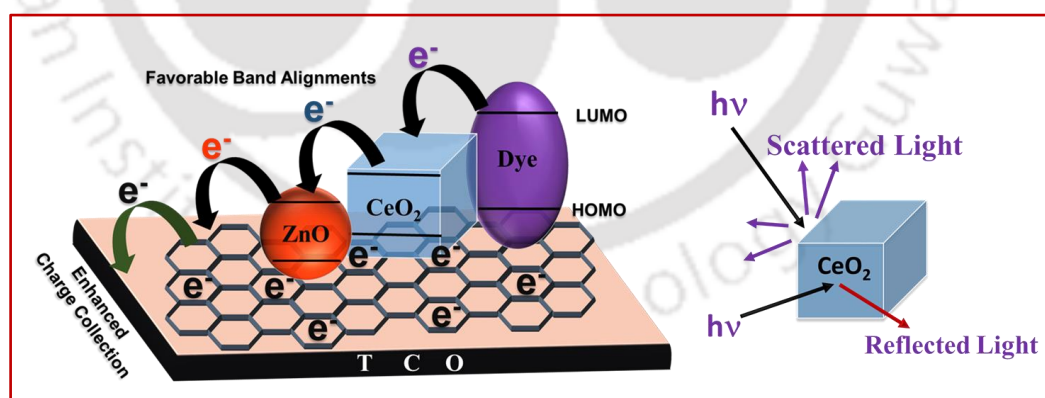
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CHAPTER 5

High quality mirror-like nano cuboidal CeO_2 coupled with reduced Graphene Oxide for superior light harnessing and charge transfer dynamics

This chapter presents a novel approach utilization of a ternary hybrid photoanode using nano cuboidal Ceria and reduced Graphene Oxide in conjunction with ZnO nanoparticle for an enhanced photovoltaic performance. Nano cuboidal CeO_2 provides better light scattering and reflection owing to its size and well defined edges and mirror-like facets. RGO on the other hand, acts as an electron sink and provides faster electron pathways thus screening the reverse electron recombination at Working Electrode/Dye/electrolyte interface.

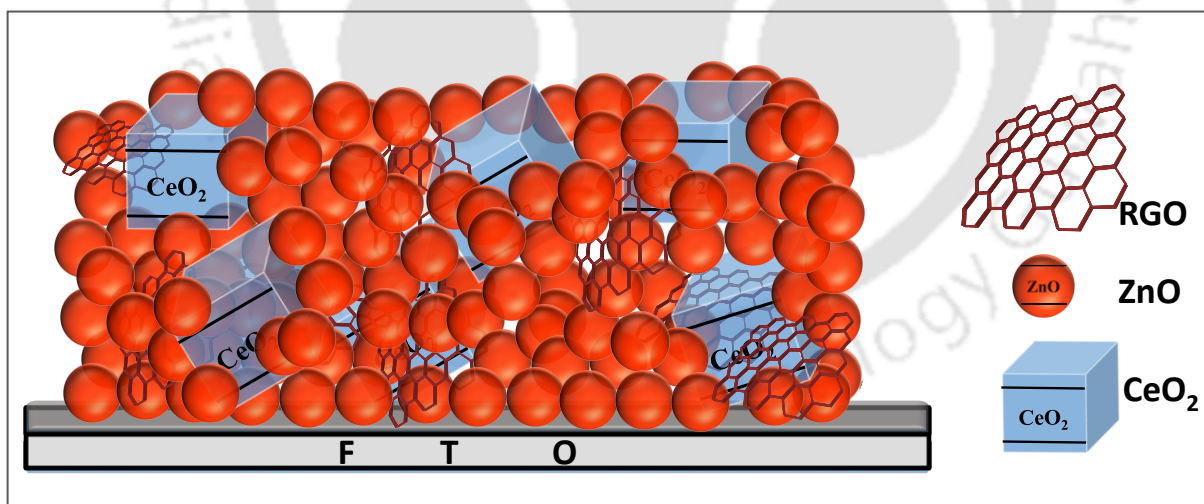


5.1 INTRODUCTION

Performance of semiconductor scaffold based photovoltaics is primarily determined by (i) light harvesting efficiency (LHE), i.e. number of photons incident followed by absorption, resulting in exciton generation, and (ii) charge injection and the efficiency of collecting the injected electrons at the back contact.^{1,2} In our approach, we have chosen ZnO as a model system owing to its ease of synthesis, having favourable band alignments with most of the popular semiconductors apart from its inherent properties such as high mobility of electron ($130\text{--}200\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$), larger diffusion length ($\sim 10^3\text{ nm}$).³ However, inadequate utilization of higher wavelength photons for small sized ($\sim 20\text{--}30\text{ nm}$) ZnO nanoparticle as well as contending and thermodynamically favourable back-transfer reactions occurring at the hetero-interfaces remains the bottle neck to good efficacy value.⁴ It is known that different materials with diverse morphologies, and high index of refraction e.g. Nb_2O_5 , SiO_2 , SnO_2 , SrTiO_3 etc. in binary composite photoanode, as well as intentionally created spherical voids display a prominent enhancement in the PCEs of the DSSCs compared to bare counterpart.⁶⁻¹³ Among various lanthanide oxides; CeO_2 , an n-type semiconductor with band gap $E_g \sim 2.9\text{--}3.2\text{ eV}$, has drawn much attention owing to its high refractive index, strong adhesion, high thermal stability, and economical synthesis routes. Cerium dioxide has found potential use in barrier layers, as an additive for UV absorber in glass for protecting light-sensitive materials and a useful material for high-refractive index film in single and multi-layer optical coatings.¹⁴⁻¹⁵ Nonetheless, formation of large aggregates and loose packing density limits the wide usage in DSSCs and bare CeO_2 furnishes a highest of $\sim 1.8\%$ PCE in DSSCs.¹⁶ Whereas, CeO_2 , used in conjunction with a primary photoanodic material with modifications showed enhancement in the device performance.¹⁷⁻¹⁸ On the other hand photo-generated charge carriers and the nonexistence of energy barrier lead to charge carrier's annihilation. Transmission of photo-generated electrons across the sensitizer scaffold network also get hindered by the charge recombination, thus affecting charge collection at the FTO.¹⁹⁻²⁰ Thus, introducing materials with high charge carrier's mobility can enhance charge separation with minimal recombination processes providing facile transport of photo-generated charges. Incorporation of conducting carbon materials into photoanode has shown promising results in enhancing the device performance.²¹⁻²⁴ Apart from 1-D carbon based structures which suffers poor point of contact with metal oxide semiconductors, 2-D allotropes offer excellent conductivity along with maximized contact. Reduced graphene oxide (RGO), exhibits a high

mobility of charge carriers ($200\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$) in two dimension, and lattice structure stability up to $1500\text{ }^\circ\text{C}$.²³ On the basis of its aforementioned advantages, RGO has been extensively used in field-effect transistor devices,²⁵ and ultrasensitive sensors,²⁶ and photovoltaic cells.²⁷⁻²⁹ The RGO sheets can act as electron sink between semiconductors and facilitates charge separation/transport, thus reducing the back transfer of electron at hetero-interfaces enhancing the device performances.

This chapter demonstrates incorporation of high quality mirror like nano-cuboidal CeO_2 ($\text{CeO}_2\text{ NC}$) and RGO into a ternary hybrid photoanode with ZnO nanoparticle which showed a $\sim 85\%$ enhancement in efficacy in ternary hybrid device (binary hybrid device showed only $\sim 40\%$) than reference device. We have performed a systematic study on the effects of $\text{CeO}_2\text{ NC}$ and optimized the amount of $\text{CeO}_2\text{ NC}$ loading in the photoanode. Additionally, to enhance the charge transfer dynamics, we have incorporated 2D- reduced graphene oxide (RGO) in the optimized device **ZC3** adopting an ultrasonication technique and found that incorporation of 2D- RGO sheets facilitated the charge transport owing to high electron mobility resulted in a reduced recombination of excitons thus enhancing the device performance. A schematic of photoanode architecture is depicted in scheme 5.1.1.



Scheme 5.1.1 Schematic representation of ternary hybrid photoanode and its components

5.2 EXPERIMENTAL METHODS

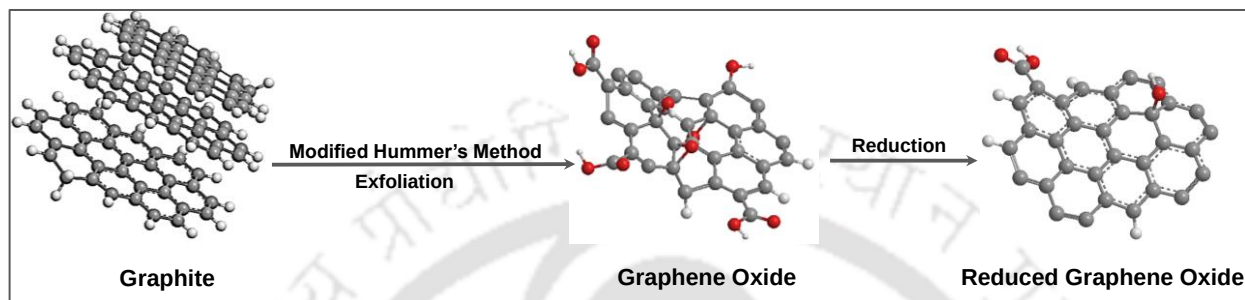
5.2.1 SYNTHETIC PROTOCOL OF NANO-CUBOIDAL CeO₂ (CeO₂ NC)

Nano-cuboidal CeO₂ (CeO₂ NC) were synthesized by hydrothermal process taking Ce (NO₃)₃. 6H₂O in alkaline solution as precursor and heated at 200 °C for 24 h in an electric oven.³⁰ In brief, 0.5g of Ce (NO₃)₃. 6H₂O was dissolved in 20 mL of distilled water containing 10% NaOH under stirring for 30 min. After that the reaction mixture was transferred into a 50 ml Teflon lined autoclave and heated at 200 °C for 24 h. The system was then allowed to cool to room temperature. The precipitate was then treated with 37% H₂O₂. The final product was collected by filtration, washed with deionized water to remove any possible ionic remnants and then dried at 60 °C.

5.2.2 SYNTHETIC PROTOCOL OF 2-D REDUCED GRAPHENE OXIDE (RGO)

Reduced graphene oxide was synthesized by chemical reduction of graphene oxide.³¹ Firstly, Graphene oxide (GO) was prepared by taking, 5 g of graphite powder and 3.74 g of NaNO₃ was added to vessel containing 374 mL of concentrated H₂SO₄ under gentle stirring kept at 0 °C, followed by addition of 22.5 g of KMnO₄ after specific interval of time over a period of 1 h and left for stirring for another 2 h at 0 °C. Then the reaction mixture was subjected to vigorous stirring at 35 °C for 72 hours. Then, 700 mL of 5 wt. % aq. H₂SO₄ solution was added very slowly under stirring and the temperature was raised to 98 °C and allowed to stir for 2 h. After that the reaction temperature was reduced to 60 °C and 9.4 mL of 48 wt. % H₂O₂ was added. The reaction mixture was then allowed to cool to Room temperature. The inorganic impurities in the solution were then purified by centrifugation. Aqueous solution of 0.5 wt. % H₂O₂ / 3 wt. % H₂SO₄ of 2000 mL was added to the obtained precipitate and ultra-sonicated for 1 h. Further, the impurities were removed by centrifugation at 10000 rpm for 20 min. The process was repeated using of a 3 wt. % HCl aqueous solution (approx. 1000 mL). After removing the impurities, GO was extracted in deionized water by Ultrasonic treatment and dried at 60 °C in a vacuum oven to obtain the GO sheets. For the synthesis of RGO, firstly, 0.2 g of GO was loaded in a round-bottom flask (250 mL) and 150 mL of water was then added to it. This dispersion was then subjected to ultra-sonication for 1h. To it 2 mL of (~ 65 mmol) NH₂NH₂. H₂O was added dropwise and refluxed at

100 °C in an oil bath for 24 h. 2-D Reduced graphene oxide gradually precipitated out as a black solid. This product was isolated by filtration over a medium fritted glass funnel, washed repeatedly with water (5×150 mL) and methanol (5×150 mL), and dried in a vacuum oven at 60 °C to obtained 2-D RGO. Complete synthesis procedure is shown in scheme 5.2.1.



Scheme 5.2.1: Schematic representation of synthesis of reduced graphene oxide from graphite

5.2.3 SYNTHESIS OF ZnO NANOPARTICLES (ZnO NPs)

Zinc oxide nanoparticles were synthesized at high degree of supersaturation to achieve a nucleation rate much greater than the growth rate following a reported procedure.³² ZnCl₂ (5.5 g) was dissolved in 200 mL of 1, 2 -ethanediol at 150 °C in an oil bath with subsequent dropwise addition of sodium hydroxide solution (5 M, 16 mL) with a gentle stirring for 30 min at 150 °C. The precipitate was then washed several times with water. Further the particles were dispersed in iso propanol and subjected to ultrasonication to disrupt the microagglomerates. The solid product was calcined in temperature programmed muffle furnace at 5 °C /min at 450 °C for 2h.

5.2.4. PREPARATION OF ZnO NP-CeO₂ NC (ZC_x, X =1-5) AND ZC₃RGO_y (Y= 0.5, 1, 1.5 %) COMPOSITES

The binary hybrid photoanode blends were prepared by taking calculated amount of CeO₂ NC and ZnO nanoparticles and ultrasonically treated for a period of 1h. To prepare 1g of composite mixture (ZC_x, x= 1,2,3,4 and 5), 10mg, 20 mg, 30mg, 40mg, and 50mg of CeO₂ NC and the balanced amount of ZnO NP were dispersed ultrasonically in ethanol. Finally, solvent was evaporated to get the solid samples and named hereafter as ZC_x (where x = 1, 2, 3, 4, 5). To prepare composite with 2-D RGO, viz. ZC₃RGO_{0.5} composite, first, 2.4 mg of RGO was sonicated in 5 ml of EtOH for 3h in a culture tube. On to that 420 mg of ZC₃ composite was added and sonicated

for 2h further to form $\text{ZC}_3\text{RGO}_{0.5}$ mixture. Rest of the ZC_3RGO_y ($y= 0.5, 1, 1.5$) mixtures were prepared following similar method taking desired amount of RGO along with ZC_3 composite.

5.2.5 DEVICE FABRICATION

Photoanodes of various composites as well as pristine material were fabricated by making homogeneous paste of each material, ZC_x viz. ZC_1 , ZC_2 , ZC_3 , ZC_4 , ZC_5 and doctor bladed over pre-cleaned FTOs. Cleaned TCO substrates were kept in Novascan UV-ozone chamber for 30 min for ozone treatment. Firstly, a ZnO compact layer was spin coated onto ozone treated TCO (zinc acetate (0.15 g), ethanolamine (42 mL) in 2-methoxyethanol (2.5 mL). Viscous homogeneous paste for photoanodes were prepared by mixing 1 g of ZnO NP or ZC_x or ZC_3RGO_y powder using terpeneol and binder i.e. ethocel in a mortar pestle and applying by doctor blade technique over compact layer coated FTO and gently heated at 120°C with subsequent calcination at 500°C for $\frac{1}{2}$ hr. The thickness of the deposited films were measured by surface profilometer and found to be $\sim 12\ \mu\text{m}$. Sensitization process was carried out by immersing the films into N719 dye solution (0.3 mM) for 8hr. After that, dye sensitized films were washed with acetonitrile and dried. Device circuit was completed by sandwiching the photoanodic films with an active area of $0.16\ \text{cm}^2$ and counter electrodes (Platinum coated FTO) using adhesive tape spacer and filling electrolyte. Counter electrode (Pt coated FTO) and I^-/I_3^- electrolyte was prepared following earlier reported procedure.¹⁸

5.3 RESULTS AND DISCUSSIONS

5.3.1 POWDER X-RAY DIFFRACTION ANALYSIS

The information of crystalline phases along with purity of as-synthesized materials and their composites were accomplished by PXRD patterns. In figure 5.3.1 (A), the XRD pattern of ZnO NP established the wurtzite phase formation (JCPDS Card No. 36-1451) whereas, CeO_2 NC showed a cubic fluorite phase (JCPDS 34-0394) with lattice planes (111), (200), (220), (311) and (222) with space group $\text{Fm}\bar{3}\text{m}$ (225). PXRD pattern for composites, as in figure 5.3.1 displayed the diffraction peaks for both ZnO nanoparticles and nano-cuboidal CeO_2 . No traces of impurity peak of other elements observed after calcination.

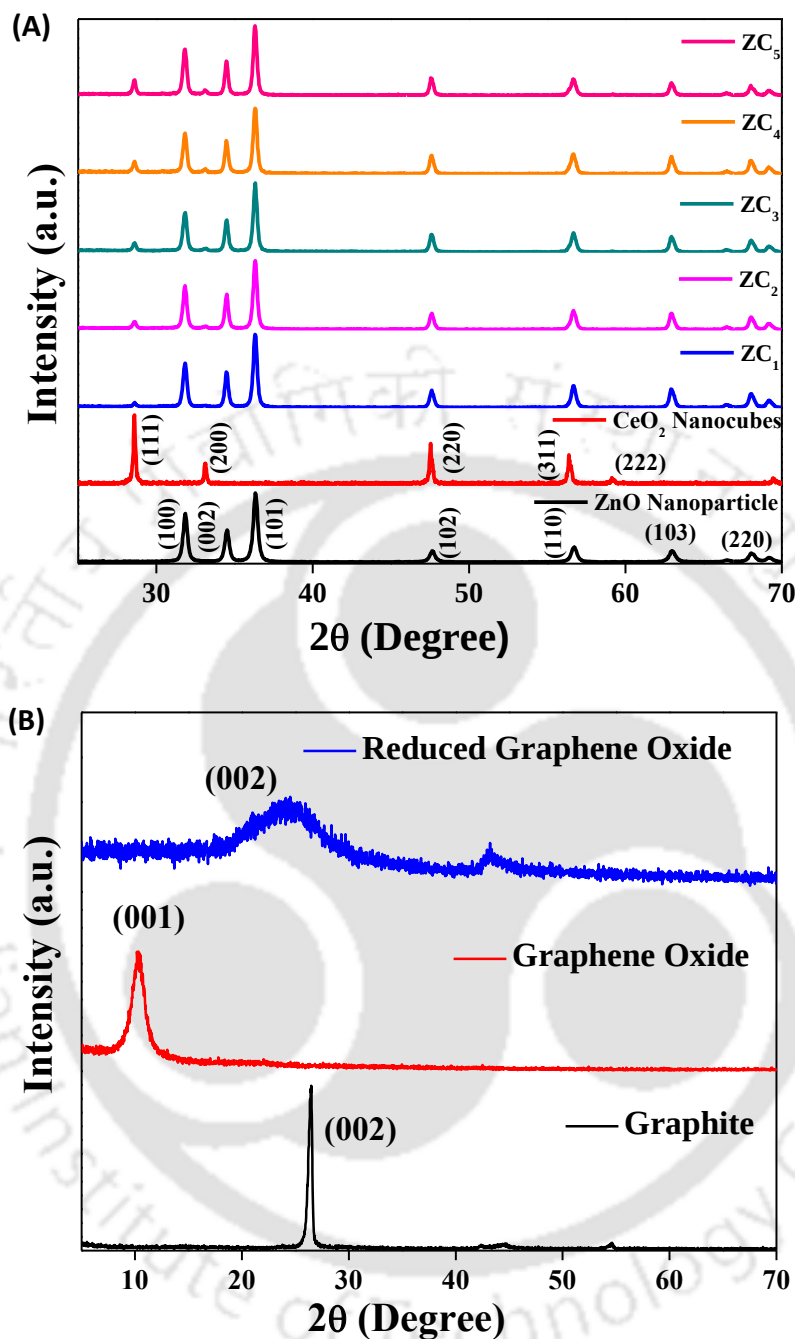


Figure 5.3.1 (A) Powder-XRD patterns for Nano-cuboidal CeO_2 (red line), ZnO nanoparticles (black line), ZnO NP_1% CeO_2 NC (ZC₁, blue line), ZnO NP_2% CeO_2 NC (ZC₂, magenta line), ZnO NP_3% CeO_2 NC (ZC₃, dark cyan line), ZnO NP_4% CeO_2 NC (ZC₄, orange line) and ZnO NP_5% CeO_2 NC (ZC₅, pink line) films on glass substrates. (B) Powder XRD patterns of graphite powder (black line), graphene oxide (red line) and reduced graphene oxide (blue line)

On the other hand, in figure 5.3.1 (B), graphite exhibits a characteristic peak of hexagonal pristine graphite at $2\theta = 26.4^\circ$ from lattice plane (002) with d-spacing ~ 0.336 nm. Upon oxidation,

the diffraction peak shifted to a lower $2\theta = 10.3^\circ$, corresponding to (001) plane of graphene oxide with much elevated d-spacing of ~ 0.858 nm, validating oxide functional group intercalation on either sides of GO. Chemically reducing GO changes the diffraction patterns, where in, the peak at $2\theta = 10.3^\circ$ disappeared and a broad peak around $2\theta = 24.3^\circ$ with a d-spacing of 0.364 nm has appeared, demonstrating a complete reduction and exfoliation of the layered RGO sheets.³³ Restoration of van der Waals' interaction between the 2D frameworks of carbon with the loss of long range order of the graphene sheets is attributed to the broad peak at 24.3° , whereas the observed significant decrease in d-spacing in case of RGO suggests the removal of oxygen/oxide functional groups from graphene sheets in RGO.³⁴

