

The current thesis represents the development of eco-friendly and economic efficient route for the optimized synthesis of AgNPs and AuNPs using an aqueous extract of *X. strumarium* and *C. bonplandianum*. For this purpose, the photoinduced route was adopted to avoid the need of even heating and stirring which was the biggest limitation of leaf extract mediated synthesis of AgNPs and AuNPs. The synthesis process of the AgNPs and AuNPs was optimized using one factor at a time approach. Thus obtained AgNPs and AuNPs were characterized through various modern characterizing techniques. The synthesized AgNPs and AuNPs were investigated for their environmental and biological applications. This work was undertaken by the author for his Ph.D. work which is divided into eight chapters.

Chapter 1 discusses the introductory remark on the nanotechnology and its origin in very brief. The different types of nanomaterials and their different approaches including both top-down and bottom-up are mentioned briefly. Since the study is focused on the green synthesis, various biological sources such as bacteria, fungi, algae, actinomycetes, yeasts, and plants used for the synthesis of AgNPs and AuNPs are discussed in detail. The literature reports revealed that the plant extract mediated syntheses avoids the need of culture, ascetic condition, nutrients, and maintenance. Therefore, the plants extract are more advantageous over other biological routes. This chapter provides the summary of the different plants used so far for the synthesis of AgNPs and AuNPs and their application reported. The literature survey revealed plant extract mediated synthesis has a great limitation of that need of heating and stirring for a long time do not signify towards a completely eco-friendly and economic route. Therefore, the current thesis work is aimed at the development of completely eco-friendly and economic route which could avoid the heating and stirring. In the present thesis work, the photoinduced route using natural sunlight was opted to develop completely eco-friendly and economic route for the synthesis of AgNPs and

AuNPs where the mechanism of AgNPs and AuNPs synthesis is given in this chapter. This chapter also highlighted the several physical and chemical properties of AgNPs and AuNPs and their broad applications. Most importantly, the current chapter discusses the need for selecting the weed plant for the synthesis of AgNPs and AuNPs. This chapter also contains the objective of the current work.

Chapter 2 provides the materials required throughout thesis work. This chapter provides the detail procedures of the preparation of leaf extracts, confirmation and quantification of polyphenolics present in leaf extracts, synthesis of AgNPs and AuNPs, GO, rGO, AgNPs-rGO-PANI, and AgNPs@rGO nanocomposites used in this study. The current chapter also covers the procedures of various applications performed such as antibacterial, antileishmanial, antioxidant, detection of iron (III), H₂O₂, GSH, and Cholesterol.

Chapter 3 deals with the eco-friendly, economic, and rapid photoinduced route for the synthesis of stable AgNPs using an aqueous extract of AEX which act as reducing as well as a stabilizing agent. The present chapter revealed that AEX could reduce the silver within 10 seconds after bright sunlight exposure. The synthesis was confirmed by UV-visible spectroscopy where the presence of a prominent SPR band at λ_{max} of 436 nm at 40 seconds corresponded to the existence of AgNPs the in reaction mixture. In this chapter, the optimum conditions for biosynthesis of AgNPs were 30 min of sunlight exposure time, 3.0% (v/v) of AEX inoculum dose and 3.5 mM AgNO₃ concentration. In the current chapter, the synthesized AgNPs was characterized by TEM, SAED, FE-SEM, EDX, XRD, AFM, and FTIR. FE-SEM and TEM study corroborated that the average size of the synthesized AgNPs was 18 nm. XRD analysis indicated the presence of fcc crystal lattice of metallic silver. FTIR analysis confirmed the involvement of polyphenolic compounds in the synthesis of AgNPs. The AFM analysis advocated the presence of AgNPs with

average roughness 8.32 nm. This chapter also provided the antibacterial and antileishmanial activity of AgNPs. In the current investigation by the available facts, a probable mechanism was also proposed to explore the possible route of the biosynthesis of AgNPs and antibacterial activity.

