SYNOPSIS

Synthesis of gold nanoparticles (AuNPs) has gained importance as they possess unique chemical, physical, biological and optoelectronic properties which depend on shape and size of nanoparticles and are exploited in a wide range of applications such as in biology, chemical sensing of single molecule, controlled release, catalysis, and immunoassays, medical, electronics, materials science, alternative energy generation, environmental restoration. To cater the demand of AuNPs, various conventional synthesis methods such as seed growth, laser/photo irradiation, chemical vapour deposition, solvolysis, thermolytic reduction, solvothermal, sonochemical, electrochemical, chemical and microwave reduction, etc., have been employed for the synthesis of AuNPs.

Conventional physical and chemical methods of AuNPs synthesis mostly rely on the use of synthetic chemicals and prolonged heating. These methods of AuNPs synthesis involve application of harsh chemicals as reducing and stabilizing agents. Studies have shown that even the purest forms of such synthesized AuNPs carry unreacted traces of the reducing or stabilizing agents, which are potential hazards to human health. Owing to the increased awareness for potential toxicity of AuNPs associated with biological applications, alternative methodologies for biocompatible AuNPs synthesis are gaining importance. Currently, nano fabrication is laying emphasis on the principle of 'green' nanotechnology which advocates the application of environmentally sound and non-polluting methods for synthesis of nanoparticles and their derivatives. There are numerous reports about the synthesis of AuNPs using 'green' method (microbes) in literature. However, microbial mediated synthesis of AuNPs is not ideal as it is having some substantial limitations such as uncontrollability over shape, size and importantly, crystallinity of AuNPs. Therefore, synthesis of AuNPs using plant extracts has gained importance as they can address all the limitation associated with microbial synthesis. To

accomplish the same, we fixed the following as the objectives of the present research work:

1. Screening of indigenous plant and fruit extracts for gold nanoparticles synthesis.
2. Synthesis of gold nanoparticles using screened plant and fruit extracts.
3. Characterization and functionalization of the gold nanoparticles.

We have tried to screen out the reducing, capping and dispersing capabilities of plant and fruit extracts for the synthesis of AuNPs in this present investigation. We have successfully synthesized AuNPs using some indigenous medicinal plant and fruit extracts such as *Mentha arvensis* leaf extract (MLE), *Fagopyrum esculentum* leaf extract (FLE), *Andrographis paniculata* (ALE), *Piper betle* leaf extract (PLE), *Cocos nucifera* (coconut water; CW), *Solanum indicum* fruit extract (SFE) and *Sapindus mukorossi* fruit extracts (SmFE) and *Calotropis procera* Aqueous fraction of latex. We have employed various methods to mediate the synthesis of AuNPs includes heat, UV irradiation, microwave irradiation and sonocatalysis. The synthesized AuNPs were extensively characterized with biophysical tools.

Overall the thesis is divided into six chapters as described below.

Chapter One: Introduction & Review of Literature.

Chapter Two: Heat Mediated Synthesis of Gold Nanoparticles Using *Mentha arvensis.*

Chapter Three: Sonocatalytic UV Light Mediated Synthesis of Gold Nanoparticles Using *Bacopa monnieri* Leaf Extract.

Chapter Four: Microwave Mediated Synthesis of Gold Nanoparticles using Plant and Fruit extracts.

Chapter Five: Sonocatalytic Synthesis of Gold Nanoparticles and Functionalized with PCL, GL and PCL-GL composites.

Chapter Six: Summary and future prospects.

Chapter One deals with brief introduction on the concept of nanotechnology and comparison of 'nano' with the macroscopic matter which is visible with the naked eye. This chapter opens with a short description of different types of nanomaterials and its properties. It also confronts about the gold history, discovery and first synthesis and usage of gold nanoparticles. It mainly describes the fundamental understanding of gold nanoparticles and their synthesis method with an emphasis of analytical and non analytical applications in various fields. At the end this chapter presents the brief overview of nanotechnology and gold nanoparticles.