5.3.2 RAMAN ANALYSIS

To explore the vibrational characteristics of materials and to identify the crystallization, structural disorder, material defects and optical properties, Raman spectra of as-synthesized materials and composites were recorded. The Raman spectrum depicted in figure 5.3.2 (A) established that both the GO and RGO displayed well documented D band (~ 1365.5 cm^{-1}), attributed to the sp^3 defects or to the breakdown of translational symmetry, and the G band ($1598.5/1585.2$ cm^{-1}) attributed to the in plane vibrations of sp^2 hybridized carbon atoms. It can be seen that the G band peak of RGO underwent a slight downshifted from 1598.5 cm^{-1} to 1585.2 cm^{-1} , owing to the “self-healing” characteristics of the RGO that recovers the hexagonal network of carbon atoms with defects confirming successful reduction of GO to RGO.³⁵ Additionally, the I_D/I_G ratio, a measure of structural disorder, was increased from 0.98 to 1.29 on passing from GO to RGO due to formation of defects occurs in addition to the removal of oxide functional groups attached to the GO surface.³⁶ Figure 5.3.2 (B) depicts a sharp and dominant peak at 439.2 cm^{-1} is assigned to E_2 (high) mode of wurtzite hexagonal ZnO lattice, a fingerprint of the degree of crystallinity. The peak at 582.1 cm^{-1} is attributed to A_1 (LO) mode, related to oxygen vacancy. The peak observed 333 cm^{-1} and 1140.1 cm^{-1} are assigned to multi-phonon second order scattering process occurred due to overtones of first order modes.¹³ On the other hand, nano-cuboidal CeO_2 depicted a first order Raman line at around 465 cm^{-1} attributed to triply degenerate Raman active optical phonon mode i.e. F_{2g} , advocating cubic fluorite crystal phase formation of CeO_2 corroborating PXRD spectra.³⁷ ZnO in figure 5.3.2 (B) displays signature peak for ZnO wurtzite

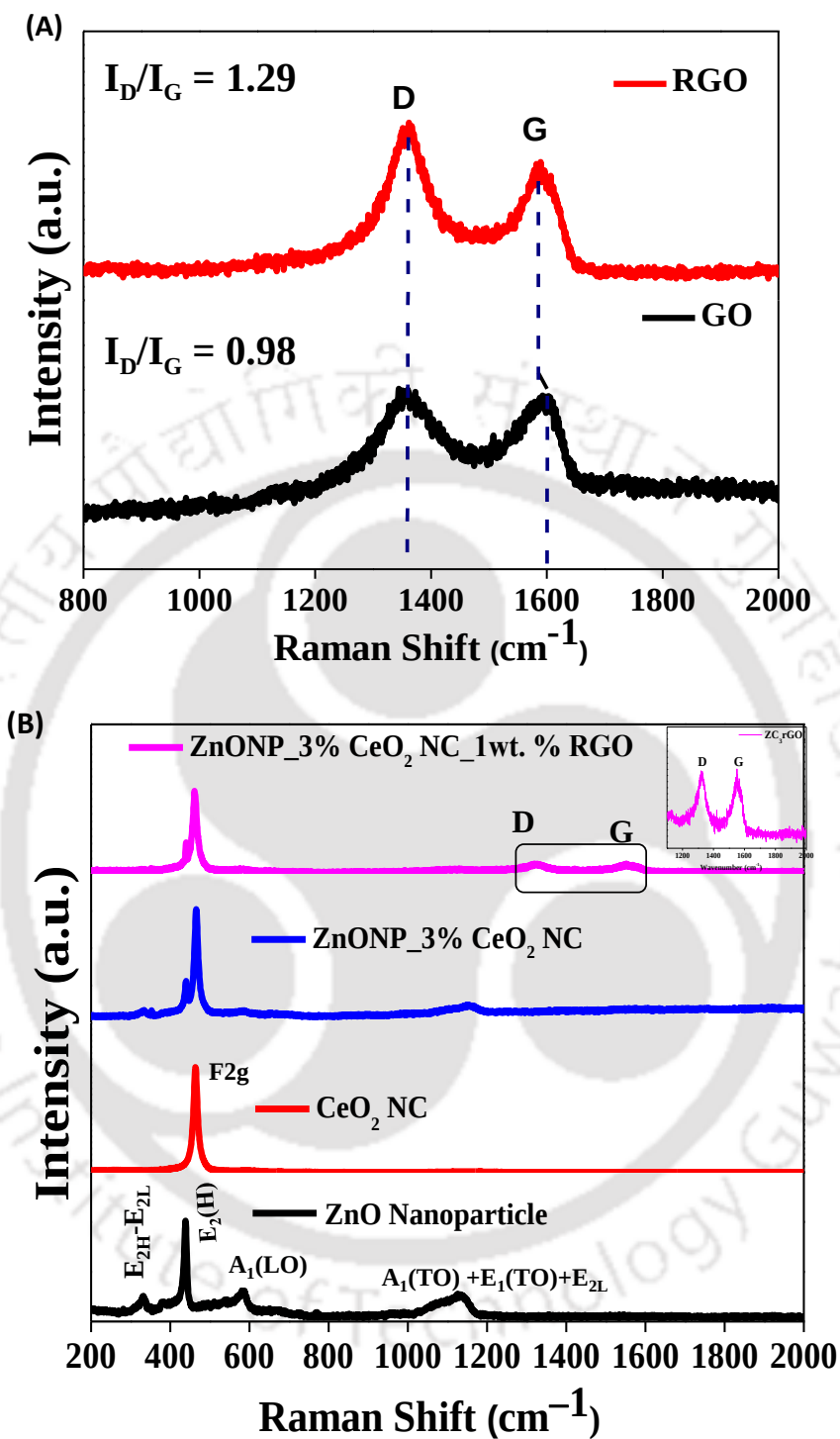


Figure 5.3.2 Raman spectra of (A) GO (black line), RGO (Red line). (B) ZnO Nanoparticle (black line), CeO₂ NC (red line), ZC₃ (blue line) and ZC₃RGO₁ (magenta line) films on glass substrate

hexagonal lattice and F_{2g} peak for CeO₂ NC, while in case of **ZC₃RGO₁**, D and G- bands corresponding to RGO with a significant frequency shifts of the graphene D-band $\sim 1325.2 \text{ cm}^{-1}$

and G-band $\sim 1552.1 \text{ cm}^{-1}$ also appeared, suggesting a synergistic charge transfer between ZnO NP/CeO₂ NCs and RGO sheets.³⁸

5.3.3 MATERIAL MORPHOLOGY

Morphological features of ZnO NP and nano-cuboidal CeO₂ (CeO₂ NC) were investigated through FESEM analysis. FESEM image of as-synthesized CeO₂ depicted in figure 5.3.3 [A-B] shows cuboidal morphology of CeO₂ with distinct and well-defined facets and edges with average dimension ranging from ~ 0.25 - $0.4 \text{ }\mu\text{m}$. Incident light can get reflected from the mirror like facets as well as edges of CeO₂ NCs and sizes, in the Mie scattering range, offers multiple scattering and increases the interaction with the absorber. As a result, more and more photo-induced electrons are generated which in turn adds to efficiency of the device. The cross-sectional FESEM image of photoanode ZC₃ [Trace (C-F)] shows that the film thickness is around $\sim 12 \text{ }\mu\text{m}$ which is in consistent with the profilometer measurements and the material morphology remains intact even after calcination at $500 \text{ }^{\circ}\text{C}$ for 30 min.

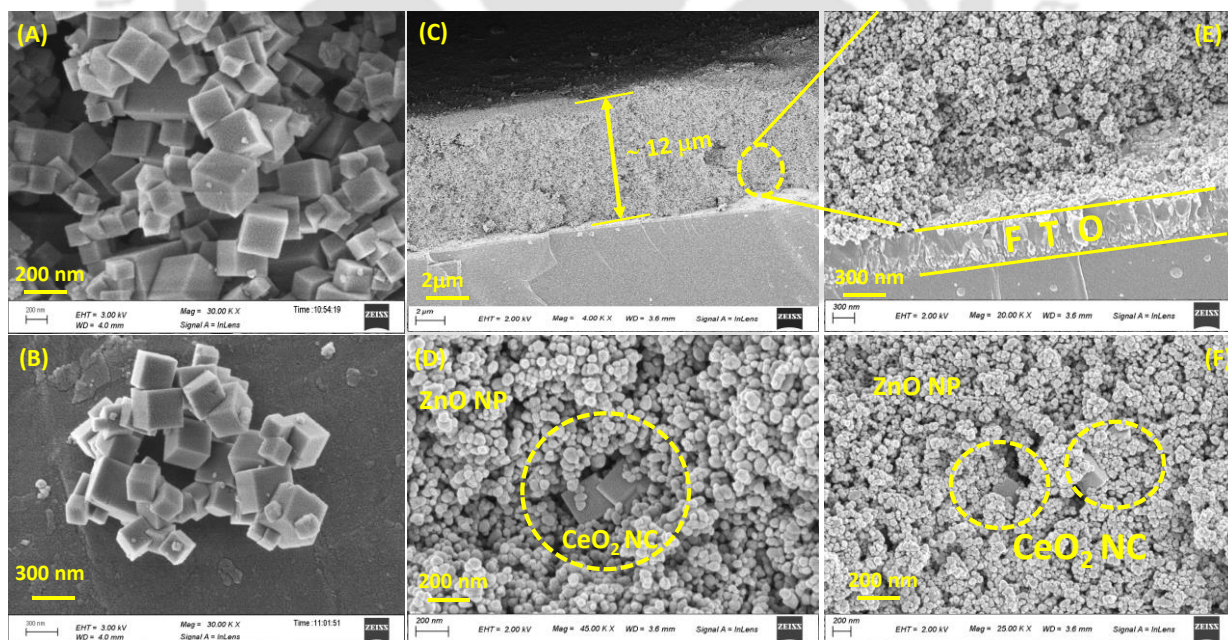


Figure 5.3.3 FESEM and magnified FESEM image of (A-B) Nano-cuboidal CeO₂ and (C-F) Cross-sectional images of ZC₃ photoanode. Scale bars are provided for better understanding

Furthermore, FETEM analysis has been performed to endorse the microstructural characteristics of as-synthesized CeO_2 NC, ZnO, and RGO. Figure 5.3.4 (A) of CeO_2 NCs shows a well-defined corner, edges, and facets. HRTEM image for CeO_2 NC, in figure 5.3.4 (B) shows distinct lattice fringes of (111) planes along with (200) planes explicitly identified from the Inverse Fast Fourier Transform (IFFT) analysis, performed for the squared parts of image (B), depicted in traces (C) and (D). Lattice fringes with the interplanar distance of about ~ 0.281 nm can be assigned for (200) crystal planes whereas, ~ 0.329 nm assigned to (111) crystal plane of as-synthesized CeO_2 NC. The SAED pattern for CeO_2 NCs [inset to figure (B)], displays a polycrystalline nature of the CeO_2 . The SAED pattern is describing the cubic fluorite crystal structure and crystal growth anisotropy as consistent with the PXRD analysis. While TEM image of ZnO NP (Trace E) shows a uniformly sized ZnO NP ranged ~ 20 - 30 nm with lattice fringes corresponding to (100) planes of wurtzite hexagonal ZnO (ZnO , $d_{100} = 0.26$ nm) are predominantly observed in HRTEM image (Trace F). SAED pattern shown in inset to figure (F) reveals polycrystalline crystalline nature of as synthesized ZnO NPs, consisting of diffuse rings with single spots superimposed where (100), (002), (101), (102), (110), (103), and (200) lattice planes were clearly indexed.

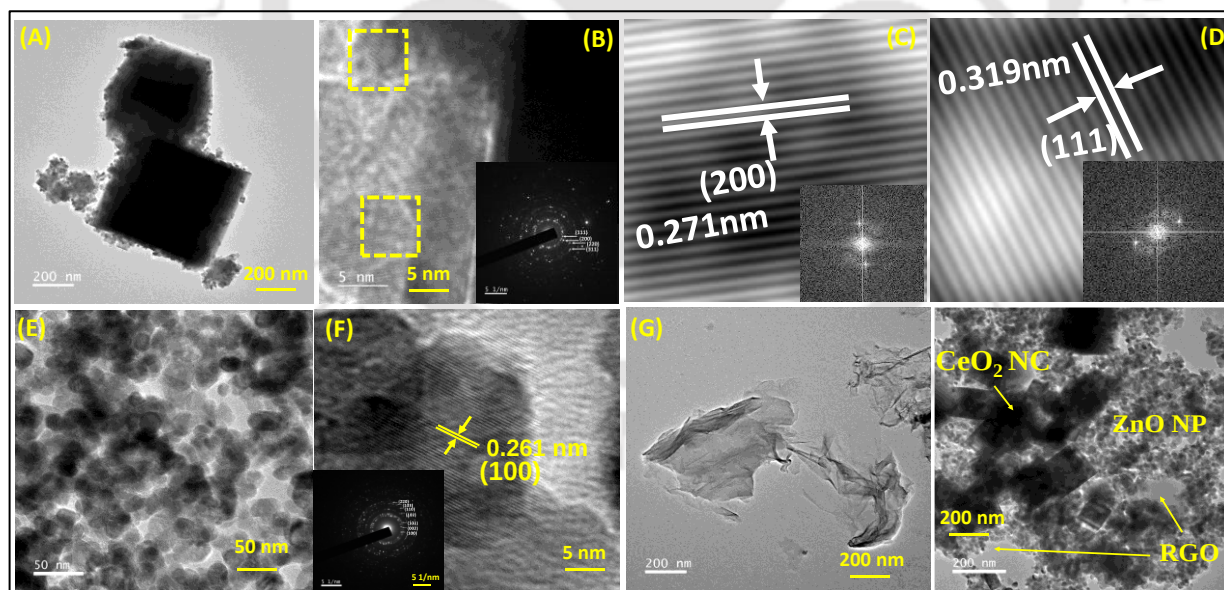


Figure 5.3.4 TEM and high resolution TEM image of as synthesized (A-D) Nano-cuboidal CeO_2 , (E-F) ZnO NP, (G) TEM image of reduced graphene oxide, and (H) TEM image of ZC_3RGO_1 composite.

Scale bars are provided for better understanding

Figure 5.3.4 (G) depicts wrinkles, lateral corrugations and scrolled morphology of RGO, indicating presence of few layers of reduced graphene sheets with localized strain and the edge of RGO sheets generated irregular defect with the formation of small fragment inferring that the material is exfoliated into mono or few-layered stacks. FETEM micrographs of ZnO NCs/RGO is shown in trace H which clearly shows uniform decking of ZnO nanoparticles as well as CeO_2 NC on both sides of the RGO sheets.

5.3.4 BET SURFACE AREA, UV-VISIBLE DRS AND EDS ANALYSIS

Porous nature of photoanode promotes diffusion of electrolyte whereas adsorption of sensitizer is directly related to surface area, both the properties are essential for efficient photovoltaics.³⁹ Brunauer-Emmett-Teller (BET) measurements were recorded for the synthesized bare as well as composite material. N_2 adsorption-desorption isotherm [figure 5.3.5] shows H3 hysteresis loops and type IV isotherm as per the BDDT (Brunauer–Deming–Deming–Teller) classification, corroborating the mesoporous nature of nano-cuboidal CeO_2 , an essential factor for device performance.⁴⁰

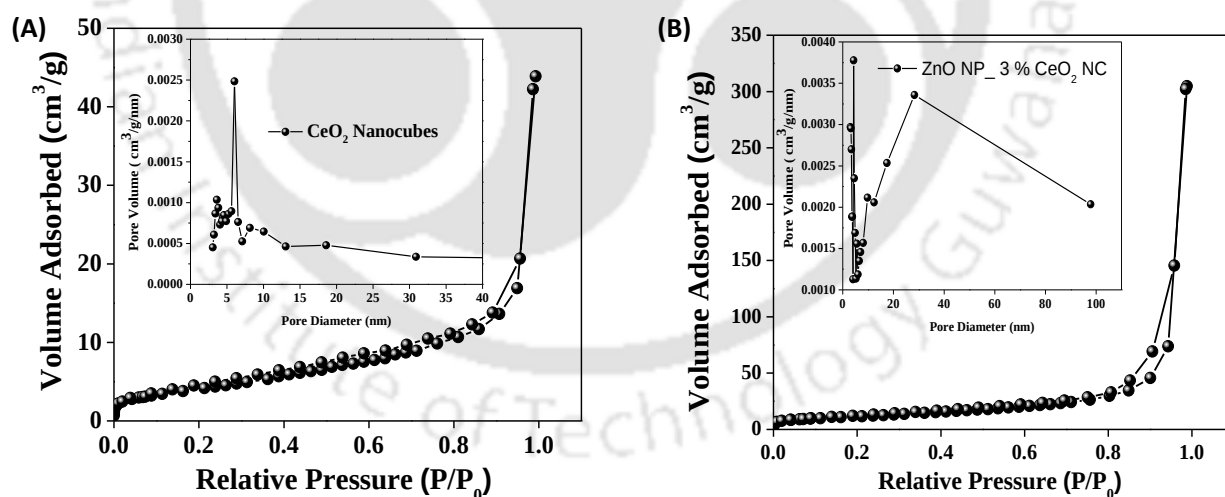


Figure 5.3.5 Nitrogen adsorption-desorption isotherms for (A) nano cuboidal CeO_2 (B) ZC_3 Photoanode. Inset depicts BJH pore size distribution plots of the respective materials

The surface area of the nano-cuboidal CeO_2 is found to be $\sim 17.1 \text{ m}^2\text{g}^{-1}$ with pores of ~ 7 - 8 nm (Inset to figure 5.3.5 A) uniformly distributed as depicted in BJH pore size distribution curve.

While, ZnO NP furnished a BET surface area $\sim 56.1 \text{ m}^2\text{g}^{-1}$. In case of composite **ZC₃** [figure 5.3.5 B], we have found that the surface area to be $\sim 53.2 \text{ m}^2\text{g}^{-1}$. The decrease in surface area is may be due to the incorporation of submicron sized CeO₂ NC which furnishes lesser BET surface area. The mesoporous nature depicted by BHJ pore size distribution curve, facilitates electrolyte diffusion. Such a porous characteristic encourages a perfect skeletal medium to adsorb sensitizers on the surface of photoanode.

It has been well established that light absorption of a photoanode is boosted by incorporating LSMs due to multiple reflection/ scattering that persuades a longer path length of the incoming photons, thus increasing the interaction of photon with the sensitizers/ absorbing units. Light scattering ability of nano-cuboidal CeO₂ has been investigated by fabricating photoanodic film of pristine ZnO NP and **ZC₁**, **ZC₂**, **ZC₃**, **ZC₄** and **ZC₅**, on FTO as shown in figure 5.6.6. UV-Vis DRS depicts that the composite photoanodic film **ZC₁** yielded a higher reflectance that gradually increases with the amount of CeO₂ NC owing to the multiple scatterings due to size/ reflections caused by mirror like facets as well as distinct edges of LSMs. Energy dispersive X-ray spectroscopic (EDS) analysis (Figure 5.6.7) of the best performing binary composite photoanode **ZC₃** depicts that LSMs are dispersed evenly throughout the blend, contributing to the efficient light harnessing.

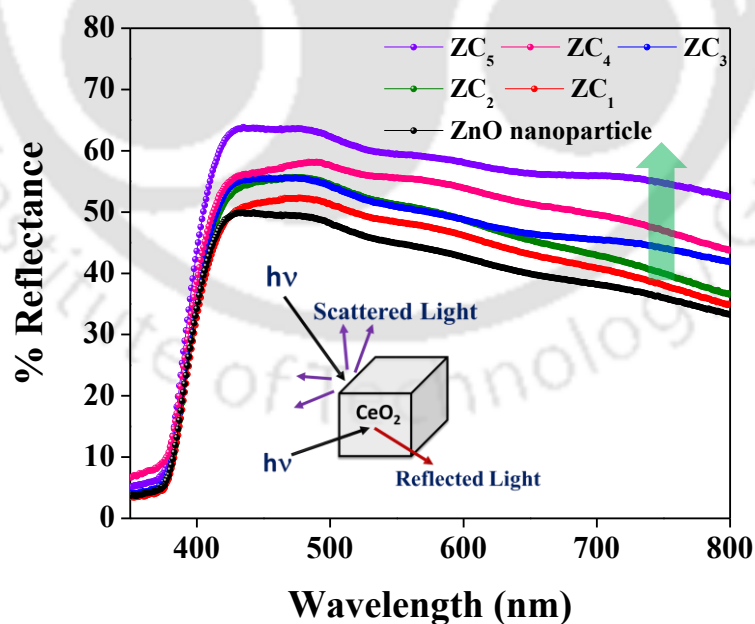


Figure 5.3.6 UV-Vis DRS spectra of ZnO NP (black line), ZnO NP_ 1% CeO₂ NC (**ZC₁**, red line) , ZnO NP_ 2% CeO₂ NC (**ZC₂**, green line), ZnO NP_ 3% CeO₂ NC (**ZC₃**, blue line), ZnO NP_ 4 % CeO₂ NC (**ZC₄**, pink line) and ZnO NP_ 5 % CeO₂ NC (**ZC₅**, navy blue line) films on glass substrates. Inset depicts the light scattering as well as reflection phenomenon from individual CeO₂ NCs