Chapter 4 deals with the selective colorimetric detection of Fe^{3+} using green synthesized AgNPs via photoinduced. The biosynthesis was confirmed by UV–visible spectroscopy where an SPR band at λ_{max} 436 nm after 40 sec and 428 nm after 30 min corresponded to the existence of AgNPs. The optimum conditions for biosynthesis of AgNPs were 30 min sunlight exposure time, 5.0% (v/v) AEC inoculum dose and 4 mM AgNO_3 concentration. The stability of synthesized AgNPs was monitored up to 9 months. The size and shape of AgNPs with average size 19.4 nm were determined by Field Emission Scanning Electron Microscope (FE-SEM) and High-Resolution Transmission Electron Microscope (HR-TEM). The crystallinity was determined by High-Resolution X-Ray Diffractometer (HR-XRD) and Selected Area Electron Diffraction (SAED) pattern. The chemical and elemental compositions were determined by Fourier Transformed Infrared Spectroscopy (FTIR) and Energy Dispersive X-ray Spectroscopy (EDX) respectively. The Atomic Force Microscopy (AFM) images represented the lateral and 3D topological characteristics of AgNPs. The XPS analysis confirmed the presence of two individual peaks 375.70 and 369.70 eV which attributed to the Ag 3d_{3/2} and Ag 3d_{5/2} binding energies corresponding to the presence of metallic silver. The biosynthesized AgNPs showed potent antibacterial activity against both gram-positive and gram-negative bacterial strains as well as antioxidant activity. Based on the results and facts, the mechanism of AgNPs synthesis colorimetric detection of Fe^{3+} , antibacterial and antioxidant activity was also proposed.

Chapter 5 describes the optimized synthesis of AuNPs with tuned size and shape. The synthesis was performed by a photoinduced route using AEX as a reducing and capping agent which is completely eco-friendly and economically viable. The development of purple color in the reaction mixture containing AEX and $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ exposed to sunlight primarily confirmed the synthesis of AuNPs. The synthesis of AuNPs was regularly monitored using UV-vis spectrophotometer which exhibited the presence of sharp UV-spectra at 530 nm within 15 min of sunlight exposure. The parameters affecting the synthesis of AuNPs such as sunlight exposure time, AEX inoculum dose and $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ concentration were optimized using one parameter at a time approach. Thus obtained AuNPs was characterized through HR-TEM, XRD, FTIR, XPS, etc. The tuning of size and shape was studied by HR-TEM analysis which revealed that on increasing the $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ concentrations, from 0.4 mM to 2.8 mM, the average size and anisotropic nature of the AuNPs increased from 11.1 to 99.5 nm. The crystallinity of the green synthesized AuNPs from 0.4 mM to 3.2 mM studied by XRD analysis which showed the presence of diffraction peaks at $2\theta = 38.1^\circ$, 44.3° , 64.6° and 77.6° . The peaks were well matched with (JCPDS) file no: 040784 and attributed to (111), (200), (220) and (311) Bragg reflections respectively. The FTIR analysis of pure tannic acid, AEX, pre and post-annealed AuNPs confirmed the involvement of polyphenolics in the synthesis of AuNPs. The elemental analysis of AuNPs was carried out using XPS analysis which corroborated the presence of two individual peaks at 86.6 and 89.3 eV which corresponded to the presence of metallic gold. Zeta potential study revealed the synthesis of negatively charged AuNPs (NC-AuNPs) having zeta potential -7.4. The NC-AuNPs showed excellent peroxidase-like mimicking activity which was utilized for the colorimetric detection of hydrogen peroxide.