Chapter Two describes heat mediated synthesis of AuNPs using ethanolic extract of *Mentha arvensis* leaves, an edible plant used as a condiment and traditional medicine in India. UV-Vis spectroscopy analysis confirmed the formation of gold nanoparticles. The different reaction parameters such as plant extract, gold solution, temperature and time were optimized for the synthesis of AuNPs. Typical bright-field TEM image of AuNPs with optimum reaction conditions, which reveals that nanoparticles are of hexagonal and nearly circular shape. The synthesized AuNPs were stable even after 6 weeks of storage at room temperature. The crystalline nature of AuNPs was confirmed with X-ray diffraction analysis. The crystallinity of AuNPs also confirmed from the typical selected area electron diffraction (SAED) and XRD pattern with bright circular rings corresponding to the (1 1 1), (2 0 0), and (2 2 0) planes corresponding to gold lattice fringes. In addition to gold, energy-dispersive X-ray analysis (EDX) showed the presence of carbon and oxygen elements. The evidence from Fourier transform infrared (FTIR) spectroscopy and energy-dispersive X-ray analysis (EDX) suggested that flavonoids and phenol compounds were involved in reduction and stability of AuNPs synthesized using

Mentha arvensis leaf extract. The UV-Vis spectroscopic analysis displayed an intense peak at 530±10 nm indicating the formation of AuNPs that can be used for biomedical applications.

Chapter Three demonstrates the green synthesis field for AuNPs synthesis using *Bacopa monnieri* leaf extract (BLE) and UV irradiation. The reducing and capping functions provided by BLE can replace synthetic reducing and stabilizing agents required for nanoparticles synthesis. UV irradiation in aqueous reaction mixtures generates hydroxyl radicals from aqueous solution and free electrons from bioactive molecules which can reduce the gold salt (Au^{3+}) to corresponding gold nanoparticles (Au^{o}). The bioactive molecules present in BLE are known to act as potential reducing agents and we speculated that they are involved in the reduction of the $HAuCl_4$ (Au^{3+}) to AuNPs (Au^{o}) by donating the free electrons or •-electrons. We observed the solution containing gold ions (Au^{3+}) and BLE turned into ruby red after 15 min of UV irradiation (~254 nm). We investigated the parameters (BLE, chlor auric acid, time) for the AuNPs synthesis. The synthesized AuNPs were extensively characterized by biophysical tools to reveal their properties. TGA spectrum of AuNPs occurs over a wide temperature range (225–580 ^{o}C) which revealed the significant weight loss (5%) of AuNPs. This clearly indicated that bioactive molecules were capped on the AuNPs and were completely degraded due to high temperature. These capped AuNPs were tested on the human cancer cell lines (HeLa, MCF-7) and were found to be biocompatible opportunities for use in drug delivery, molecular imaging and therapy.

Chapter Four confronts the 'green' opportunity for the production of gold nanoparticles with a very less time. This chapter deals with investigations of reducing and stabilizing capabilities of *Fagopyrum esculentum* leaf extract (FLE), *Piper betle* leaf extract (PLE), *Cocos nucifera* (CW), *Solanum indicum* fruit extract (SFE) and *Sapindus*

mukorossi fruit extracts (SmFE) and Aqueous fraction (AF) of *Calotropis procera* latex for the synthesis of the AuNPs. We have used the microwave irradiation for the AuNPs synthesis. Microwave (MW) dielectric heating is a fast emerging and widely accepted new processing technology for a variety of inorganic synthesis and biomedical applications. Compared to the conventional heating, MW irradiation shortens reaction times and improve yield without causing any appreciable alteration in the composition of products of a chemical reaction. In contrast to general heating treatment, MW synthesis favors homogeneous heating through the entire bulk of the reaction mixture in a container, leading to a more homogeneous and easy nucleation of noble metal nanoparticles. UV-visible spectroscopy analysis indicated the successful formation of gold nanoparticles. We have optimized the parameters for the synthesis of AuNPs using FLE (0.4% FLE, 1 mmol/L $HAuCl_4$ and 16 s MW irradiation time), PLE (2% PLE, 0.5 mM $HAuCl_4$, and 18 s MW irradiation time), CW (0.250 mM HAuCl4 for 17 s), SFE (0.03% FLE, 0.5 mM $HAuCl_4$ and 20 sec MW irradiation time), SmFE (8% PFE, 1 mM $HAuCl_4$ and 25 sec of MW irradiation time) and *C. procera* (AF) (3% procera latex, 1mM $HAuCl_4$ and 40 sec MW irradiation).

We have employed the TEM technique to visualize the size and shape of formed AuNPs and showed shapes of triangular, hexagonal, rod shaped and spherical. XRD pattern suggested that the AuNPs synthesized by plant materials were crystalline in nature. Intense diffraction peaks were clearly observed at (111), (200) and (220) corresponding to the Bragg's angles at 38.1°, 44.4° and 64.5°, respectively. FT-IR, NMR and EDX analyses demonstrated the presence of biomolecules on the surface of AuNPs arising from the strong reducing molecules such as phenolic compounds, flavonoids and antioxidants which are involved in the reduction of gold salts to AuNPs. Cytotoxicity studies revealed that there is no significant toxicity of AuNPs on the proliferation of cells.