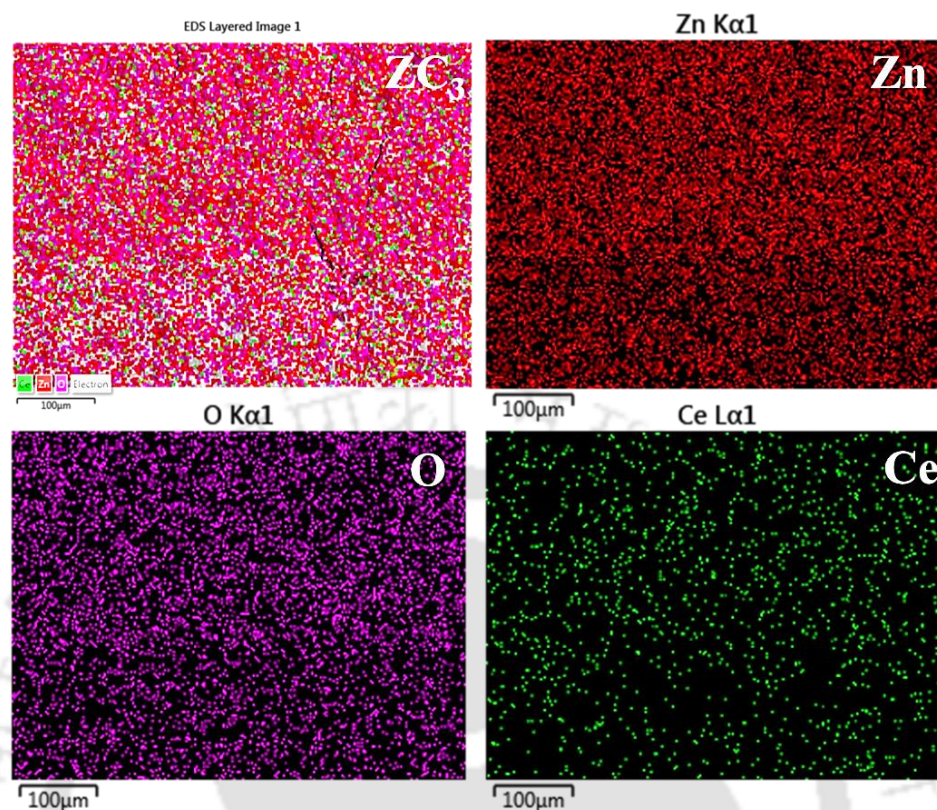


Figure 5.3.7. Energy Dispersive X-ray spectra of ZnO NP_3% CeO₂ NC photoanode

5.3.5 TIME RESOLVED PHOTOLUMINESCENCE ANALYSES

Decay analysis for dye sensitized photoelectrodes and dye, are carried out with excitation source of ~ 475 nm diode laser are shown in Fig. 5.3.8. The decay curves are fitted with a bi-exponential function and average exciton lifetime, $\langle \tau \rangle$ values have been evaluated (Table 5.3.1) by the equation (1),⁴¹

$$\langle \tau \rangle = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2} \dots \dots \dots (1)$$

The PL decay curves in Figure 5.3.8 (A) displays a faster decay patterns for dye when anchored onto semiconductor/composite scaffolds, while, **ZC₃RGO₁** displayed a fastest decay pattern among all, revealing an effective electron injection from LUMO of N719 to CB of semiconductors and a better charge separation as well as faster transport offered by honey comb like 2D RGO sheets in ternary hybrid photoanode, results in a very small $\langle \tau \rangle$ value. Calculated $\langle \tau \rangle$ for dye decreases from ~ 44.4 ns to ~ 29.6 ns (ZnO_N719), ~ 22.3 ns (**ZC₅_N719**) and lowest

of ~ 21.6 ns in case of **ZC₃RGO₁**, supports enhanced charge separation and injection in case of composite photoanode films via suitable band edge alignments [Figure 5.3.8 (B)].⁴²

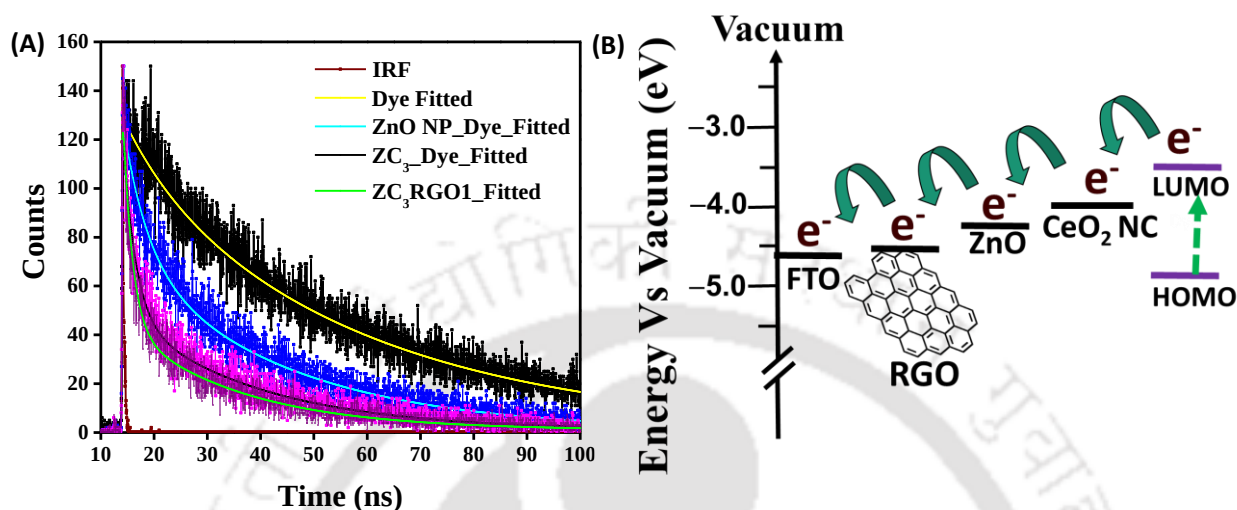


Figure 5.3.8. (A) Photoluminescence decay spectra of bare N719 film on FTO (black line), N719_ZnO NP film on FTO (blue line), N719_ZC₃ film (pink line) and N719_ZC₃RGO₁ (purple line) on FTO (B) Schematic of electron transfer process in the ternary composite

Table 5.3.1: Calculated fitting parameter (χ^2), lifetime components (τ_1 , τ_2), pre-exponential factors (α_1 , α_2), average lifetimes ($\langle\tau\rangle$) and rate of injection (k_{inj}) for fabricated sensitized photoanode. All values except χ^2 are rounded off to the nearest integer

Samples	χ^2	τ_1 (ns)	τ_2 (ns)	α_1 (%)	α_2 (%)	$\langle\tau\rangle$ (ns)
Dye	1.136	9.1	44.6	3.8	96.2	44.4
ZnO NP - Dye	1.013	4.6	30.1	12.2	87.8	29.6
ZC ₁ -Dye	1.020	3.6	29.4	11.8	88.1	29.0
ZC ₂ -Dye	0.990	2.7	26.9	11.9	88.0	26.6
ZC ₃ -Dye	0.996	2.3	25.1	16.6	83.4	24.7
ZC ₄ -Dye	1.078	2.2	24.7	19.9	80.1	24.2
ZC ₅ -Dye	1.017	1.6	22.7	15.2	84.8	22.3
ZC ₃ RGO ₁ -Dye	1.027	1.7	22.0	17.5	82.4	21.6

The kinetics of electron injection (k_{inj}) from N719 to ZnO, **ZC₃** and **ZC₃RGO₁** (Best performed devices) is evaluated using equation (2) and calculated parameters are given in Table 1:⁴¹

$$k_{inj} = \frac{1}{\langle \tau \rangle_{composite}} - \frac{1}{\langle \tau \rangle_{dye}} \dots \dots \dots (2)$$

The higher value of k_{inj} in case of **ZC₃RGO₁** ($\sim 2.3 \times 10^8 \text{ s}^{-1}$) photoelectrode [**ZnO** $\sim 1.1 \times 10^8 \text{ s}^{-1}$ and **ZC₃** $\sim 1.7 \times 10^8 \text{ s}^{-1}$] advocates a faster electron transfer rates in RGO incorporate ternary composite photoanode that results in a reduced recombination processes in favor of photovoltaic performance.

5.3.6 PHOTOVOLTAIC CHARACTERISTICS OF THE SOLAR CELLS

In order to study the effect of high quality mirror-like nano-cuboidal CeO₂ as well as 2D reduced graphene oxide sheets in photovoltaic devices, a series of devices are fabricated with different content of CeO₂ NC and RGO in the photoanode (see experimental section). The energy conversion efficiency was determined using J–V plots of as fabricated photoanodes against Pt coated FTO as counter electrode using I[−]/I₃[−] as electrolyte and the parameters are presented in figure 5.3.9 and results obtained are tabulated in Table 5.3.2. It is observed that bare ZnO nanoparticle alone showed a PCE of $\sim 3.10 \%$. It has been found that on incorporation of 1 % CeO₂ NC into ZnO NP viz. **ZC₁**, the PCE of the device impressively enhanced to $\sim 3.80\%$. This increase in the PCE is mainly attributed to the increase in J_{sc} and V_{oc} of the device [as shown in table 5.3.2]. Short circuit current density or J_{sc} is mainly affected by the efficiency of charge separation/transport, and light absorption, while the V_{oc} is mainly associated with the Fermi Level (E_f) of ZnO and the Nernst potential of the redox shuttle as well as recombination occurring at various interfaces. In case of composite photoanode i.e. **ZC₁**, CeO₂ NCs having mirror like facets and size in Mie scattering range helps incoming photons to get reflected/scattered in different directions, therefore, letting it spend longer time within the photoanode before eventually get absorbed by sensitizer [Figure 5.3.6]. Increased interaction between the incident light and sensitizer leads to increase in photo-induced electron generation, in turn J_{sc} . On the other hand the conduction band position of CeO₂ lies above that of ZnO, serving as an energy barrier for photo-injected electrons reducing the probability of recombination thus increasing V_{oc} as well as Fill factor. The rise in efficacy has been observed till 3 % loading of CeO₂ NC which furnished highest PCE $\sim 4.36 \%$ with $J_{sc} \sim 11.96 \text{ mA/cm}^2$, a $V_{oc} \sim 647 \text{ mV}$, a $FF \sim 56.5 \%$. Whereas, loading of 4 % CeO₂ NC, degrades the device performance (as can be seen in Table 5.3.2).

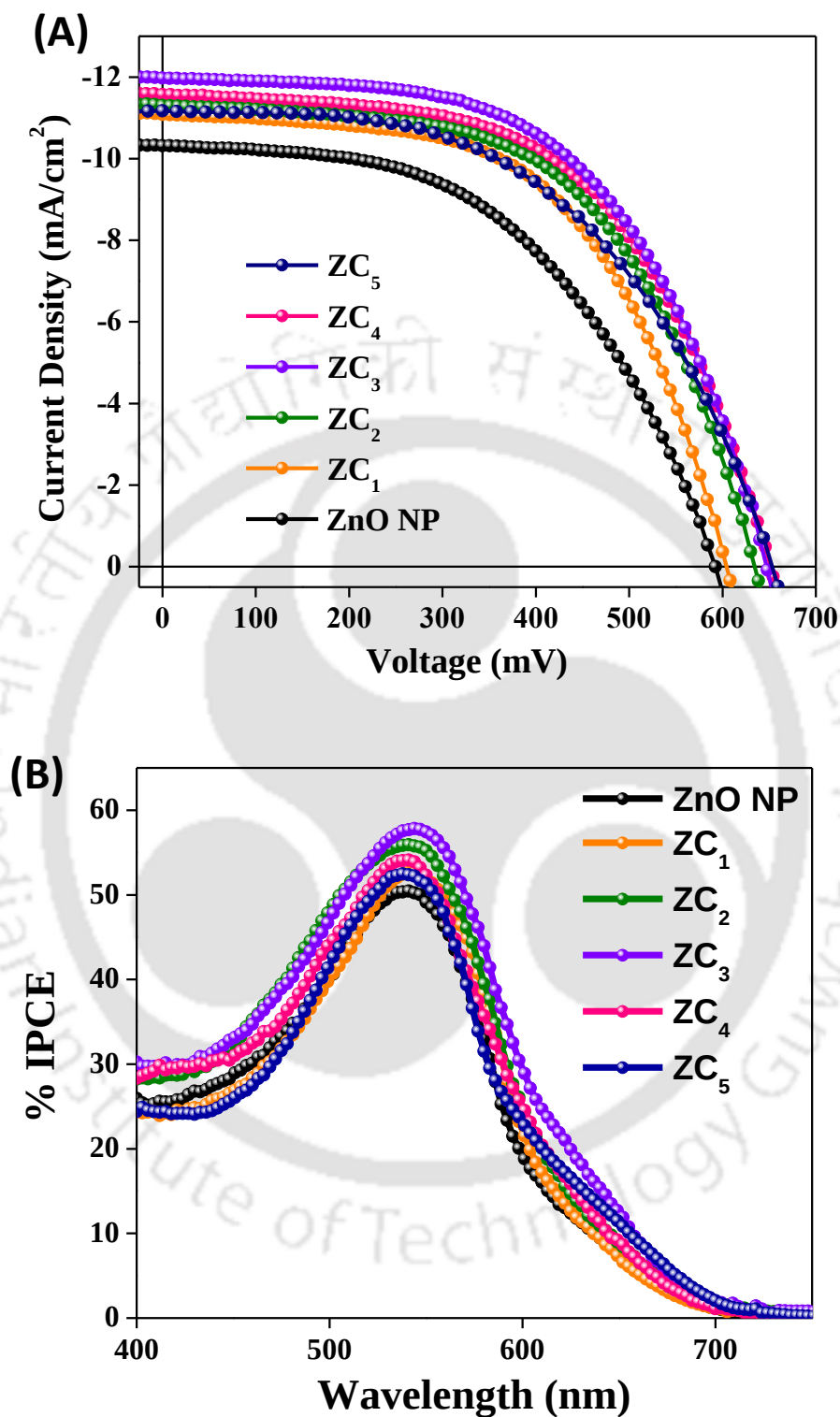


Figure 5.3.9 (A) Short circuit current density–voltage (J–V) (B) IPCE plots for devices with ZnO NP film (black line), ZnO NP_ 1% CeO_2 NC (ZC_1 , orange), ZnO NP_ 2% CeO_2 NC (ZC_2 , olive line), ZnO NP_ 3% CeO_2 NC (ZC_3 , violet line), ZnO NP_ 4% CeO_2 NC (ZC_4 , pink line) and ZnO NP_ 5% CeO_2 NC (ZC_5 , blue line) photoanodes

Table 5.3.2. Photovoltaic performance parameters for the **ZC_x** (X=1-5%) devices

Device	J _{sc} (mA/cm ²)	V _{oc} (mV)	FF (%)	Efficiency (%) ^a	IPCE (%)
ZnO NP Bare	10.32	593	50.6	3.10	50.1
ZnONP_1wt% CeO ₂	11.08	604	56.7	3.80	52.5
ZnONP_2wt% CeO ₂	11.29	634	56.4	3.99	55.7
ZnONP_3wt% CeO ₂	11.96	647	56.5	4.36	58.2
ZnONP_4wt% CeO ₂	11.58	651	56.8	4.24	54.1
ZnONP_5wt% CeO ₂	11.17	653	56.8	3.82	52.1

^a Data reported here are the results of the best performed devices out of five devices for each configuration

We have seen that though there is not much change in V_{oc} and fill factor, there is a gradual decrease in J_{sc} in **ZC₄** as well as **ZC₅**. Although, **ZC₅** photoanode displays a higher diffused reflectance, the device performance is the lowest. To probe the current scenario we have carried out chemisorption analysis.¹³ As can be seen, there is a gradual decrease in dye adsorption moving from **ZC₁** ($\sim 3.51 \times 10^{-6}$ mol.cm⁻²) to **ZC₂** ($\sim 3.37 \times 10^{-6}$ mol.cm⁻²), **ZC₃** ($\sim 3.24 \times 10^{-6}$ mol.cm⁻²), **ZC₄** ($\sim 2.93 \times 10^{-6}$ mol.cm⁻²), **ZC₅** ($\sim 2.82 \times 10^{-6}$ mol.cm⁻²) as compared to pristine device ZnO ($\sim 3.64 \times 10^{-6}$ mol.cm⁻²). We have seen that nano-cuboidal CeO₂ which as higher particle size contributes to a low BET surface area (figure 5.3.5) as compared to ZnO NP. Although, incorporation of CeO₂ NC resulted in a decreased dye adsorption (low BET surface area), has been compensated by higher light scattering, thereby absorption properties up to 3%, achieving highest PCE. However, when incorporated more than 3% CeO₂, though, high light scattering, reduced adsorption of dye effecting the performance of the photoanode. Moreover, with increase in concentration of LSMs probability of back scattering at the FTO junction also increases, hindering the penetration probability of incident photons thus causing a loss of incident radiation.⁴³ It is observed that with the incorporation of CeO₂ NC, open circuit voltage (V_{oc}) also increases [Table 5.3.2]. Higher V_{oc} for hybrid photoanodes can be endorsed to the more negative CB position of CeO₂ as compared to ZnO that helps in reduced reverse recombination of photo-injected electrons at hetero-interface.⁴¹

On the other hand, incorporation of RGO enhances the device performance substantially as can be seen from figure 5.3.10 and table 5.3.3. Reduced graphene oxide is a well-known two dimensional materials that acts as electron sink and helps in faster charge transport, reduces recombination as well.

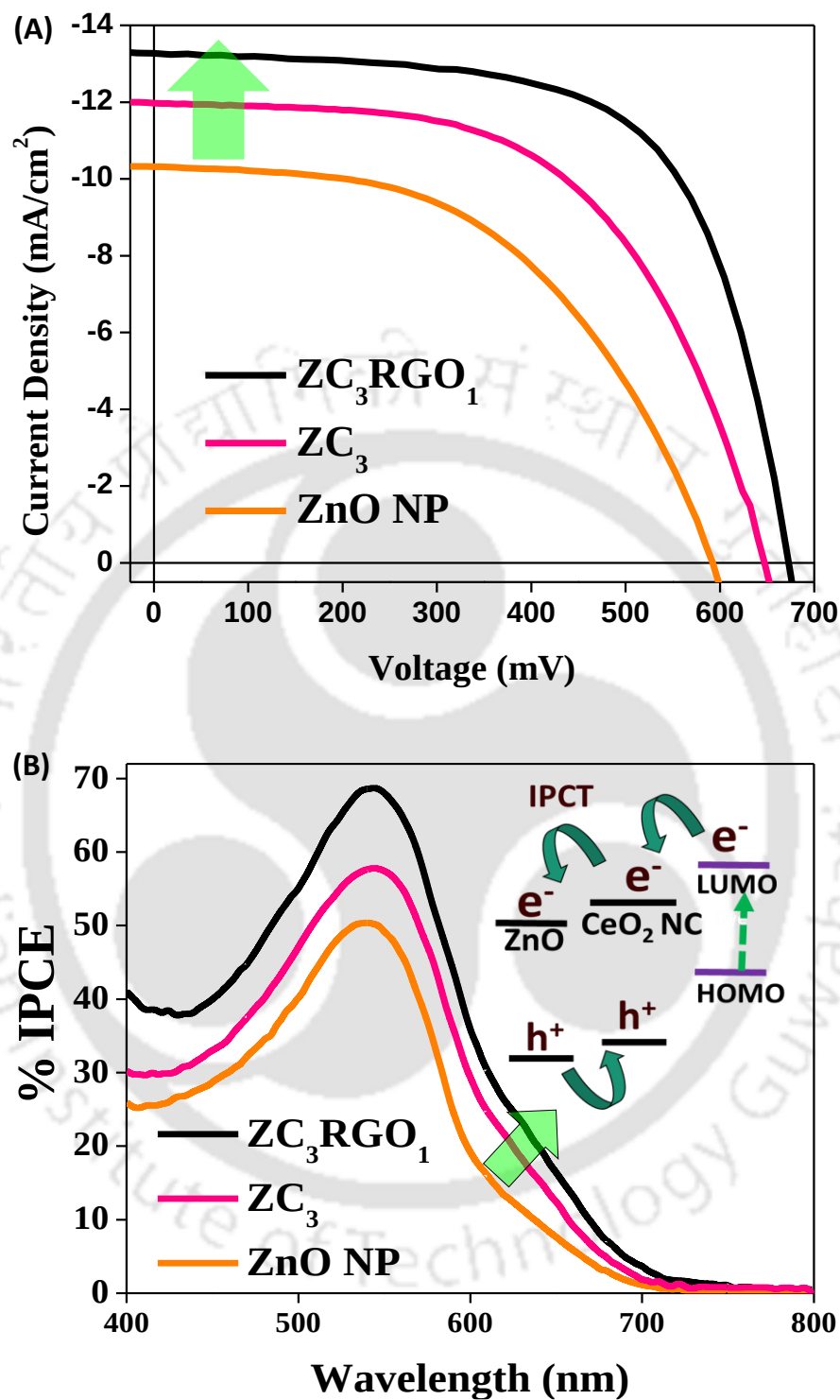


Figure 5.3.10 (A) Short circuit current density–voltage (J - V) (B) IPCE plots for devices with ZnO NP film (orange line), ZnO NP_ 3% CeO_2 NC (ZC_3 , pink line), ZC_3RGO_1 (black line)

Incorporation of RGO in the ZC_3 photoanode [Table 5.3.3] drastically increased the power conversion efficiency reaches a maximum value with 1wt% RGO yielding PCE $\sim$ 5.76 % with J_{sc}

~ 13.27 mA/cm², a $V_{oc} \sim 677$ mV, a FF ~ 64.1 %. As compared to binary hybrid photoanode i.e. **ZC₃**, ternary hybrid photoanode based device furnished a $\sim 32\%$ increase in efficacy value. It can be seen from EDX analysis of **ZC₃RGO₁** [figure 5.3.11] that 2D- RGO sheets are homogeneously distributed throughout the scanned area. RGO provides a facile charge transport and collection through 2D graphene sheets with a favorable work function with ZnO and FTO thus causing lesser recombination/back transfer processes occurring in the devices. The value of open circuit voltage i.e. V_{oc} can be described as in equation 3.⁴⁴

$$V_{oc} = E_{red} - E_{CB} - \gamma \frac{k_B T}{e} \ln \left(\frac{N_e}{n} \right) \dots \dots \dots (3)$$

Where, γ is a characteristic constant of tailing states of semiconductor, k_B is the Boltzmann constant, T is temperature (25 °C), e is elementary charge, and N_e is the effective density of states at the CB. Under similar conditions, E_{red} , γ , and N_e would not change considerably, so the parameters influencing V_{oc} are E_{CB} and n , with the latter closely related to the charge recombination. Higher the electron density (n) in the CB of ZnO, higher will be the V_{oc} .