Chapter 6 represents the eco-friendly and zero cost photoinduced approach for the synthesis of more stable AuNPs using AEC as a reducing and capping agent. The reaction mixture of AEC and $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ when exposed to sunlight turned purple which primarily confirmed the biosynthesis of AuNPs. The biosynthesis was monitored by UV-vis spectroscopy which exhibited a sharp SPR band at 530 nm after 10 min of sunlight exposure. The parameters affecting the synthesis were optimized where 24 min of sunlight exposure time, 4.0% (v/v) of AEC inoculum dose and 1.6 mM $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$ concentration was found to be the optimum conditions for biosynthesis of AuNPs. The HR-TEM study revealed that as the metal ion concentrations increased from 0.4 mM to 3.2 mM, the average size and anisotropic nature of the AuNPs increased. The crystalline nature of the AuNPs synthesized from 0.4 mM to 3.2 mM was also confirmed by XRD analysis where the Bragg's diffraction pattern at (111), (200), (220) and (311) corresponded to the face-centered cubic crystal lattice of metallic silver. The involvement of polyphenolics in the synthesis of AuNPs was confirmed by the comparing the FTIR analysis of pure tannic acid, AEC, pre and post-annealed AuNPs. The XPS analysis corroborated the presence of two individual peaks attributing to the Au $4f_{7/2}$ and Au $4f_{5/2}$ binding energies which corresponded to the presence of metallic gold. The AuNPs thus obtained showed as a peroxidase-like mimicking activity which catalyzed the oxidation of TMB to oxTMB with the development of blue color and absorption spectra at 652 nm. However, the presence of GSH caused further reduction of oxTMB. This detection experiment showed the good linear relationship between 1 μM to 40 μM with the limit of detection 0.013 μM . In addition to this, the greater recovery of GSH from human blood serum advocated that the developed system was simple and sensitive for the real sample analysis.

Chapter 7 The current study aims at the development of an electrochemical sensor based on silver nanoparticles-reduced graphene oxide-polyaniline (AgNPs-rGO-PANI) nanocomposite for the sensitive and selective detection of hydrogen peroxide (H_2O_2). The nanocomposite was fabricated by simple in situ synthesis of PANI at the surface of rGO sheet which was followed by stirring with AEC biosynthesized AgNPs to form a nanocomposite. The synthesis of AgNPs, GO, rGO, PANI, rGO-PANI, and AgNPs-rGO-PANI nanocomposite and their interaction were studied by UV-vis, FTIR, XRD, SEM, EDX and XPS analysis. AgNPs-rGO-PANI nanocomposite was loaded (0.5 mg/cm^2) on glassy carbon electrode (GCE) where the active surface area was maintained 0.2 cm^2 for the investigation of electrochemical properties. It was found that AgNPs-rGO-PANI-GCE corroborated high sensitivity towards the reduction of H_2O_2 than AgNPs-rGO which occurred at -0.4 V vs. SCE due to the presence of PANI (AgNPs have direct electronic interaction with N atom of the PANI backbone) which enhanced the rate of transfer of electron during the electrochemical reduction of H_2O_2 . The calibration plots of H_2O_2 electrochemical detection was established in the range of $0.01 \text{ }\mu\text{M}$ to $1000 \text{ }\mu\text{M}$ ($R^2 = 0.99$) with a detection limit of 50 nM , the response time of about 5 sec at a signal-to-noise ratio ($S/N = 3$). The sensitivity was calculated as $14.7 \text{ }\mu\text{A mM}^{-1} \text{ cm}^{-2}$ which indicated a significant potential as a non-enzymatic H_2O_2 sensor.

Chapter 8 The present work deals with the peroxidase like-mimetic activity of AuNPs@rGO. The AuNPs@rGO was fabricated using AEC synthesized AuNPs and rGO obtained by the reduction of GO prepared by modified hummer's method. The utilization of negatively charge AEC synthesized AuNPs has not been reported yet for the fabrication of AuNPs@rGO for peroxidase-like mimetic activity. Several characterizing techniques such as UV-visible spectroscopy, FTIR, XRD, and TEM advocated the successful fabrication of AuNPs@rGO. The

TEM images revealed the clear sheets of rGO and uniformly distributed AuNPs over its surface. Thus prepared AuNPs@rGO showed an excellent peroxidase-like activity which influenced by the change in pH, and temperature. The other variables affecting the catalytic activity of the AuNPs@rGO like the concentration of TMB, and AuNPs@rGO amount were also optimized for securing optimum peroxidase-like activity of AuNPs@rGO. The fabricated AuNPs@rGO showed its catalytic activity as that of natural peroxidase enzyme because of its efficiency at lower pH and 40 °C temperatures which were used in the colorimetric detection of H₂O₂ and cholesterol in human blood serum. In the current investigation, the typical limit of detection for H₂O₂ and ChO were 0.0268 and 0.062 mM respectively. Overall, a simple, cost-effective, rapid, highly sensitive and selective colorimetric method was proposed for the potential detection of cholesterol which would be helpful for the medical diagnosis and biochemistry based applications.