The small size of AuNPs synthesized with these plant leaf extracts provides an opportunity for safe delivery to sub cellular organelles and applications in molecular imaging and therapy.

Chapter Five confronts the sonocatalytic mediated synthesis of AuNPs. In this study, we determined the optimum conditions for synthesis of AuNPs by using ethanolic extract of *A. paniculata* as ALE, $HAuCl_4$, amplitude, ultrasonication and pH time for the spherical synthesis of the AuNPs. Biomolecules such as flavonoids and phenolic compounds found in *A. paniculata* are involved in the reduction of gold ions to AuNPs. The properties of synthesized AuNPs were extensively characterized with biophysical tools. The crystalline nature of the synthesized AuNPs was confirmed from the selected area electron diffraction (SAED) pattern with bright circular rings corresponding to the (1 1 1), (2 0 0), and (2 2 0) planes. We observed the different coloured colloidal solutions for AuNP–PCL, AuNP–GL, and AuNP–PCL–GL composites. The successful functionalization of PCL, GL, and PCL–GL onto the AuNPs was confirmed from XRD and FT-IR analyses. The cytotoxic studies revealed that the maximum dose (100 µmol/L) of synthesized AuNPs showed insignificant toxicity on HeLa and MCF-7 cells. The rapidness and eco-friendly method mentioned here for the synthesis of AuNPs provides an opportunity for application in drug delivery and molecular imaging.

Chapter Six presents the overall summary of the investigations, and the scope for further studies. This chapter present the outline of synthesis of AuNPs using some indigenous medicinal plant and fruit extracts from North East India, includes *Fagopyrum esculentum* leaf extract (FLE), *Piper betle* leaf extract (PLE), *Cocos nucifera* (coconut water; CW), *Solanum indicum* fruit extract (SFE) and *Sapindus mukorossi* fruit extracts (SmFE) and *Calotropis procera* Aqueous fraction of latex. This chapter also confronts various methods to mediate the synthesis of AuNPs such as heat, UV irradiation,

microwave irradiation and sonocatalysis. The work presented in the thesis has been peer reviewed and resulted in the following international journal publications and reprints are included under section of list of publication:

1. **Babu PJ**, Sharma P, Saranya S, Bora U. UV Light mediated synthesis of gold nanoparticles using ethonolic leaf extract of *Bacopa monnieri*. Materials Letters. 2012; 93: 431–434.
2. **Babu PJ,** Sharma P, Bora U. *Sapindus mukorossi* aqueous fruit extract as reducing, capping and dispersing agents in synthesis of gold nanoparticles. (Accepted for publication in Micro and Nano Letters, 2012).
3. **Babu PJ,** Saranya S, Sharma P, Tamuli R, Bora U. Sonocatalytic Synthesis of Gold Nanoparticles Using Ethnolic Extract of *Andrographis paniculata* and Functionalization with Gelatin-Polycaprolactone Composites. Front Mater Sci. 2012**;** 6(3): 236–249.
4. **Babu PJ**, Das RK, Gogoi N, Sharma P, Bora U. Microwave mediated rapid synthesis of gold nanoparticles using *Calotropis procera* latex and study of optical properties. ISRN Nanomaterials. 2012: 1–6.
5. **Babu PJ**, Sharma P, Saranya S, Tamuli R, Bora U. *Piper betle* Mediated Green Synthesis of Biocompatible Gold Nanoparticles. International Nano Letters. 2012; 2:18–28.
6. **Babu PJ,** Sharma P, Kalita MC, Bora U. Green Synthesis of Biocompatible Gold Nanoparticles Using *Fagopyrum esculentum* Leaf Extract. Front Mater Sci. 2011**;** 5(4): 379–387**.**

7. **Babu PJ,** Das RK, Kumar A, Bora U. Microwave Mediated Synthesis of Gold Nanoparticles Using Coconut Water. Int J Green Nanotechnol Biomed. 2011; 3:13–21.
8. **Babu PJ,** Sharma P, Borthakur BB, Das RK, Nahar P, Bora U. Synthesis of Gold Nanoparticles Using *Mentha arvensis* Leaf Extract. Int J Green Nanotechnol Phys and chem. **2010;** 2(2): 62–68.

Manuscripts in Communication

9. **Babu PJ,** Saranya S, Sharma P, Tamuli R, Bora U. Green Synthesis and Characterization of Biocompatible Gold Nanoparticles Using *Solanum indicum* Fruits (Minor Review under progress in Nanomaterials and Nanotechnology, 2012).