Table 5.3.3. Photovoltaic performance parameters for the **ZC₃RGO_Y** (Y= 0.5, 1, 1.5 %) devices

Device	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	Efficiency (%) ^a
ZC ₃ rGO _{0.5}	12.39	680	62.6	5.25
ZC ₃ rGO _{1.0}	13.27	677	64.1	5.76
ZC ₃ rGO _{1.5}	11.67	667	65.1	5.06

^a Data reported here are the results of the best performed devices out of five devices for each configuration

Incorporation of RGO enhanced the charge extraction into the external circuit more easily reducing the recombination, thus increases the electron density in CB of ZnO, enhancing V_{oc} [Table 5.3.3] as corroborated by the EIS data as shown later. On the other hand, increase in fill factor can be attributed to the decrease in series resistance by introduction of 2D- RGO sheets in the photoanode that provides faster transport of the photo-generated charge carriers. It can be seen that going from photoanode with RGO content from 1wt% to 1.5wt% there is a decrease in device performance [table 5.3.3]. The decrease in the efficiency at a high RGO loading is due to i) RGO can absorb some visible light (figure 5.3.12 A), which led to a light harvesting competition between Dye and RGO, thus the number of photo-generated electrons decreases under illumination, ii) the

excessive RGO can act as a kind of recombination center instead of providing an electron transfer pathway, and the short circuit will happen easily. The combined factors cited above lead to a trade-off for the performance of the RGO doped devices.

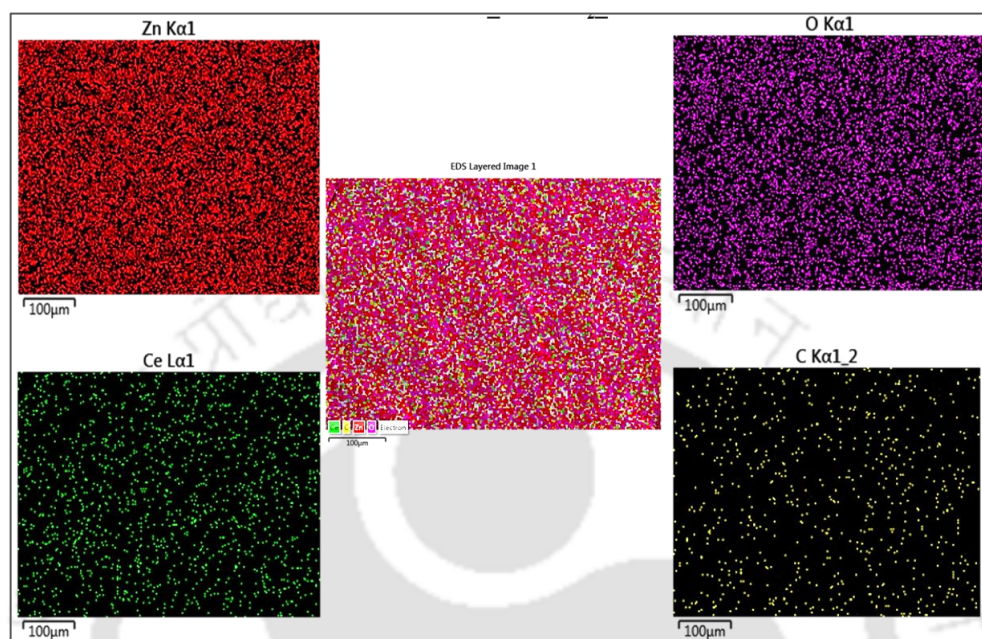


Figure 5.3.11. Energy Dispersive X-ray spectra of ZC_3RGO_1 photoanode

To probe the solar light to electron conversion efficacy IPCE measurements were carried out. IPCE of a device dependent upon factors like light harvesting efficiency (LHE) of a photoelectrode, the charge injection and collection efficacy. Figure 5.3.9 (B) represents a maximum IPCE value of $\sim 50.1\%$ for bare ZnO NP based photovoltaic device as a result of prominent dye sensitization in the visible range. On incorporation of CeO_2 NC it has been found that the IPCE values first increased, reached a maximum of $\sim 57.5\%$ (for ZC_3 photoanode) and then decreased for further increase of CeO_2 concentration [Table 5.3.2]. IPCE spectrum shows an increase in the light harvesting efficacy in red region for devices loaded with CeO_2 NC advocate confinement of incident light within composite photoanodes accredited to the repeated reflection/scattering capacity of sub-micron sized CeO_2 NC having the sharp edges and mirror like facets. Enhancement in the IPCE values on moving from reference ZnO to ZC_3 devices is owing to the increased number of events i.e. absorption followed by excitation of dye due increased interaction of incident light and absorber with an optimal dye loading. Furthermore, ZnO and CeO_2 has a uniquely aligned band edge structure which helps efficient separation of photo-generated

charge carriers due to an inter particle charge transfer process (IPCT) as shown in the inset to figure 11, further confirm by quenching of PL intensity of ZnO Based photoanode when combined with CeO₂ and RGO [figure 5.3.14 B].⁴⁵

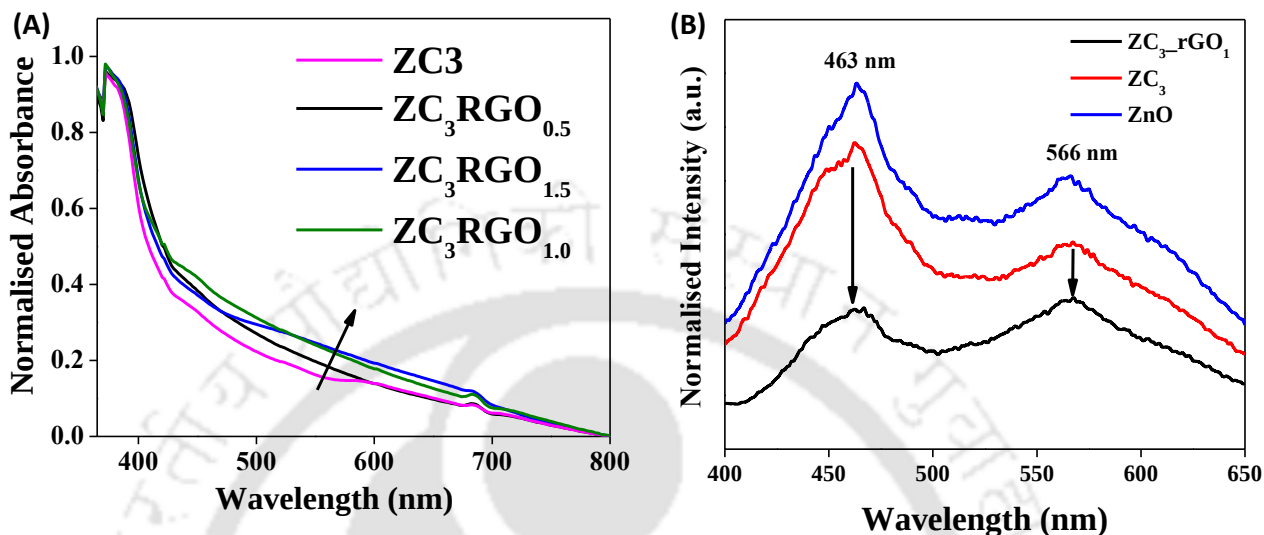


Figure 5.3.12. (A) UV-vis absorption spectra of RGO based ZC₃ Photoanodes (B) PL spectra of ZnO, ZC₃ and ZC₃RGO₁ based photoanode

Whereas, higher loading of CeO₂ NC tends to show a lower IPCE due to decreased loading of light absorbing materials [as can be seen from chemisorption and J_{sc} values] where scattering ability of photoanode is superseded by dye intake. On the other hand, on RGO loading it has been observed that IPCE values increased impressively corroborating results of J-V measurements. The increase in IPCE is attributed to better charge separation, transport and collection offered by 2D-RGO sheets. The work function of RGO is well matched with conduction band positions of ZnO and CeO₂ as well as FTO as shown in inset to figure 5.3.8 B. The photo-generated electrons can be well separated and transported through the 2D-RGO bridges and collected at the FTO as seen in the TRPL studies. On the other hand, when the concentration of RGO is increased, the conversion efficiency decreases corroborating similar results to the of J_{sc} values, owing to the masking of incident light by RGO so before light reach to the sensitizer, RGO can absorb some visible light decreasing the efficacy. Moreover, the electron diffusion and transport become poor, as the excessive RGO will generate more charge trap on the surface of RGO/ semiconductor and decreases charge collection efficacy.⁴⁶ The photovoltaic performances of best performed devices for comparison are shown in table 5.3.4.

Table 5.3.4. Photovoltaic performance parameters for the fabricated devices

Device	J_{sc}^a (mA/cm ²)	V_{oc}^a (mV)	FF ^a (%)	PCE ^a (%)	IPCE (%)
ZnO NP Bare	10.32	593	50.6	3.10	50.1
ZnO NP_3wt% CeO ₂	11.96	647	56.5	4.36	57.5
ZnONP_3wt%CeO ₂ _1wt% RGO	13.27	677	64.1	5.76	68.3

^a Values reported for the best performed devices out of five identical devices.

5.3.8 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPIC (EIS) ANALYSIS:

To better elucidate the results obtained from J-V measurements, EIS measurements have been carried out at V_{oc} (frequency range $\sim 10^{-1}$ Hz to 10^4 Hz) under the dark conditions and depicted in figure 5.3.13 (A) and (B) as well as 5.3.14 (A) and (B). Equivalent circuit diagram is shown in inset to figure 5.3. 12 (A) with the fitted data listed in Table 5.3.5.⁴⁷ The impedance due to back transfer of photo-induced electron at semiconductor/ dye/ electrolyte interface is referred to the semicircle at the intermediate frequency region ($\sim 10^{-1}$ – 10^2 Hz) in the Nyquist plots. R_{CT2} , is known as recombination resistance (R_{rec}), corresponds to this semicircle. Bigger the semicircle or greater the value of R_{CT2} , greater is the hindrance offered to photo-injected electrons to get recombined with the oxidized species in electrolyte.

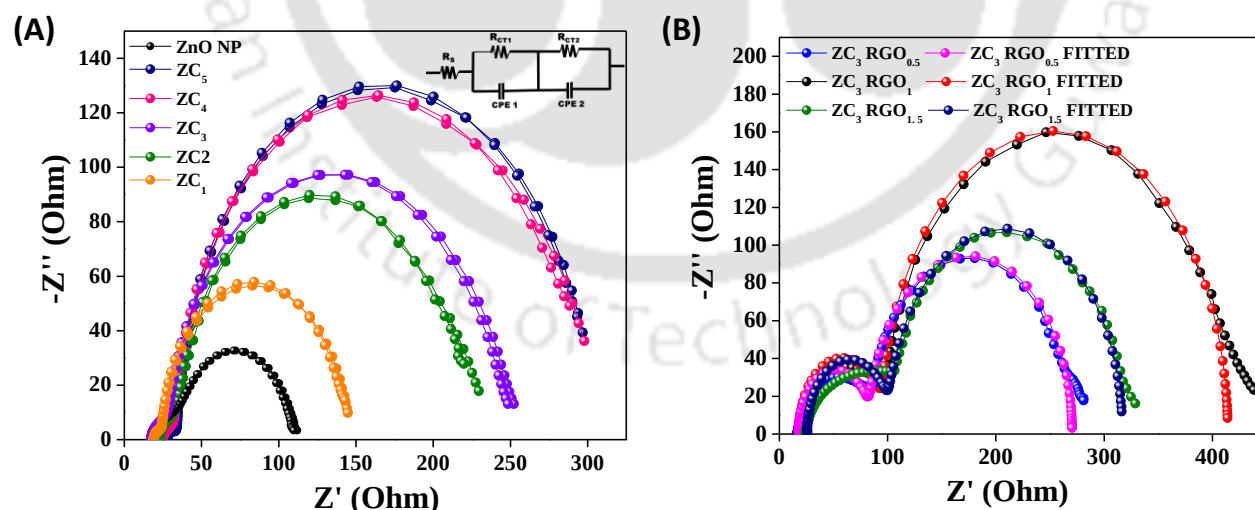


Figure 5.3.13 Nyquist plots for (A) ZnO NP (black symbol), ZC₁ (orange symbol), ZC₂ (olive symbol), ZC₃ (violet symbol), ZC₄ (pink symbol), ZC₅ (blue symbol) and (B) ZC₃RGO_{0.5} (royal blue symbol), ZC₃RGO₁ (black symbol), ZC₃RGO_{1.5} (olive symbol) film based devices

The increased value of R_{CT2} signifies a reduced recombination at the **ZC_x**/ dye/ electrolyte interface compared to ZnO based cell alone lead to a higher V_{oc} for the CeO₂ NC incorporated based devices as shown in figure 5.3.13 (A).

On the other hand, incorporation of RGO into the device **ZC₃**, has substantially increased R_{CT2} value as a result of which the device performances also enhanced as shown in figure 5.3.13 (B). This is due to the fact that 2D- RGO sheets facilitates interfacial electron transfer, lowering the reverse tunnelling probability of injected electrons on semiconductors. Whereas, R_s , the series resistance accounting for the transfer resistance of the FTO and the electrolyte decreases on incorporation of RGO indicating a better charge transport/collection efficacy of the devices through 2D- RGO sheets. It can be seen in figure 5.3.13 (B) that with higher RGO content, the R_{CT2} value decreases inferring a higher recombination probability as well as reduced device performance. This may be due to excess of RGO can agglomerate thus providing recombination sites for back recombination.

Nyquist plots of best performed devices and corresponding Bode plot for the devices are depicted in figure 5.3.14 (A) and (B). The peak at mid frequency region, for RGO loaded **ZC₃**, **ZC₃** photoanodes appeared at a frequency lower than that of bare counterpart (from 8.29 to 2.03 Hz). The photo-generated electron life time of photoanodes, τ_e is calculated as, $\tau_e = (2\pi f_p)^{-1}$, where f_p is the peak frequency maxima in the middle frequency regime and presented in Table 5.3.5. This increase in the τ_e advocates the results obtained from Nyquist plot. A favourable alignment between ZnO, CeO₂ band-edge allows migration of holes to CeO₂, thus decreasing e^-h^+ recombination resulting in increase in the τ_e . Whereas, RGO owing to its higher electron mobility and favourable work function with FTO facilitate better charge transport and collection, causing further reduced recombination. Moreover, mesoporous nature of the photo electrodes **ZC₃** as well as **ZC₃RGO₁** facilitates the penetration of electrolyte through the photoanode scaffold for regeneration of oxidized dye molecules thus preventing recombination processes, in turn increasing the FF in the devices. A schematic representation of charge transfers processes through well matched band positions occurring in the ternary device is shown in scheme 5.3.1.

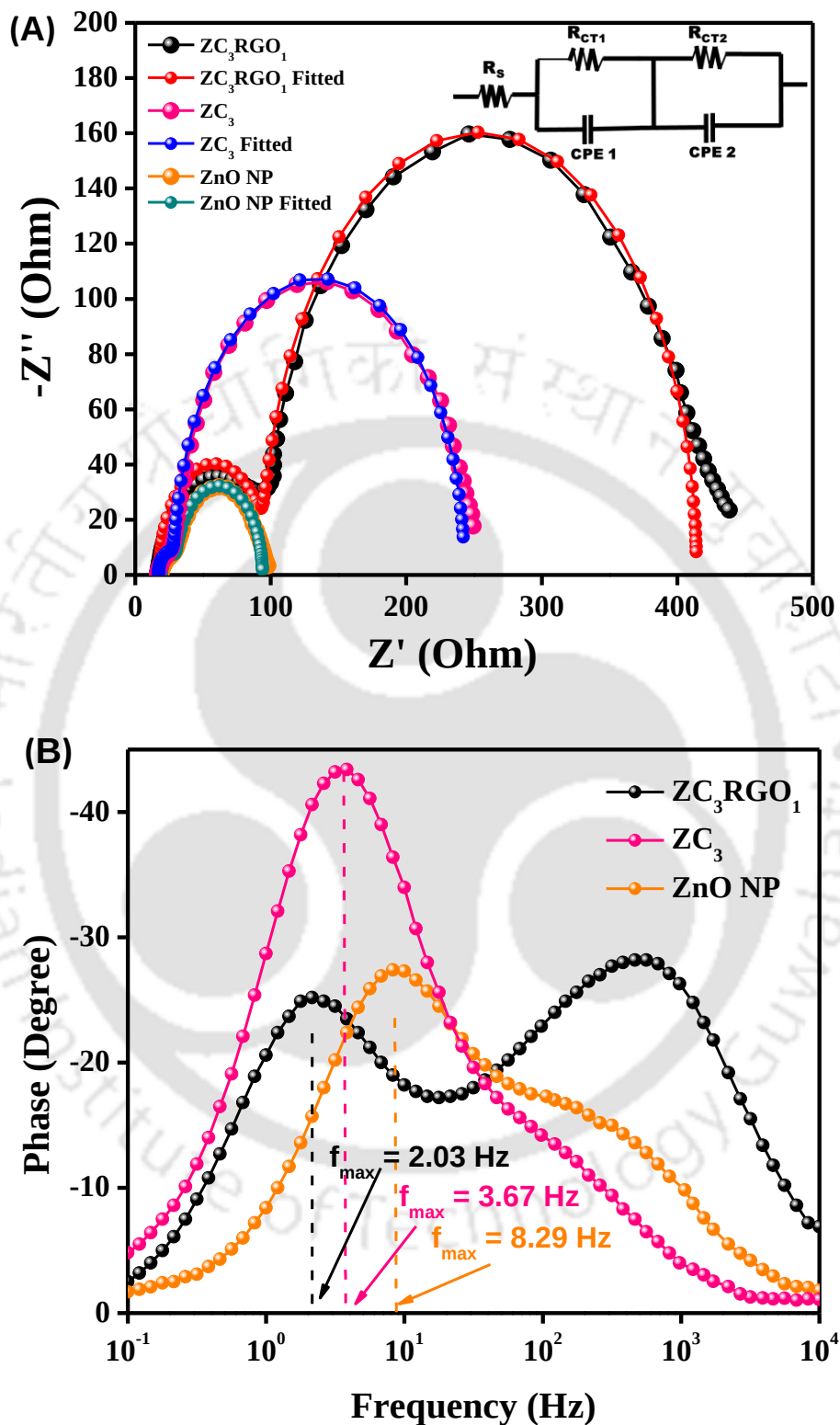
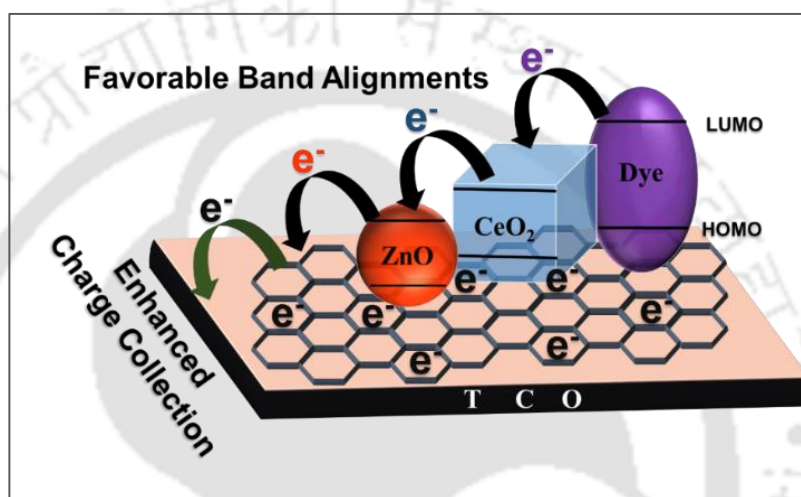


Figure 5.3.14 (A) Nyquist and (B) Bode plots for ZnO NP (orange symbol), ZC_3 (pink symbol), ZC_3RGO_1 (black symbol) film based devices. Inset to 12(A) represents equivalent circuit diagram

Table 5.3.5. Fitting parameters of EIS analysis for the fabricated devices obtained from EIS analysis (^a Nyquist and ^b Bode plot)

Device	R_s^a (Ohm)	R_{ct1}^a (Ohm)	R_{rec}^a (Ohm)	f_p^b (Hz)	τ_e^b (ms)
ZnO NP	19.38	10.73	63.6	8.29	19.2
ZnONP_3% CeO ₂ NC	17.18	12.03	212.8	3.67	43.3
ZnONP_3% CeO ₂ NC_1 wt% RGO	16.05	73.6	312.2	2.03	78.4



Scheme 5.3.1. Schematic of Charge transfer processes occurring in ternary device

The electron recombination kinetics has been further investigated by carrying out the transient open circuit voltage decay (OCVD) measurement. From illumination condition, once the light is turned off under open circuit condition, decay of the V_{oc} is due to electron recombination solely.⁴⁸ From figure 5.3.15, it is evident that the ZnO NP based photoanode has a faster decay as compared to **ZC₃** and **ZC₃RGO₁** based devices corroborating the faster recombination kinetics in the device. The V_{oc} decay becomes significantly slow on incorporation of 2D- RGO inferring a better charge transport and impeded recombination of photo-generated electrons as can be seen from EIS measurements. Further, dark-current measurements have been performed to corroborate the results obtained in EIS. Generally, dark current generates due recombination of photo-injected electrons on a semiconductor with oxidized electrolyte species.⁴⁹

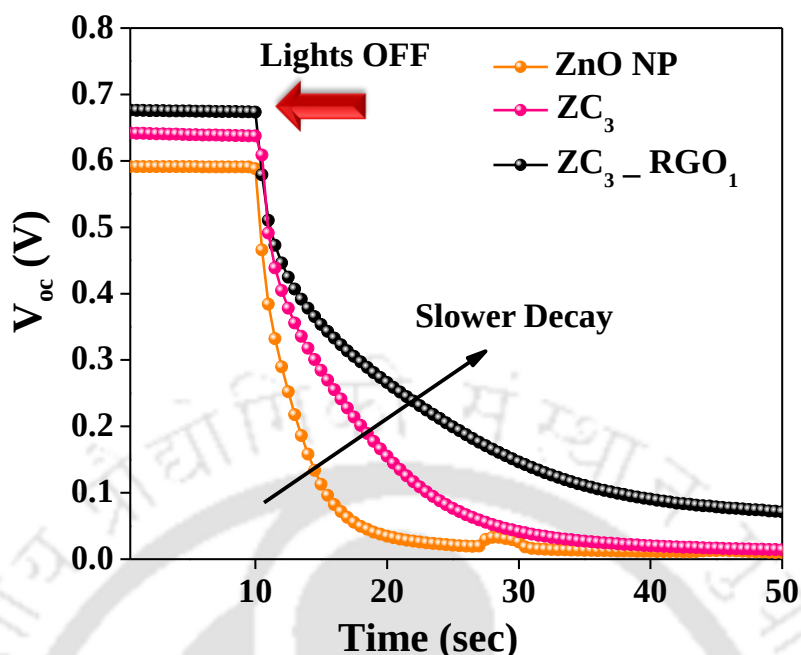


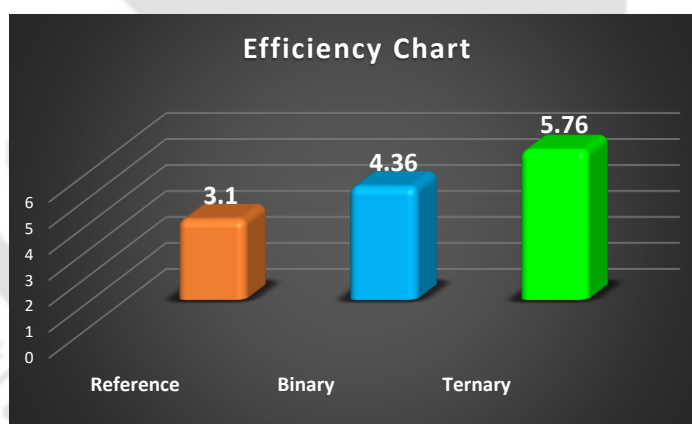
Figure 5.3.15. OCVD curves for the fabricated devices composed of ZnO NP film (orange line), ZC₃ film (pink line), and ZC₃RGO₁ film (black line) based photoanodes

5.4 CONCLUSIONS

In brief, a cost effective light scattering material i.e. nano-cuboidal CeO₂ with well-defined edges and high quality mirror like facets have been synthesized and introduced as composite material into ZnO NP based photoanode and its effect on photovoltaic behaviour has been evaluated. CeO₂ NC owing to its size in the Mie scattering range boosts the light harvesting efficiency through enhanced interactions of incident light with the absorber i.e. dye, by multiple scattering as well reflections from mirror like facets within the photoanode ensemble. Additionally, uniquely aligned band positions of ZnO and CeO₂ allow efficient separation of photo-induced charges through IPCT, thus increases the charge injection rate and reducing the recombination probability. CeO₂ owing to its CB position act as a partial energy barrier to the photo-injected electrons at ZnO. Moreover, inclusion of 2D- RGO to the optimized binary hybrid devices by a convenient ultrasonication technique, substantially increased the device efficacy owing to the better charge injection, transport as well as collection through 2D RGO sheets. Higher recombination resistance (R_{rec}) values and photo-generated electron life time i.e. τ_e , for nano-cuboidal CeO₂ and 2D- RGO loaded devices signifies a reduced reverse tunnelling probability of

photoinjected electron, increasing the charge collection efficiency, in turn PCE of the devices. Some of the highlights of this work are as follows,

- ✚ First report on the demonstration of **mirror like nano-cuboidal CeO₂** coupled with **2D-RGO** in the performance parameters of a ternary hybrid photoanode with ZnO nanoparticle
- ✚ A nearby ~ 6% power conversion efficiency has been achieved for photoanode with optimized CeO₂ NC concentration loaded with 1wt% RGO which is ~ 85% higher than the reference device and ~ 32% higher than binary hybrid device.
- ✚ CeO₂ nanocubes serves as a light scattering materials for efficient light absorption as well as partial energy barrier for minimum back recombination at hetero-interfaces.
- ✚ Inclusion of 2D RGO sheets resulted in an increased charge injection kinetics ($k_{\text{inj}} \sim 2.3 \times 10^8 \text{ s}^{-1}$ for ternary, $1.1 \times 10^8 \text{ s}^{-1}$ for reference device) of the devices.



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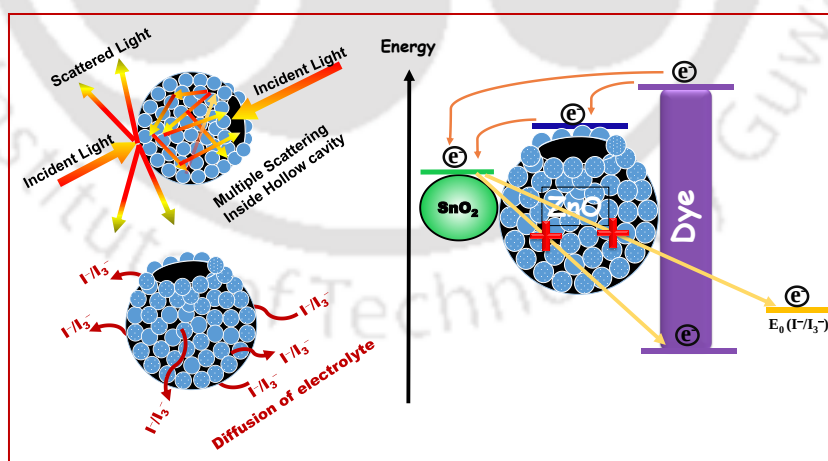
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CHAPTER 6

Nano-amassed mesoporous zinc oxide hollow microspheres as synergy boosters for efficient energy harvesting in SnO_2 based dye-sensitized solar cell

This chapter presents utilization of a micron sized ZnO hollow sphere (HS) formed by assembly of nanocrystalline units in a SnO_2 nanoparticle based dye-sensitized solar cell. Nano-amassed micron sized ZnO HS can boost the light harvesting capability of the photoanode without sacrificing surface area by as well as optical confinement of incident light by multiple reflections within its cavity as well as an enhanced light scattering effects. Improvement in the fill factors of the composite based devices is endorsed to the facile penetration of electrolyte through the pores of nano-amassed meso-ZnO HS, which increases the regeneration probability of oxidized dye.



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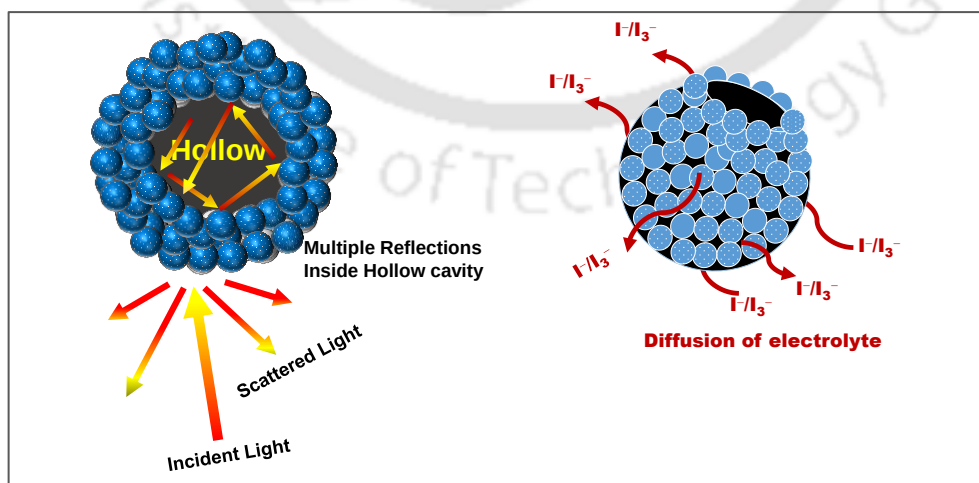
Banik *et al.*, 2018, 3, 14482.

6.1 INTRODUCTION

Numerous wide band gap semiconductors such as ZnO,¹ SnO₂,²⁻⁴ WO₃,⁵ Nb₂O₅,⁶ SrTiO₃⁷ etc. have been explored as the potential photoanodic materials alternative to traditional TiO₂ in DSSCs. Among them SnO₂ and ZnO has been found to be most appealing. SnO₂, a stable, n-type semiconductor has two distinct advantages over TiO₂ in terms of higher electron mobility⁸ (SnO₂ ~ 100–200 cm² V⁻¹ s⁻¹, TiO₂ ~ 0.1–1 cm² V⁻¹ s⁻¹) and wider band gap (SnO₂ ~ 3.6 eV, TiO₂ ~ 3.2 eV).⁹ The higher electron mobility of SnO₂ promotes faster transport of photo-injected electron to the collector electrode i.e. fluorine doped tin oxide (FTO),¹⁰ thus reducing the recombination probability of photo-induced electrons, whereas higher band gap tends to create fewer oxidative holes at the valence band minimizing the dye degradation rate and improves long term stability of DSSCs.¹¹ Furthermore, SnO₂ forms homo-junction with the FTO substrate, thus resolves the high contact resistance issue originated from the hetero-junction formed between other metal oxides (like TiO₂, ZnO) and FTO.¹² Despite these advantages, solar cells using SnO₂ as photoanodes suffer from a low energy-conversion efficiency as compared to TiO₂. The inferior photovoltaic performance of SnO₂ based DSSCs can be endorsed to i) faster electron recombination kinetics at semiconductor/sensitizer/electrolyte interface and a lower open circuit voltage (V_{oc}) value owing to intrinsically lower conduction-band edge of SnO₂ as compared to that of TiO₂, ii) reduced adsorption of dyes having carboxylic acid as an anchoring group at SnO₂ surface, due to lower isoelectric point, IEP ~ 4-5 of SnO₂ as compared to TiO₂ ~ 6-7.¹³ Lower dye adsorption in turn decreases the optical density of the photo-anodic film and its ability to absorb light resulting in a lower number of photo-induced electrons which limits photo current in the devices.¹⁴ “Bare SnO₂ nanoparticle based devices made from SnO₂ nanoparticles only (size ~ 20 nm) with mostly used Ru-based N719 dye rarely show power conversion efficiencies more than PCE ~ 2%.”¹⁵⁻¹⁷ A very convenient strategy to overcome the adverse issues in case of SnO₂ based photoanode is to make composite photo-anodic architecture with other wide band gap metal oxides such as TiO₂,¹⁸ MgO,¹⁹ and ZnO.²⁰⁻²³ It has been seen that in case of SnO₂ based devices, composite photoanode architecture has shown substantial improvement in device performances, resulting from a reduced reverse tunneling probability of photo-generated electrons. In composite photoanode systems, it is believed that a proper combination of electronic structures of constituents (e.g. the conduction band edge, CB edge) and distribution of electron accepting states in the conduction band is a critical factor for a good device performance.²⁴ Zinc Oxide, a typical n type semiconductor, has

higher band edge position as compared to that of SnO_2 with a band gap of ~ 3.37 eV and has the distribution of electron accepting states in the conduction bands similar to SnO_2 i.e. s-orbital.²⁵⁻²⁶ Moreover, zinc oxide is less acidic as compared to SnO_2 , [ZnO (Iso electric point, IEP ~ 9), SnO_2 (IEP ~ 4 -5)] and can achieve diverse morphologies with high crystallinity,²⁷⁻³⁰ making it as a suitable candidate for a composite mixture photoanode for SnO_2 based DSSCs. Apart from the electronic properties, efficient light harvesting is an essential property for a well performing photoanode.³¹ Incorporation of light scattering materials can boost the power conversion efficiency (PCE) in DSSCs by increasing the light harnessing ability of the photoanode films.³²⁻³³ Among them, hollow structures as light scattering materials not only provides higher light absorption probability but also facilitates the diffusion of electrolyte to regenerate the oxidized dye efficiently.³⁴⁻³⁵

This chapter demonstrates the bi-functional effect of nano-amassed micron sized ZnO hollow spheres loading on SnO_2 photovoltaic. Nano-amassed micron sized *meso*- ZnO hollow spheres provide a high surface area with better light harvesting ability owing to its mesoporous nature and hollow architecture. Moreover, ZnO hollow spheres provide pathways for infiltration of liquid electrolyte responsible for regeneration of sensitizer and simultaneously acts as a partial energy barrier owing to high conduction band position in reducing the reverse tunneling probability of photo-induced electrons in semiconductor/sensitizer/electrolyte interface. A schematic of the hollow structure and pathways of scattering and electrolyte diffusion have been shown in scheme 6.1.1.



Scheme 6.1.1 Schematic representation showing light scattering and electrolyte diffusion pathways in a hollow mesoporous structure

6.2 EXPERIMENTAL METHODS

6.2.1 SYNTHESIS OF SnO₂ NANOPARTICLES (SnO₂ NP)

SnO₂ nanoparticles were prepared by adopting a reported protocol.³⁶ In the synthetic procedure, first, 5 mmol of SnCl₂·2H₂O (A.R.) in 50 mL EtOH is dissolved and kept stirring for 30 min. In a 250 mL round-bottom (RB) two-necked flask 50 mL distilled H₂O was added and kept at 100 °C with water-cooled condenser in one end and a dropping funnel at the other. Then the prepared SnCl₂ solution was added slowly to the 250 mL flask containing 50 mL water through dropping funnel under vigorous stirring and the system was kept at 100 °C for 12 h with continuous stirring. The resultant product was centrifuged and washed with distilled H₂O and EtOH for two to three times and dried at 60 °C in an oven. Finally, the powder was calcined at 500 °C for 1 h to obtain the final products for further characterizations.

6.2.2 SYNTHESIS OF NANO-AMASSED MESOPOROUS HOLLOW ZnO MICROSPHERES (*meso* - ZnO HS)

Meso-porous hollow ZnO microspheres have been synthesized using a one-step reflux route following a reported protocol.³⁷ Typically, 2.973 g of zinc nitrate hexahydrate was dissolved in 100 mL of PEG 200 under stirring conditions. Resulting solution was then transferred into a 250 mL RB flask and progressively heated to 160 °C. The system was kept for 6 h under refluxing process and then allowed to cool naturally. The products were collected by centrifugation and washed with absolute EtOH and distilled H₂O for several times and kept at 60 °C for drying. Finally, the brown powders were subjected to calcination for 4 h at 500 °C in a muffle furnace to get the final products.

6.2.3 DEVICE FABRICATION

All the photoanodes were fabricated by making a homogenous paste of SnO₂ NP and SnO₂ NP-ZnO HS composite viz. SZ₁₀, SZ₂₀, SZ₃₀. FTOs were cleaned using soap solution, Milli-Q water and ultrasonically treated in acetone and 2-propanol for 15 min each and then dried. Ozone treatment was done on the cleaned FTO substrates for 30 min using Novascan UV-Ozone chamber.

First, a thin compact layer of SnO₂ was deposited onto the pre-cleaned FTO³⁸ by spin coating a solution of 0.2M SnCl₄·5H₂O in 2-methoxy ethanol followed by calcination at 500 °C. For the preparation of homogeneous pastes, 0.5 g of SnO₂ NP or SnO₂ NP_ZnO HS composites viz. **SZ₁₀**, **SZ₂₀**, **SZ₃₀** were ground with a mixture of acetic acid (0.05ml), acetylacetone (0.1ml), terpineol and PEG-PPG-PEG in an mortar pestle. This homogenous paste was applied SnO₂ compact layer coated FTO using doctor blade technique and the films were dried at 120 °C, followed by calcination at 500 °C for 30 min. The thickness of the photoanode layers were found to be in the range of 13–15 μm, as measured by surface profilometer. These substrates were then immersed for 8 h into N719 dye solution in acetonitrile: *tert*-butanol (7:3) (0.3 mM). Sandwiching the photoanodes and Pt-CE using as a spacer between the electrodes and adding I[−]/I₃[−] electrolyte solution completed the device fabrication. The I[−]/I₃[−] redox mediator was prepared using 0.05 M I₂, 0.5 M LiI, and 0.5 M 4-*tert*-butylpyridine and 0.1 M guanidium thiocyanate in a solvent mixture of acetonitrile: valeronitrile (8.5:1.5, v/v). The active area for all devices were kept 0.16 cm².

6.3 RESULTS AND DISCUSSIONS

6.3.1 POWDER X-RAY DIFFRACTION ANALYSIS

Powder X-ray diffraction (PXRD) patterns were recorded to confirm the phase purity and crystallinity of pristine SnO₂ nanoparticle, ZnO HS and SnO₂_ZnO HS composites viz. **SZ₁₀**, **SZ₂₀** and **SZ₃₀** as shown in Figure 6.3.1. All of the diffraction peaks from lattice planes (110), (101), (200), (111), (211), (220), (002), (310), (112), (301), (202) and (321) were indexed to the formation of tetragonal phase (JCPDS File Card No. 41-1445) of SnO₂ NP with $a = b = 0.474$ nm and $c = 0.317$ nm. The average crystallite sizes of the nanoparticles were evaluated using the Scherrer equation³⁹ from the full-width at half maxima of (110) peak of SnO₂ and is found to be ~ 11.40 nm. On the other hand ZnO HS shows diffraction peaks from lattice planes (100), (002), (101), (102), (110), (103), (112) and (201) and were indexed to the formation of hexagonal wurtzite phase (JCPDS File Card No. 36-1451) of ZnO with no traceable impurity peaks.

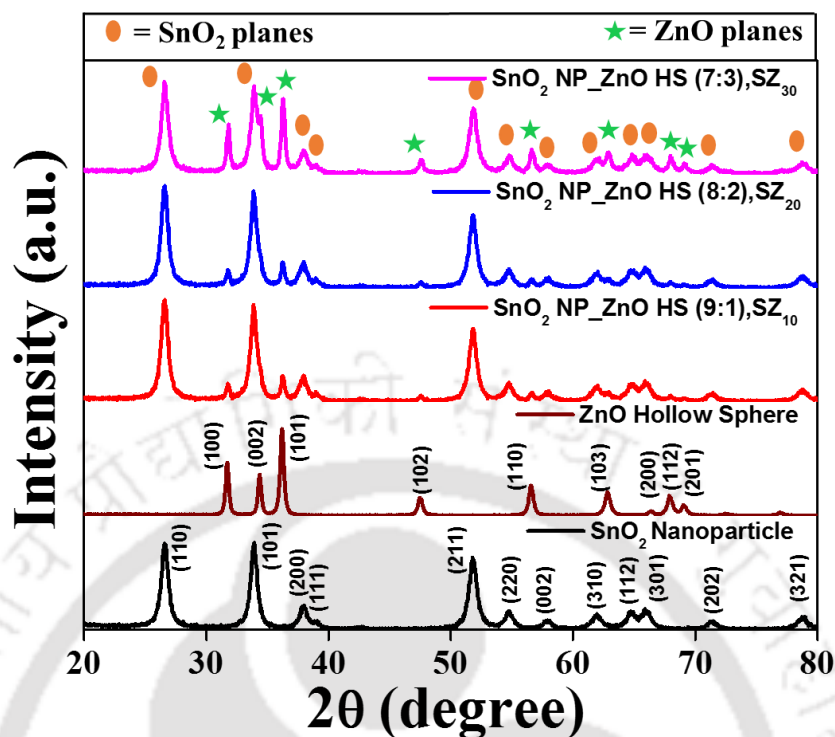


Figure 6.3.1 Powder XRD patterns for SnO₂ nanoparticle film (SnO₂ NP, black line), SnO₂ NP_ZnO HS (9:1) SZ₁₀ (red line), SnO₂ NP_ZnO HS (8:2), SZ₂₀ (blue line) and SnO₂ NP_ZnO HS (7:3), SZ₃₀ (magenta line) films on glass substrates

Notably, the recorded PXRD pattern for composites SZ₁₀, SZ₂₀ and SZ₃₀ shows the diffraction peaks assignable to wurtzite phase of ZnO crystal as well as tetragonal phase of SnO₂ and no other additional impurity peaks observed. It has been seen that with increase in ZnO content, the intensity of ZnO peaks also becomes prominent. To examine any change in average crystallite size of SnO₂ nanoparticle upon ZnO hollow sphere loading the average crystallite sizes of composites SZ₁₀, SZ₂₀, SZ₃₀ were calculated monitoring (110) lattice plane of SnO₂ NP. However, it was observed that with 10%, 20% and 30% loading of ZnO HS did not alter the crystallite size of SnO₂ NP significantly (SnO₂ NP ~ 11.40 nm, SZ₁₀ ~ 11.40 nm, SZ₂₀ ~ 11.39 nm, SZ₃₀ ~ 11.65 nm), indicates crystallinity of SnO₂ NP is retained even after loading of ZnO HS.

6.3.2 RAMAN ANALYSIS

Raman spectroscopy is used to investigate the vibrational characteristics of materials and to identify the crystallization and structural defect. Figure 6.3.2 shows the typical Raman spectra of photoanodes fabricated with SnO₂ nanoparticle and SnO₂ NP_ZnO HS composites viz. SZ₁₀, SZ₂₀, SZ₃₀ at room temperature. For SnO₂ nanoparticle samples a sharp and dominant peak

observed at 633 cm^{-1} is assigned to A_{1g} vibrational mode and peak observed at 773 cm^{-1} is assigned to B_{2g} vibrational mode of tetragonal SnO_2 lattice. A_{1g} (633 cm^{-1}) and B_{2g} (773 cm^{-1}) are related to the symmetric and antisymmetric stretching modes of Sn-O bond.⁴⁰ In case of the composite samples **SZ₁₀**, **SZ₂₀** and **SZ₃₀**, the Raman spectra displayed the presence of both metal oxides, giving evidence of the composite nature of the mixtures. In case of composite **SZ₁₀**, along with the signature peaks of SnO_2 nanoparticle, a sharp and dominant peak was observed at 438 cm^{-1} , assigned to the E_2 (high) mode of wurtzite hexagonal ZnO lattice. This mode is a fingerprint of the hexagonal wurtzite ZnO associated with oxygen displacement.⁴¹ Another suppressed peak at 582 cm^{-1} is ascribed to A_1 (LO) mode, probably occurred due to oxygen vacancy.⁴² As can be seen from the spectra, with the increase in ZnO content from **SZ₁₀** to **SZ₃₀** the peak intensities of the corresponding vibrations of ZnO lattice also increases. It is observed that upon ZnO HS addition there is no shift in peak positions of tetragonal SnO_2 lattice as well as no peaks for any tertiary phases or impurity occurred, corroborating the powder XRD data.

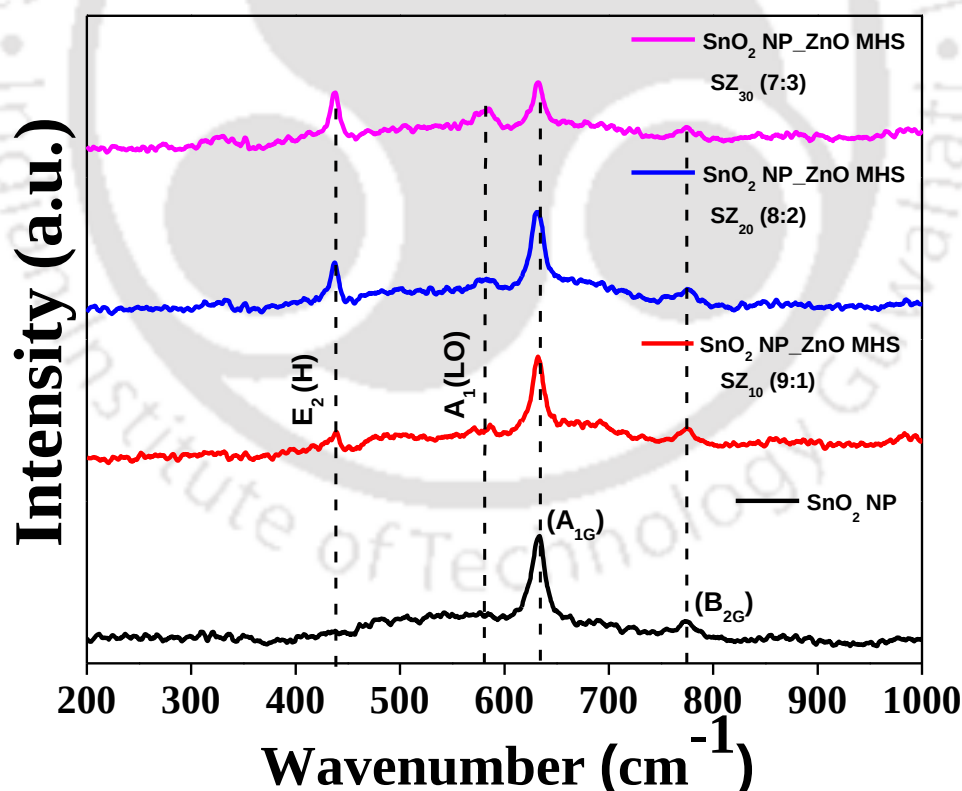


Figure 6.3.2 Raman spectra of SnO_2 nanoparticle film (black line), SnO_2 NP_ ZnO HS (9:1) **SZ₁₀** (red line), SnO_2 NP_ ZnO HS (8:2), **SZ₂₀** (blue line) and SnO_2 NP_ ZnO HS (7:3), **SZ₃₀** (magenta line) all on glass substrates

6.3.3 MATERIAL MORPHOLOGY

The morphological features of the as synthesized materials and photoanodes was studied by carrying out FESEM analysis. Figure 6.3.3 (A) depicts the FESEM images of as synthesized *meso*-ZnO HS. It has been observed that ZnO hollow spheres have an average size dimension of $\sim 1\mu\text{m}$. From the FESEM image, Fig 6.3.3 (B), it is clearly evident that as synthesized hollow spheres are composed of self-assembled small ZnO nanoparticles with diameter of $\sim 30\text{-}50\text{ nm}$. The ZnO hollow spheres are formed by polymer assisted Ostwald ripening of single crystalline ZnO nanoparticles.³⁷ The hollow nature of the micron sized material favours trapping of light within the cavity as well as efficient light scattering in the photoanode while nanoparticles provides comparably higher surface area than solid structures for efficient dye loading. Magnified image of ZnO hollow spheres endorses its porous nature uniformly distributed pores within the hollow spheres to facilitate the diffusion of electrolyte along the material to regenerate the oxidized dye which is a critical factor in performance the photovoltaic device.³⁵

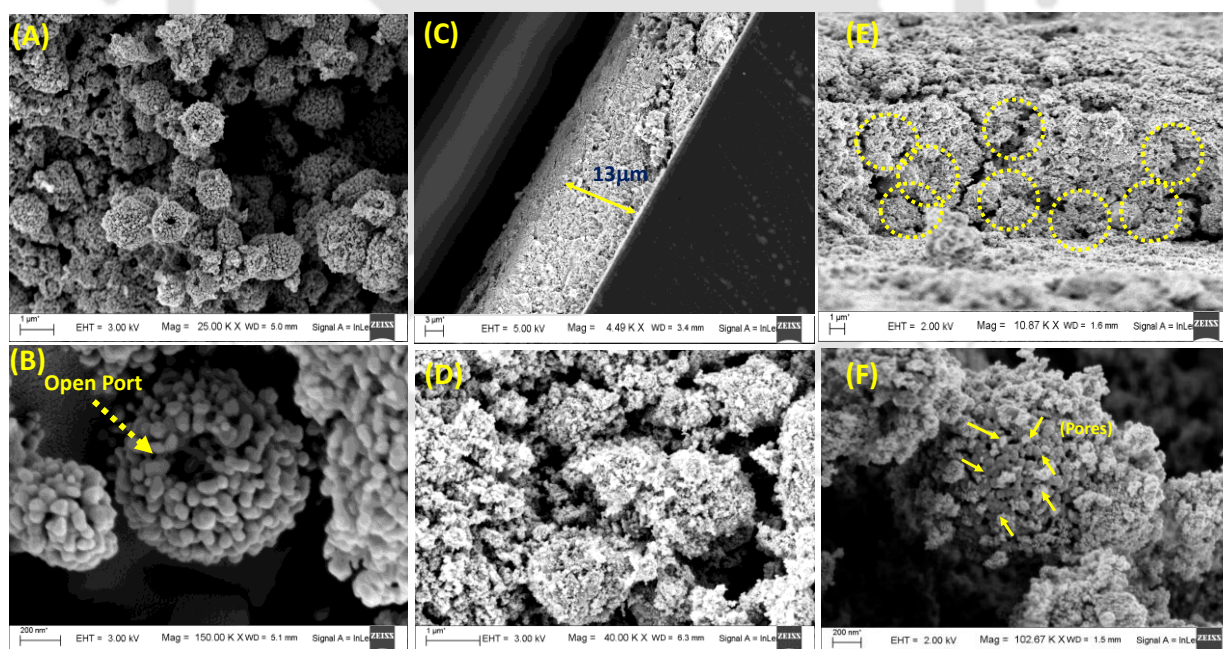


Figure 6.3.3 FESEM and magnified FESEM image of (A-B) *meso*-ZnO HS
(C-F) Cross-sectional images of *SZ*₂₀ photoanode

A detailed top view and cross-sectional FESEM images of fabricated SnO₂ NP_ ZnO HS (8:2), *SZ*₂₀ photoanode (best device performance) have been depicted in Figure 6.3.3 (C-F) at

different magnifications. It can be clearly seen from the cross sectional image that overall thickness of fabricated film is $\sim 13\text{--}15\text{ }\mu\text{m}$ (as seen in profilometer measurements) and shows evenly distributed ZnO HS throughout the region. From the FESEM image of the photoanode it is seen that ZnO HS is well distributed throughout the specified region and the hollow architecture of ZnO HS can be seen from the magnified FESEM images [trace **E** fig. 6.3.3] that facilitates the penetration of electrolyte efficiently.

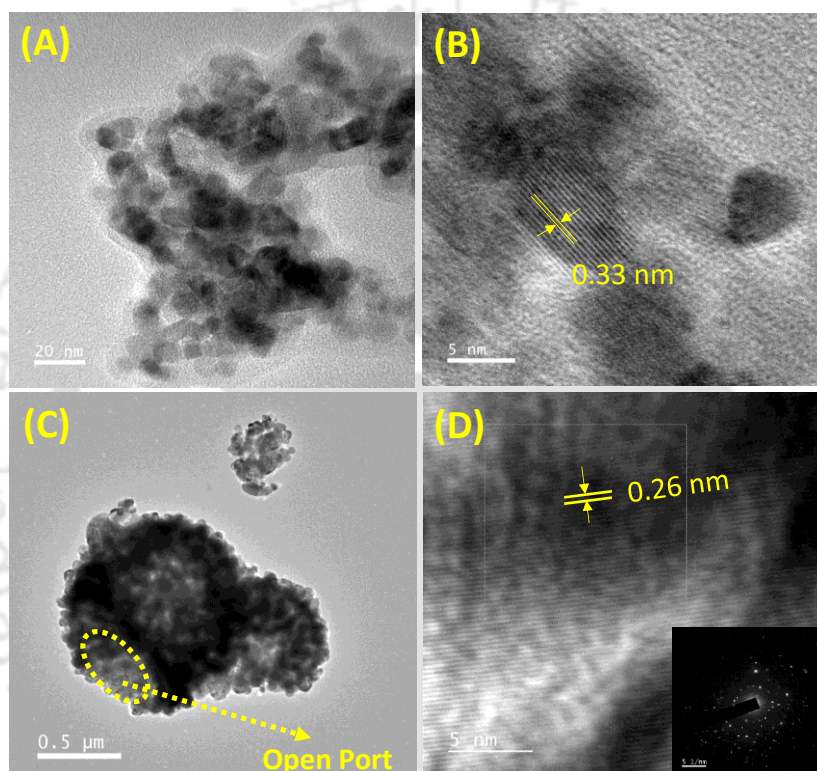


Figure 6.3.4 (A) TEM image of as synthesized SnO₂ nanoparticle. Trace (B) represents the HRTEM image of a SnO₂ displaying growth along lattice plane (110) (C) TEM image of as synthesized ZnO hollow spheres and Trace (D) depicts High resolution TEM image of meso-ZnO HS. Inset shows the SAED pattern of ZnO HS

Figure 6.3.4 represents the TEM images of as synthesized SnO₂ nanoparticles and *meso*-ZnO hollow spheres after ultra-sonication for 1.5hr in ethanol. The average size of SnO₂ nanoparticles as in figure 6.3.4 (A) is found to be in the range of $\sim 10\text{ nm}$. Figure 6.3.4 (B) shows the high-resolution TEM (HRTEM) image of a single SnO₂ nanoparticle with a well-resolved lattice pattern, indicative of its crystalline nature, a prerequisite for the efficient photo-injected charge migration. The SnO₂ nanoparticles exhibit lattice fringes with an interplanar distance (d-spacing) of 0.33 nm that can be indexed as (110) plane, as shown in the HRTEM image. TEM

images [Figure 6.3.4] of the as synthesized *meso*-ZnO hollow spheres sample clearly shows the micrometer size range of the samples in accordance with FESEM analysis. It can be seen from the TEM image that *meso*-ZnO hollow sphere composed of interconnected smaller ZnO nanoparticles (average size ranging from ~ 30 -50 nm) that assembled into a hollow morphology and excellent porosity which is useful for light scattering. Trace (D) depicts the HRTEM of nano-building blocks of *meso*-ZnO HS showing an interplanar distance of $d \sim 0.26$ nm, corresponding to (100) plane. Selected area electron diffraction (SAED) pattern for *meso*-ZnO HS [inset to trace (D)], infers to the single crystalline nature of wurtzite ZnO crystalline structure. The single crystalline nano-building blocks in *meso*-ZnO HS microstructure are responsible for better charge transport as well as provide high surface area for adsorption of sensitizer.

6.3.4 BET SURFACE AREA ANALYSIS

Porous structure and surface area are the two essentials for a material to be used as a photoanodic material in DSSCs. Porous structure provides light trapping as well as electrolyte diffusion while the later tends to increase the dye adsorption providing higher number of species accountable for photo-generated electrons thus increases photocurrent.⁴³ The porous structure and pore size distribution of the as-prepared ZnO hollow spheres are investigated by performing the Brunauer-Emmett-Teller (BET) measurement. As shown in Figure 6.3.5, N₂- physisorption isotherm exhibits type IV isotherm and H3 hysteresis loops according to the Brunauer–Deming–Deming–Teller (BDDT) classification, and thus confirm the characteristic mesoporous nature of ZnO HS, a prerequisite for DSSC applications.⁴⁴⁻⁴⁵

The BET surface area of the ZnO HS was observed to be $\sim 40.3 \text{ m}^2\text{g}^{-1}$. The BJH pore size distribution curve shows the uniformly distributed pores in the range of ~ 15 nm, as can be seen from FESEM analysis. Owing to the mesoporous nature and high surface area, *meso*-ZnO HS can offer sufficient adsorption sites for the dye as well as the electrolyte can easily infiltrate through the holes to regenerate the oxidised sensitizer for a better functioning of the devices which is limited in case of solid hierarchical structures, as depicted in the schematic [inset to fig 6.3.5]. Whereas, the BET surface area for SnO₂ nanoparticle is found to be $46.5 \text{ m}^2/\text{g}$.

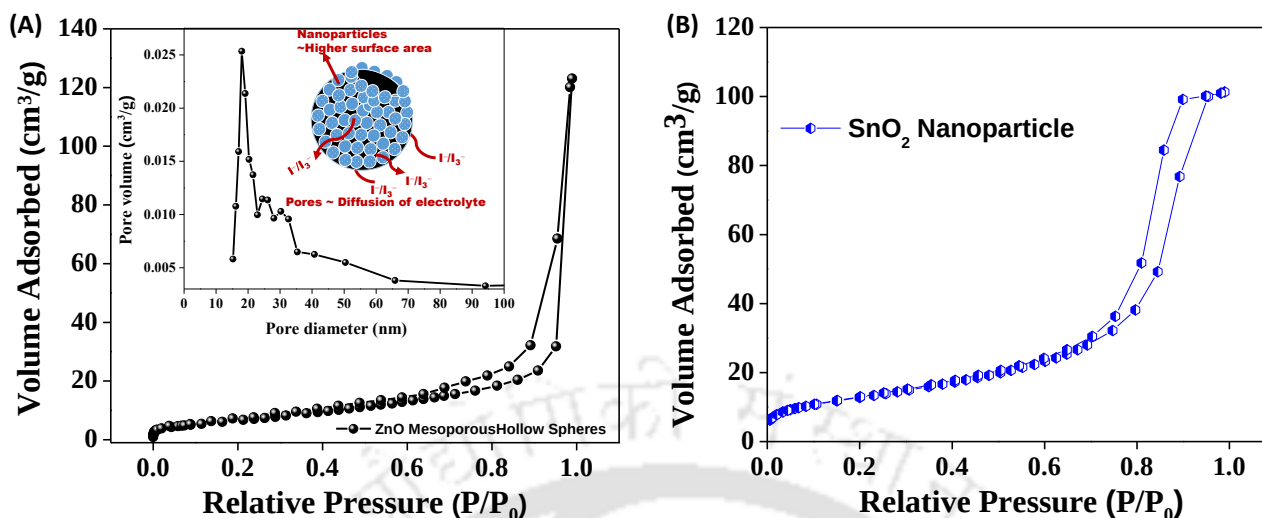


Figure 6.3.5 Nitrogen adsorption-desorption isotherms for (A) *meso*-ZnO hollow spheres. Inset to trace (A) shows BJH pore size distribution plot for *meso*-ZnO hollow spheres and the schematic depicts electrolyte diffusion pathways through the pores (B) SnO₂ nanoparticles

6.3.5 UV-VISIBLE DIFFUSED REFLECTANCE ANALYSIS

Figure 6.3.6 depicts the diffused reflectance measurements carried out for photoanode films based on pristine SnO₂ NP (black line), SZ₁₀ (red line), SZ₂₀ (blue line) and SZ₃₀ (magenta line) deposited on glass substrates prior to dye sensitization. The composite photoanodic film SZ₁₀, containing with 10% ZnO HS shows higher diffused reflectance than the pristine SnO₂ film owing to the multiple reflections of the incident light within the interior cavity of the hollow structure, enhanced scattering in-between hollow spheres and from the ensemble as well.⁴⁶ The diffused reflectance further increases with the increase in ZnO HS content and composite with 30 % ZnO HS (SZ₃₀) exhibits highest reflectance among all the photoanodes in the wavelength range 600–800 nm. It is observed from the EDX analysis (figure 6.3.8) that *meso*-ZnO HS is homogeneously distributed throughout the composite photoanode (champion photoanode, SZ₂₀), contributing to the effective light harvesting through trapping of light by multiple reflection within the cavity as well as by increasing the propagation length by scattering from the ensemble. Pictorial representation of various light scattering pathways in the hybrid photoanode has been depicted in Scheme 6.3.1. Inset to figure 6.3.6 depicts the digital images of different photoanode fabricated using SnO₂ nanoparticle, SZ₁₀, SZ₂₀, SZ₃₀. It has been observed, though SZ₃₀ photoanode shows

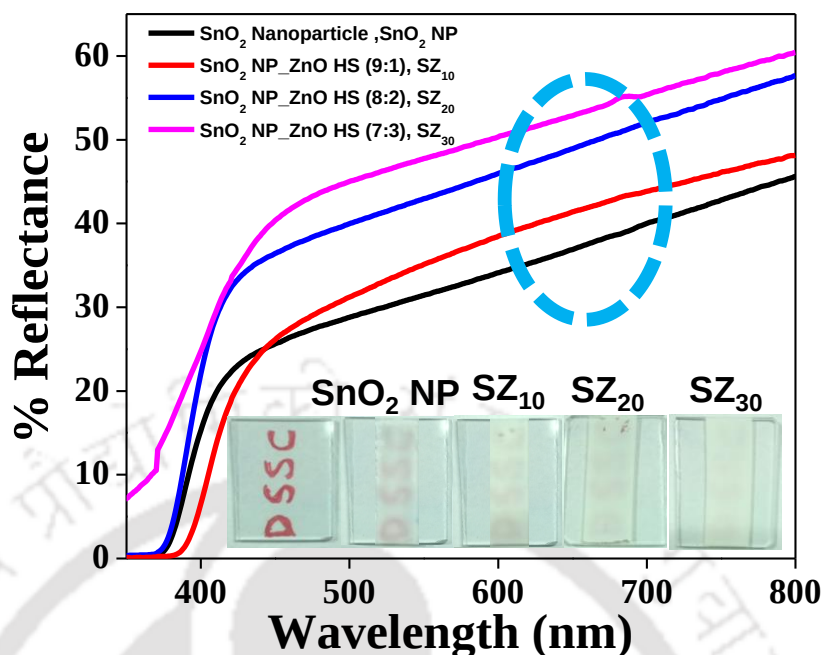
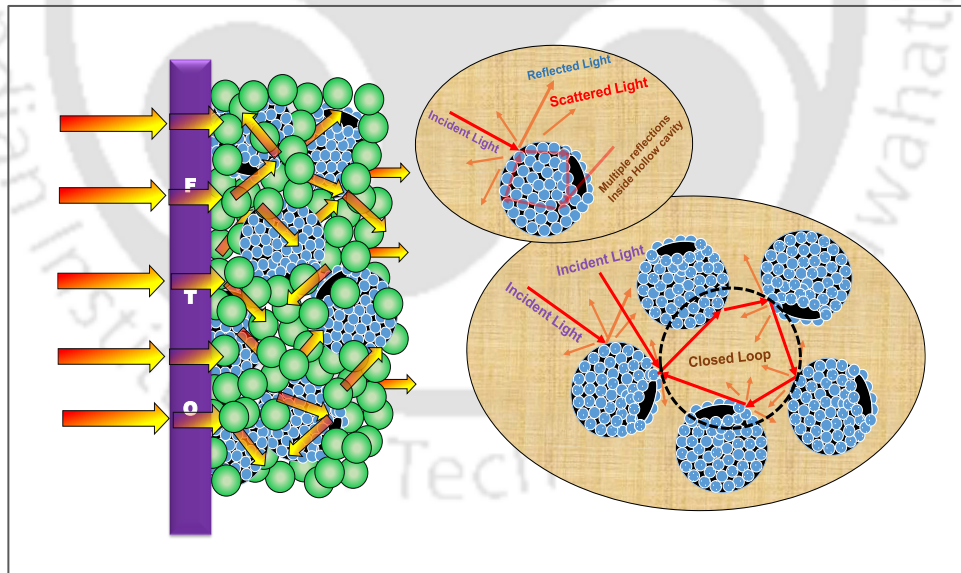


Figure 6.3.6 Ultraviolet-Visible DRS of photoanodes SnO₂ NP film (black line), SnO₂ NP_ZnO HS (9:1), SZ₁₀ (red line), SnO₂ NP_ZnO HS (8:2), SZ₂₀ (blue line) and SnO₂ NP_ZnO HS (7:3), SZ₃₀ (magenta line) on FTO. Inset depicts the digital images of fabricated photoanode with SnO₂ NP, SZ₁₀, SZ₂₀ and SZ₃₀ and a blank FTO for comparison



Scheme 6.3.1 Light scattering pathways in the composite photoanode. Note that incoming photon flux undergoes multiple reflections within the hollow cavity of *meso*-ZnO HS as well as from the ensemble thereby increasing the optical path length. Please note that the light scattering pathways shown here are relative representations only

highest reflectance but at the same time the opaqueness of the photoanodic film increases with increase in concentration of micron sized *meso*-ZnO HS thus preventing the penetration of incident

light, causing adverse effect to the photovoltaic performance. Moreover, amount of back scattered light at FTO junction will increase with ZnO HS content causing hindrance to light penetration.

6.3.6 PHOTOVOLTAIC CHARACTERISTICS OF THE SOLAR CELLS

To explore the potential of hybrid photoanodes in harvesting solar energy, photovoltaic performance of the fabricated SnO₂ NP as well as composite **SZ₁₀**, **SZ₂₀**, **SZ₃₀** based devices are evaluated against Pt counter electrode using I⁻/I₃⁻ redox electrolyte and photovoltaic parameters are summarized in Table 6.3.1. From figure 6.3.7 (A) it is seen that photovoltaic device with pristine SnO₂ nanoparticle exhibited a J_{sc} of ~ 7.82 mA/cm², V_{oc} of ~ 384 mV and FF of ~ 35% affording a PCE of ~ 1.15%. On the other hand ZnO hollow spheres loaded SnO₂ NP composite based devices viz. **SZ₁₀** afforded a PCE of ~ 3.29% with J_{sc} ~ 9.58 mA/cm², V_{oc} ~ 612 mV, FF ~ 56%, and **SZ₂₀** afforded a PCE of ~ 4.37% with J_{sc} ~ 11.01 mA/cm², V_{oc} ~ 632 mV, FF ~ 63% whereas device with 30% ZnO HS, **SZ₃₀** showed lower performance yielding a J_{sc} ~ 8.89 mA/cm², a V_{oc} ~ 638 mV, a FF ~ 64.6% and a PCE ~ 3.67%. The increase in the device efficiency in case of composite photoanode can be mainly attributed to increase in the photocurrent density and open circuit potential. The enhanced J_{sc} in case of composite photoanode **SZ₁₀** and **SZ₂₀** is accredited to better light harvesting capability by photoanodes incorporated with nano-amassed micron sized *meso*-ZnO HS and a reduced recombination of photo generated electrons at semiconductor/sensitizer/electrolyte interface. From the chemisorption analysis it is seen that there is a slight increase in the dye loading capacity of the composite photoanode which may be due to comparable surface area and higher iso-electric point (IEP) value of nano-amassed *meso*-ZnO HS (SnO₂ ~ 4.21 × 10⁻⁸ mol.cm⁻², **SZ₁₀** ~ 4.78 × 10⁻⁸ mol.cm⁻², **SZ₂₀** ~ 4.91 × 10⁻⁸ mol.cm⁻², **SZ₃₀** ~ 4.46 × 10⁻⁸ mol.cm⁻²). Hence the light harvesting in case of composite photoanode is solely due to the higher light scattering properties of the composite photoanode thereby allowing trapping of the incident light within its cavity and increasing the optical path of incident light by scattering phenomenon promoting interaction between incident photons and the dye molecules. The enhanced light scattering by the *meso*-ZnO hollow spheres as well as multiple reflections within the ensemble increases the probability of harvesting the incident light, eventually absorbed by the dye molecule, in return boosting the photo-generated current i.e. J_{sc}. Secondly, the impeded reverse

tunneling probability of photo-generated electron imposed by the higher conduction band level of ZnO as compared to SnO₂ also adds to the increase in J_{sc} .

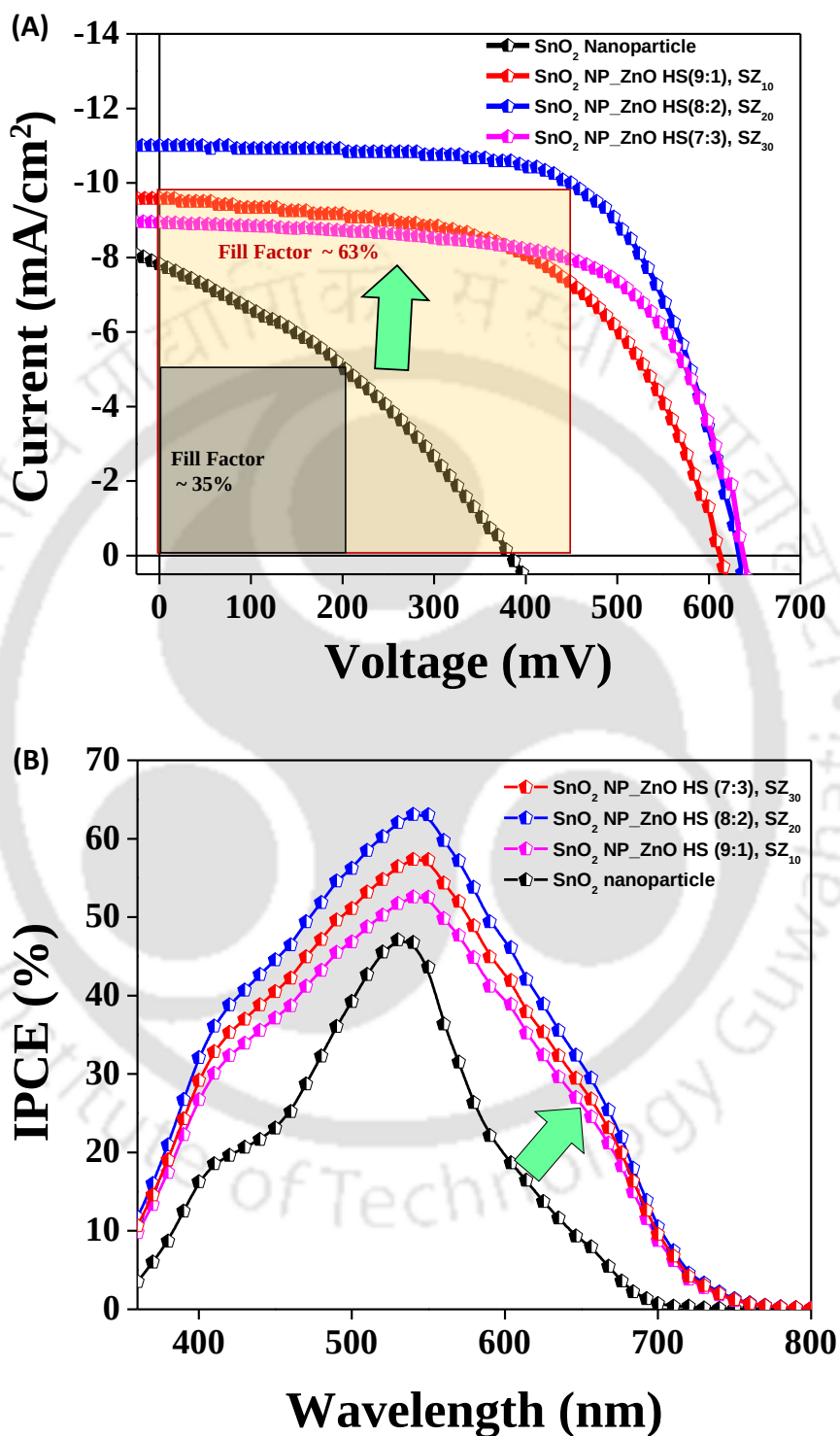


Figure 6.3.7 (A) J–V plots and (B) IPCE plots for DSSCs with SnO₂ nanoparticle film (black line), SnO₂ NP_ZnO HS (9:1) SZ₁₀ (red line), SnO₂ NP_ZnO HS (8:2), SZ₂₀ (blue line) and SnO₂ NP_ZnO HS (7:3), SZ₃₀ (magenta line) photoanodes

Table 6.3.1. Photovoltaic performance parameters for the devices

DSSC photoanode	Thickness (μm)	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF (%)	PCE^a (η, %)	IPCE_{max} (%)
SnO ₂ NP	13.94	7.82	383.4	35.1	1.15	46
SZ ₁₀	14.10	9.58	612.3	56.1	3.29	56
SZ ₂₀	13.89	11.01	632.3	62.8	4.37	62
SZ ₃₀	13.71	8.89	638.2	64.6	3.67	52

^a Data reported for the best performed devices out of five identical devices. Thickness of the champion devices were found to be within the range of reference device as measured by profilometer

The lower value of V_{oc} shown by SnO₂ NP based devices, is due to faster recombination of photo-generated electron from conduction band (CB) of SnO₂ nanoparticle to the redox mediator resulting from the reactive low-energy trap states of SnO₂. Whereas, in case of composite photoanodes we observed a dramatic increase in open circuit potential or V_{oc} (Table 6.3.1). Open circuit voltage or V_{oc} of a dye-sensitized solar cell can be defined as the potential difference between the fermi level of the metal oxide semiconductor and the redox potential of the redox shuttle. The increase in the V_{oc} in case of composite photoanodes can be accredited to the shift of conduction band edge of SnO₂ on addition of ZnO resulting in a higher quasi fermi level as well as reduced back recombination of photo-generated electrons from the CB of SnO₂. The decrease in chemical capacitance of SnO₂ results in a decrease in combined capacitance of mixed electrode, thus shifts the CB position toward the vacuum level.⁴⁷

On the other hand, a significant increase in fill factor (FF) from $\sim 35\%$ (SnO₂ nanoparticle) to $\sim 56\%$ (SZ₁₀) and to $\sim 65\%$ (SZ₃₀) in case of composite photoanode devices has been observed. A good fill factor of a device is indicative of a well-behaved diode structure, where in the voltage and current increases proportionately obtaining the maximum power output from a solar cell. In the present work, increase in the fill factor with the introduction of *meso*-ZnO HS can be attributed to a lower recombination of photo-induced electrons that leads to an improved charge separation. The higher conduction band position of *meso*-ZnO HS serves as a partial energy barrier in reverse tunneling of photo-induced electrons with electrolyte thereby increasing efficiency⁴⁸⁻⁴⁹ whereas the pores of *meso*-ZnO HS provides a highway to regenerate the oxidized species in the respective layers by the redox couple.⁵⁰ Although the scattering ability of photoanode SZ₃₀ is more as compared to the other composite photoanodes, but increase in concentration of ZnO HS from 20% to 30% the device performances deteriorate. This decrease in the device performance can be attributed to increased opaqueness of the photoanode thus hindering the light penetration as a result

the overall photovoltaic performance decreased. With the increase in the amount of nano-amassed *meso*-ZnO HS the amount of back scattered light also increases, leading to a lower light absorption ability.

In order to estimate the photocurrent features of the DSSCs, photocurrent action spectra of the DSSCs are recorded against a wavelength range of 360–800 nm. In principle, the IPCE characteristic of a photovoltaic device depends upon (i) light harvesting efficiency (LHE) of the photoanode, (ii) the quantum yield of photo-induced electron injection and (iii) the efficiency of collecting these injected electrons.⁵¹ Figure 6.3.7 (B) displays photosensitization in the whole visible region achieved by the dye with maximum IPCE values of ~ 46%, ~ 56%, ~ 62% and ~ 52% at ~ 525 nm for SnO₂ nanoparticle, **SZ₁₀**, **SZ₂₀** and **SZ₃₀** based devices respectively. The higher IPCE values at longer wavelength observed in the IPCE spectra in case of composite photoanodes viz. **SZ₁₀**, **SZ₂₀**, **SZ₃₀**, depict an enhanced light harvesting and scattering ability of micron sized ZnO HS which adds to increases the overall PCE of the devices. The better light harnessing ability is accredited to the efficient sensitization of photoanodes with *meso*-ZnO hollow spheres and light confinement within the photoanodes of composite devices owing to the hollow architecture as well as light scattering ability of micron sized *meso*-ZnO HS. These features lead to the enhanced absorption of solar light and an increase in the quantum yield of photo-generated electron injection in the composite devices. Further, the efficient regeneration of the oxidized dye molecule by the electrolyte, due to the facilitated electrolyte diffusion through pores of *meso*-ZnO HS in the photoanodes, reduces the recombination rate and increases the photo-generated charge collection thus improves the IPCE.

From the EDS mapping Figure 6.3.8, it is clearly seen that *meso*- ZnO HS are homogeneously distributed throughout the specified region, leading to a better light trapping and scattering, resulting in a higher light harvesting ability as compared to the pristine SnO₂ nanoparticle based photoanode. The decreased IPCE value in case of **SZ₃₀** as compared to **SZ₂₀** is due to higher back scattering by micron sized *meso*-ZnO HS at the FTO junction as well as increased opaqueness of the photoanodic film device resulting in a reduced charge collection efficacy.

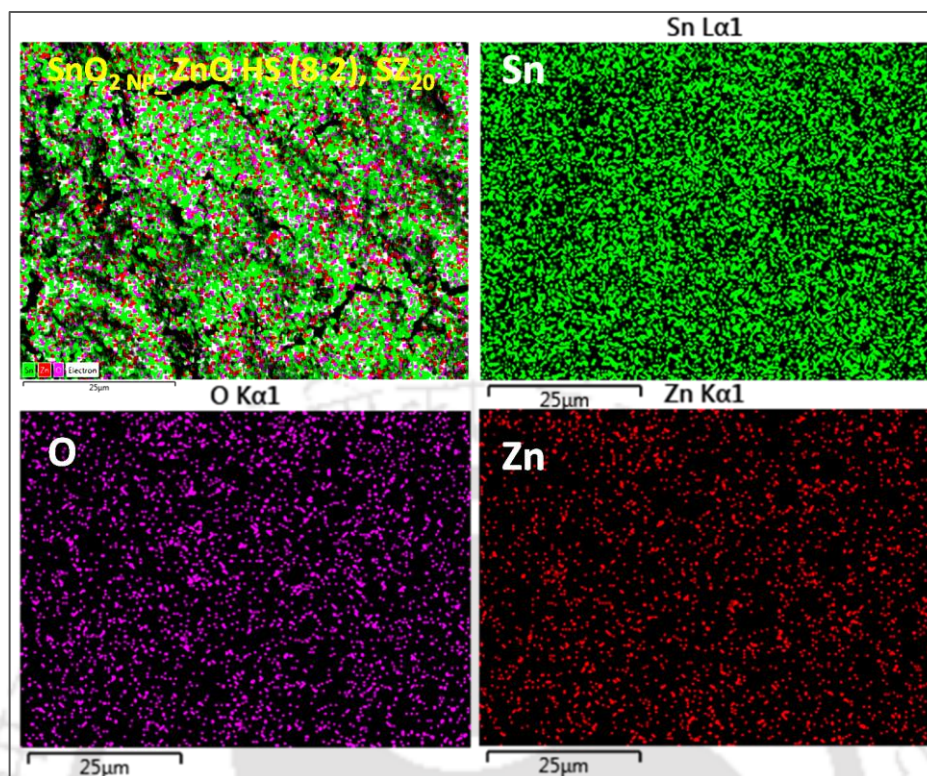


Figure 6.3.8. Energy Dispersive X-ray spectra of best performing composite photoanode viz. SnO_2 NP_ZnO HS (8:2), SZ_{20}

6.3.7 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPIC (EIS) ANALYSIS

Kinetics and energetics of electron transport and interfacial recombination properties in fabricated bare as well as composite DSSCs have been investigated by carrying out EIS measurements for the best-performing devices in a frequency range of 0.1 Hz to 100 KHz under the dark conditions at an external bias equivalent to open circuit voltage (V_{oc}) as shown in figure 6.3.9 (A) and (B) and the fitting data are given in Table 6.3.2. EIS for the DSSCs typically explicates the characteristic charge transfers occurring at various interfaces in different frequency regions, viz. at the counter electrode and electrolyte interface (1–100 KHz), at the semiconductor/sensitizer/electrolyte interface (0.1–1 KHz), and the diffusion of electrolyte (0.1–0.01 KHz).⁵²

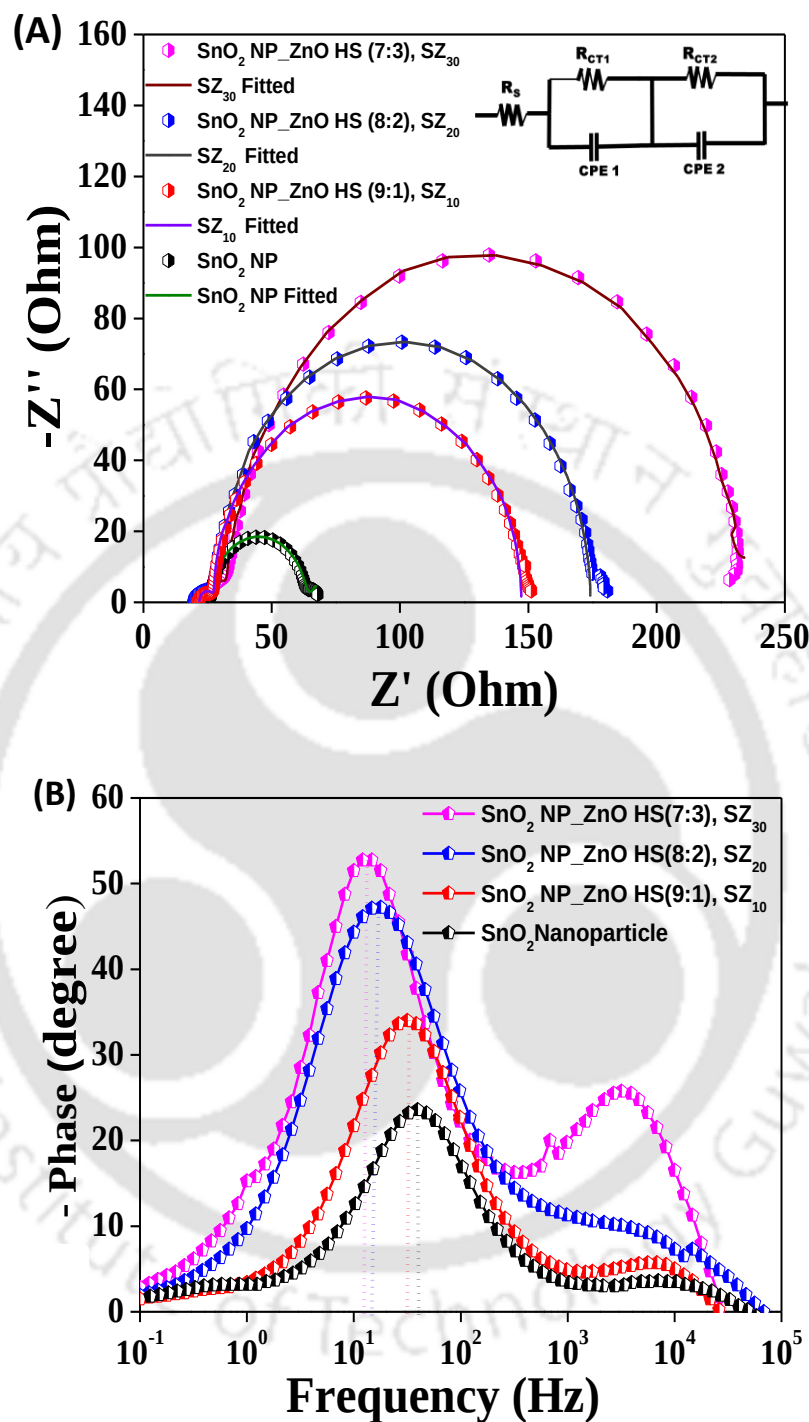


Figure 6.3.9 (A) Nyquist and (B) Bode plots for the fabricated DSSCs composed of SnO₂ nanoparticle film (black line), SnO₂ NP_ ZnO HS (9:1) SZ₁₀ (red line), SnO₂ NP_ ZnO HS (8:2), SZ₂₀ (blue line) and SnO₂ NP_ ZnO HS (7:3), SZ₃₀ (magenta line) devices. Inset to (A) represents the equivalent circuit diagram

In the equivalent circuit, resistance R_s is the sheet resistance related to resistance of the TCO, CE material, and the resistance of electrolyte, R_{ct1} is the charge-transfer resistance of the

counter electrode, CPE1 is the constant-phase element of the counter electrode, R_{ct2} is charge-transfer resistance of the working electrode; CPE2 is the constant-phase element of the working electrode. In typical Nyquist plot, the semicircle in the mid frequency region reveals the charge recombination resistance, which is attributed to the charge-transfer resistance (R_{ct2}) at the metal oxide/sensitizer/electrolyte interface.

Table 6.3.2. Sheet resistance (R_s), Charge recombination resistance at metal oxide/sensitizer/electrolyte interface (R_{ct2}), Maximum peak frequency (f_p), Electron life time (τ_e) values for DSSCs i.e. SnO_2 NP and SnO_2 NP-ZnO HS composite Based Photoanodes viz. **SZ₁₀**, **SZ₂₀**, **SZ₃₀** as obtained from Nyquist plot ^a and Bode phase plot ^b

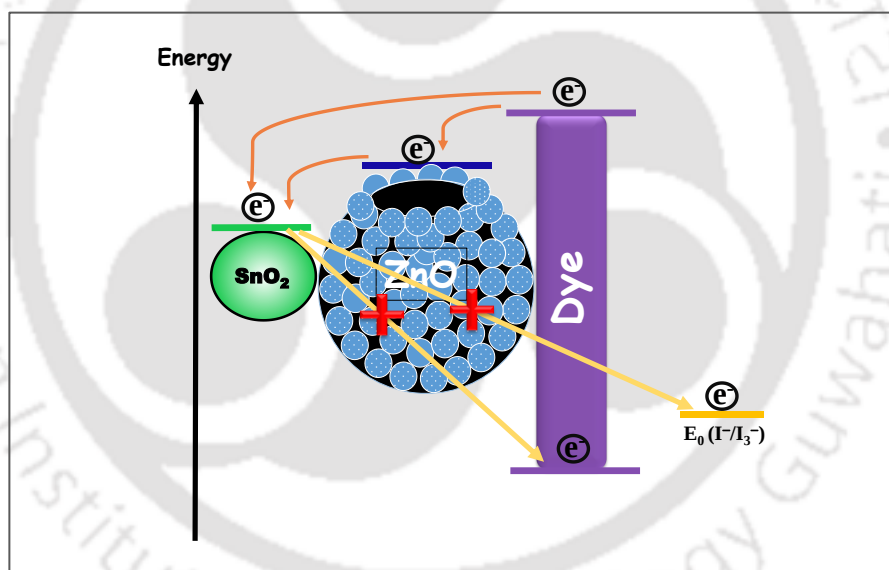
DSSC photoanode	R_s^a (Ohm)	R_{ct2}^a (Ohm)	f_p^b (Hz)	τ_e^b (ms)
SnO_2 NP	22.51	39.5	40.3	3.9
SnO_2 NP _ ZnO HS (9:1), SZ₁₀	21.83	121.2	31.4	5.1
SnO_2 NP _ ZnO HS (8:2), SZ₂₀	20.11	146.3	14.6	10.9
SnO_2 NP _ ZnO HS (7:3), SZ₃₀	21.65	183.5	12.4	12.6

EIS measurements are performed only for the best performed devices

As can be seen from the table **6.3.2**, the charge recombination resistance, R_{ct2} in case of SnO_2 nanoparticle device is quite low ~ 39.5 ohm only, which is due to higher recombination of photo-generated electron at SnO_2 /dye/electrolyte interface corroborating the current-voltage analysis. Whereas, in case of composite photoanode the value of R_{ct2} is much higher than pristine SnO_2 nanoparticle and further increases i.e. from ~ 121.2 ohm in case of **SZ₁₀** to ~ 146.3 ohm in **SZ₂₀** and highest in **SZ₃₀** ~ 183.5 ohm with increase in *meso*-ZnO HS content.⁵³ This observation can be attributed to inhibited recombination of photo-generated electron with introduction of ZnO hollow sphere having higher conduction band level as depicted in scheme **6.3.2**. Moreover, mesoporous ZnO hollow sphere also facilitates the electrolyte diffusion for efficient regeneration of oxidized sensitizer molecule thus preventing recombination of photo-generated electron with oxidized sensitizer.

Corresponding Bode phase plots for the fabricated devices are represented in Figure **6.3.9 (B)**. Two peaks at two different frequency region endorses the two diode interfaces present in DSSC. The characteristic phase angle peak, at the mid-frequency region are located at ~ 40.3 Hz, ~ 31.4 Hz, ~ 14.6 Hz, ~ 12.4 Hz for pristine SnO_2 nanoparticle, **SZ₁₀**, **SZ₂₀** and **SZ₃₀** devices respectively. From the Bode phase plot, the values of photo-induced electron life time τ_e in CBs of

different photoanode based cells can be estimated using the relation $\tau_e = 1/(2\pi f_p)$, where f_p is the observed maximum peak frequency in the mid-frequency region.⁵³ It has been found that the τ_e for different photoanodes are 3.9 ms, 5.1 ms, 10.9 ms, 12.6 ms for SnO₂ nanoparticle, **SZ**₁₀, **SZ**₂₀ and **SZ**₃₀ devices. The gradual increase in the photo-induced electron lifetime for the composite based devices as compared to pristine SnO₂ photoanode based device with increase in *meso*-ZnO HS content also validates the interference created by addition of *meso*-ZnO hollow sphere in the photoanode, acting as a partial barrier for photo-induced electrons to undergo recombination with the oxidized sensitizer and redox mediator at semiconductor/sensitizer/electrolyte interface. Moreover, a type II band alignment formed between well matched band positions of SnO₂ and ZnO heterostructures results in a charge carrier separation (electrons on SnO₂ and holes on ZnO) leads to reduced recombination and thus increases charge carrier lifetimes as shown in scheme 6.3.2.⁵⁴



Scheme 6.3.2 Schematic representation of the inhibited electron interception in case of SnO₂ NP_ ZnO HS composite photoanode at semiconductor/dye/electrolyte interface

The electron recombination kinetics was further investigated by carrying out the transient open circuit voltage decay (OCVD) measurement. Once the light is turned off under open circuit condition, the decrease in electron density in the CB and thus, decay of the V_{oc} is due to electron recombination solely.⁵⁵ The V_{oc} decay rate directly determined by the recombination rate. It is evident from the V_{oc} decay as shown in figure 6.3.10, the SnO₂ nanoparticle based photoanode

has a faster decay as compared to other composite photoanode corroborating the faster recombination kinetics in the device. The V_{oc} decay becomes significantly slow as we move from **SZ₁₀** to **SZ₃₀** inferring a better charge transport and impeded recombination of photo-generated electrons on *meso*-ZnO HS loading. Although the charge transport properties of device with photoanode **SZ₃₀** is better than **SZ₂₀**, till it furnishes lower efficiency that is mainly due to the less dye adsorption as well hindrance in light penetration resulting in a lower photo-generated electron thus decreases photo-generated current whereas the better performance of **SZ₂₀** device can be accredited to optimal concentration of *meso*-ZnO HS loading with combined effect of efficient light harvesting through optical absorption and confinement as well as better charge transport properties at the interface.

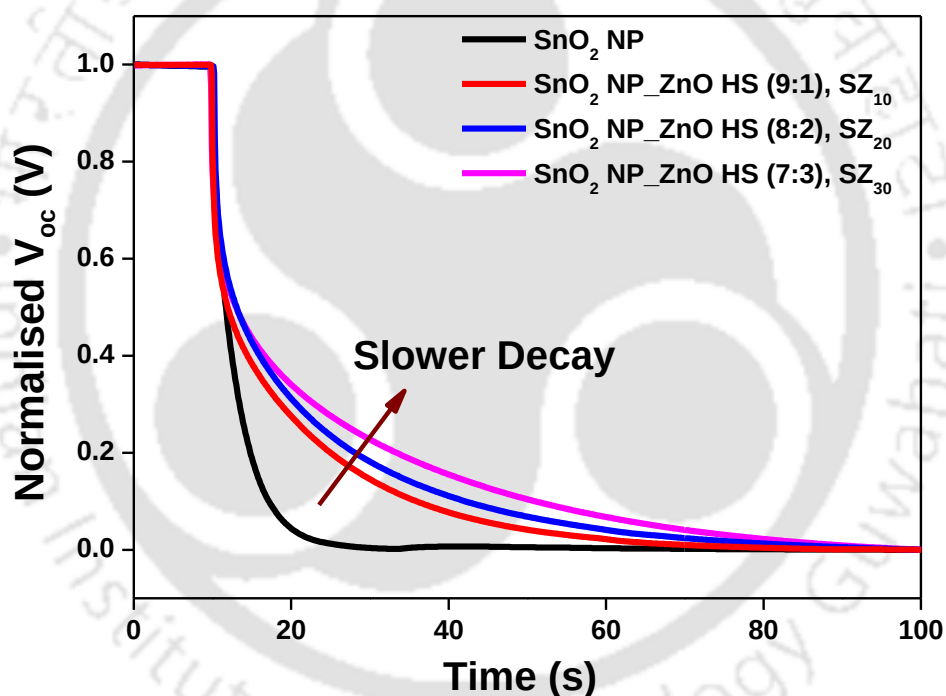


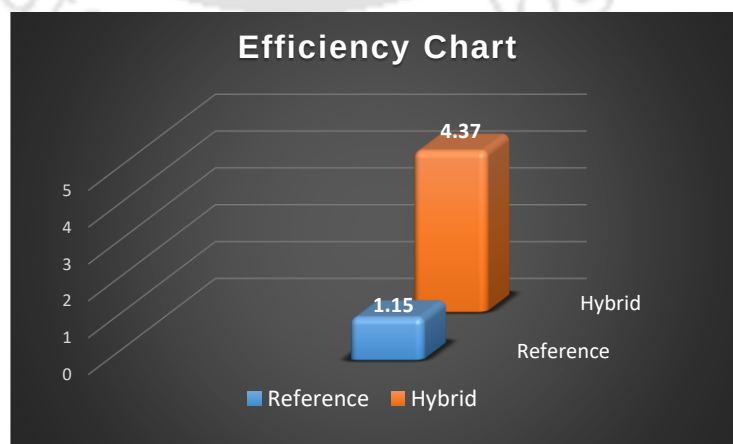
Figure 6.3.10. Normalized V_{oc} decay curves for the fabricated DSSCs composed of SnO_2 nanoparticle film (black line), SnO_2 NP_ ZnO HS (9:1) **SZ₁₀** (red line), SnO_2 NP_ ZnO HS (8:2), **SZ₂₀** (blue line) and SnO_2 NP_ ZnO HS (7:3), **SZ₃₀** (magenta line) based photoanodes

6.4 CONCLUSIONS

In summary, a simplistic and convenient approach for superior light harvesting and impeded reverse tunneling of photo-generated electrons in SnO_2 nanoparticle based DSSC was

demonstrated by introducing a cost effective, easily synthesizable nano-amassed *meso*-ZnO HS. Micron sized *meso*-ZnO HS can effectively scatter the incident light as well as traps the light inside the cavity by multiple reflections thus increasing the probability of harvesting the incident light within the photoanode, eventually absorbed by the dye molecule, thus boosting the device efficacy. On the other hand, *meso*-ZnO HS can act as a partial energy barrier for reverse tunnelling of photo-induced electron at the working electrode/sensitizer/electrolyte interface owing to its higher CB position and also facilitates the diffusion of electrolyte through pores for regenerating the oxidized sensitizer molecule thus preventing recombination of photo-generated electrons. Some of the highlights of this work are as follows,

- ✚ A near **~4-fold increase** in the power conversion efficiency (PCE, η) is displayed by SnO₂ NP_ ZnO HS [for an optimized weight ratio (8:2)] composite photoanode device as compared to pristine SnO₂ NP device.
- ✚ Mesoporous nano-amassed ZnO hollow spheres acts as a light scattering center owing to micron size dimension without compensating the surface area as well as a partial energy barrier for impeded reverse tunneling probability of photo-induced electron at semiconductor/dye/electrolyte interface.
- ✚ **Around ~100% increase** in the fill factors in case of composite based devices is due to facilitated diffusion of electrolyte through the pores of *meso*-ZnO HS, thus increasing the regeneration probability of oxidized dye.



6.5 REFERENCES

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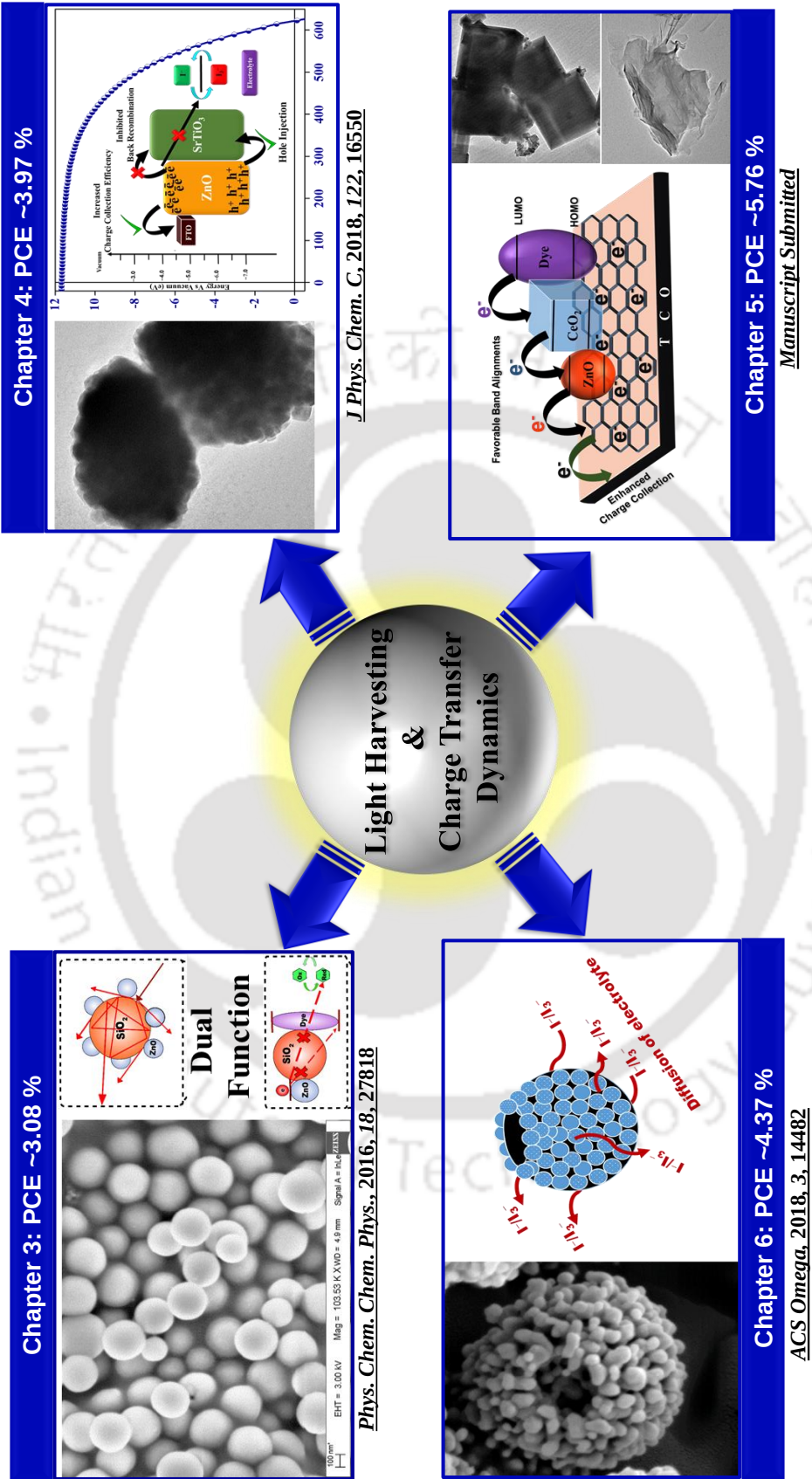


THESIS OVERVIEW & FUTURE SCOPE

Thesis overview :

This thesis presents a number of new prospects related to solar energy harvesting utilizing light scattering phenomenon in dye-sensitized solar cell. Various semiconductor/oxide materials of submicron/micron size dimension have been utilized in the photoanodic section in conjunction with the small sized nanoparticle to form basic architecture of photoanode. Apart from light scattering, utilizing semiconductor materials with favorable energy band positions which can form hetero-junctions led to efficient photo-generated charge separation. Moreover, materials with inherent high charge carrier mobility has also been utilized for better charge transport properties in devices in respective chapter.

- *In **Chapter 3**, we have utilized insulating silica nanospheres of sub-micron sized in a binary hybrid photoanode with zinc oxide nanoparticle. Binary hybrid devices yielded a ~22% enhancement in power conversion efficiency (PCE) owing to better light harvesting and impeded back transfer of photo-injected electrons at hetero-interface.*
- *In **Chapter 4**, we have utilized nanocube assembled SrTiO₃ microspheres (STO NCMS) in conjunction with ZnO nanoparticles. Scattering of light by bigger STO NCMS improves the light harvesting efficiency of the devices whereas, hetero-junction formed between the well-matched band positions results in a better charge separation yielding a ~2-fold increase in the PCE as compared to reference device.*
- *In **Chapter 5**, we have utilized a ternary hybrid composite utilizing mirror-like nanocuboidal CeO₂ (CeO₂ NC) and 2D-reduced graphene oxide (2D-RGO) sheets in conjunction with ZnO nanoparticle and introduced in the photoanodic segment. Ternary hybrid photoanode based device showed a ~ 85% enhancement in efficacy (binary hybrid device showed only ~ 40%) than reference device owing enhanced light harvesting and charge transport properties.*
- *In **Chapter 6**, we have utilized nano-amassed mesoporous zinc oxide hollow microspheres as synergy boosters for efficient energy harvesting in SnO₂ nanoparticle based dye-sensitized solar cell. An optimized binary hybrid photoanode displayed a near ~ 4-fold increase in the power conversion efficiency as compared to pristine SnO₂ NP device owing to better light scattering, inhibited recombination at hetero-interfaces as well as facilitated electrolyte penetration in devices.*



Future Scope:

A good number of research findings are obtained from this thesis in terms of design and development of photoanodic architectures for efficient light harvesting in dye-sensitized solar cell. The materials used in photoanode section of dye-sensitized solar cell are primarily synthesized via hydrothermal or reflux route. The device architecture utilized in the current thesis has a simplified fabrication technique as well as cost effective and can easily be utilized in large-scale processes with much advanced instrumentations. Utilization of two semiconductor with well-matched band positions forming heterojunctions yields lesser photo-induced charge recombination probability. Certainly, many areas worth further extensive research attention in this domain. Few research areas for future work base on our investigations are presented as follows:

- To enhance light absorption capability, UV absorber LSMs can be doped with certain metals/ non-metals so as to introduce mid-gap energy states thus increasing the visible light absorptivity along with the light scattering ability.
- Metal nanoparticles with excellent localized surface plasmon resonance (LSPR) properties can be coupled with LSMs in the photoanode for an enhanced light absorptivity.
- Along with the LSMs which helps to increase the light absorption at higher wavelength regions, rare earth upconversion nanoparticles can be coupled so as to increase the absorptivity in the Infra-Red (IR) region to enhance the efficiency of the device. This domain for photovoltaics is yet to be explored to a large extent.

Journal Articles:

Included in Thesis

1. **Avishek Banik**, Mohammad Shaad Ansari, Mohammad Qureshi, Superior light harnessing and charge injection kinetics utilizing mirror-like nano cuboidal ceria coupled with reduced graphene oxide in zinc oxide nanoparticle based photovoltaics, **Solar Energy**, 2019, **185**, 89.
2. **Avishek Banik**, Mohammad Shaad Ansari, Suhaib Alam, Mohammad Qureshi, Thermodynamic Barrier and Light Scattering Effects of Nanocube Assembled SrTiO₃ in Enhancing the Photovoltaic Properties of Zinc Oxide Based Dye Sensitized Solar Cells **J. Phys. Chem. C**, 2018, **122**, 16550.
3. **Avishek Banik**, Mohammad Shaad Ansari, Mohammad Qureshi,, Efficient Energy Harvesting in SnO₂-Based Dye-Sensitized Solar Cells Utilizing Nano-Amassed Mesoporous Zinc Oxide Hollow Microspheres as Synergy Boosters **ACS Omega**, 2018, **3**, 14482.
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Not Included Thesis:

1. Mohammad Shaad Ansari, **Avishek Banik**, Suhaib Alam, Mohammad Qureshi, Combined effect of in-situ grown p-type CuSbS₂ / n-type CdS coupled with hierarchical ZnO nano disks for improved photovoltaic light harvesting efficiency, **J. Power Sources**, 2019, **425**, 204.
2. Adit Kumar Shah, Tushar Kanta Sahu, **Avishek Banik**, Devipriya Gogoi, Nageswara Rao Peela, Mohammad Qureshi, Reduced graphene oxide modified CuBi₂O₄ as an efficient and noble metal free photocathode for superior photoelectrochemical hydrogen production, **Sustainable Energy Fuels**, 2019, **3**, 1554.
3. Tushar Kanta Sahu, Adit Kumar Shah, **Avishek Banik**, Mohammad Qureshi, Enhanced Surface and Bulk Recombination Kinetics by Virtue of Sequential Metal and Nonmetal Incorporation in Hematite-Based Photoanode for Superior Photoelectrochemical Water Oxidation, **ACS Appl. Energy Mater.**, 2019, **2**, 4325.
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- substrates: enhanced photovoltaic and selective sensing applications **J. Mater. Chem. A**, 2018, **6**, 15868.
5. Mohammad Shaad Ansari, Ramesh Maragani, **Avishek Banik**, Rajneesh Misra, Mohammad Qureshi, Enhanced photovoltaic performance using biomass derived nano 3D ZnO hierarchical superstructures and a D-A type Cs-Symmetric triphenylamine linked bisthiazole **Electrochimica Acta**, 2018, **259**, 262.
 6. Tushar Kanta Sahu, Sonia Arora, **Avishek Banik**, Parameswar Krishnan Iyer; Mohammad Qureshi, Efficient and rapid removal of environmental malignant Arsenic (III) and industrial dyes using reusable, recoverable ternary Iron Oxide – ORMOSIL - Graphene Oxide composite **ACS Sustainable Chem. Eng.**, 2017, **5**, 5912.
 7. Mohammad Shaad Ansari, **Avishek Banik**, Mohammad Qureshi, Morphological tuning of photo-booster g-C₃N₄ with higher surface area and better charge transfers for enhanced power conversion efficiency of quantum dot sensitized solar cells **Carbon**, 2017, **121**, 90.
 8. Ramesh Maragani, Mohammad Shaad Ansari, **Avishek Banik**, Rajneesh Misra, Mohammad Qureshi, Cs-Symmetric Triphenylamine-Linked Bisthiazole-Based Metal-Free Donor–Acceptor Organic Dye for Efficient ZnO Nanoparticles-Based Dye-Sensitized Solar Cells: Synthesis, Theoretical Studies, and Photovoltaic Properties **ACS Omega**, 2017, **9**, 5981.
 9. Dipankar Barpuzary, **Avishek Banik**, Gaurangi Gogoi, Mohammad Qureshi, Noble metal-free counter electrode utilizing Cu₂ZnSnS₄ loaded with MoS₂ for efficient solar cells based on ZnO nanowires co-sensitized with CuInS₂–CdSe quantum dots **J. Mater. Chem. A**, 2015, **3**, 14378.
 10. Dipankar Barpuzary, **Avishek Banik**, Aditya Narayan Panda, Mohammad Qureshi, Mimicking the Heteroleptic Dyes for an Efficient 1DZnO Based Dye-Sensitized Solar Cell Using Homoleptic Ruthenium(II) Dipyrrodo-Phenazine Complex as a Photosensitizer **J. Phys. Chem. C**, 2015, **119**, 3892.

Conferences and Workshops Attended

1. International conference Nanotechnology: Ideas, Innovations & Initiatives (ICN:3I) 2017, Indian Institute of Technology Roorkee, Uttarakhand, India (**Oral presentation**)
2. 5th National Workshop on NEMS/MEMS and Theranostics Devices-2019, Department of Nanotechnology, Indian Institute of Technology Guwahati, Guwahati, India (**Poster presentation**).

3. *International Conference on Frontiers in Chemical Sciences (FICS)*, 2018, Indian Institute of Technology Guwahati, Guwahati, India (**Poster presentation**).
 4. *4th National Workshop on NEMS/MEMS and Theranostics Devices-2018*, Department of Nanotechnology, Indian Institute of Technology Guwahati, Guwahati, India (**Poster presentation**).
 5. *International Conference on Sophisticated Instruments in Modern Research (ICSIMR)*, 2017, Indian Institute of Technology Guwahati, Guwahati (**Poster presentation**)
 6. *5th International Conference on Advanced Nanomaterials and Nanotechnology (ICANN)*, 2017, Indian Institute of Technology Guwahati, Guwahati (**Poster presentation**)
 7. *20th CRSI national symposium in chemistry*, 2017, Department of Chemistry, Gauhati University, Guwahati, India (**Poster presentation**)
 8. *National Conference on Frontiers in Chemical Sciences (FICS)*, 2016, Indian Institute of Technology Guwahati, Guwahati, India (**Poster presentation**).
 9. *4th International Conference on Advanced Nanomaterials and Nanotechnology (ICANN)*, 2015 at Indian Institute of Technology Guwahati, Guwahati, Assam, India (**Attended**).
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