SUMMARY

The present thesis described the development of photoinduced route for the green synthesis of AgNPs and AuNPs. Thus, the developed route proved to be rapid, complete eco-friendly and economically efficient which avoided the involvement of hazardous reducing agents, additional stabilizing agent, sophisticated and high cost instruments. This route avoided the need of aseptic condition, nutrient and proper maintenance. In addition to this, the photoinduced route also avoided the need of even heating and stirring also which made it swift and energy efficient and hence removed the limitation of leaf extract mediated synthesis of AgNPs and AuNPs. For the synthesis purpose, two weed plants (*X. strumarium* and *C. bonplandianum*) were selected on the basis of their phytochemicals constituent and their aqueous extracts (AEX and AEC) were prepared. The extracts were used for the synthesis of AgNPs and AuNPs. The synthesis processes were optimized using one parameter at a time approach. Thereafter, the synthesized AgNPs and AuNPs were characterized using different modern techniques. Thus prepared AgNPs and AuNPs from both extracts i.e. AEX and AEC were investigated against several applications. AgNPs was investigated for antibacterial, antileishmanial, antioxidants and detection of metal ions. However, the AuNPs was investigated for peroxidase-like mimetic activity. The AgNPs and AuNPs thus produced from AEX and AEC respectively were compared on the basis of results obtained. It was concluded that the AgNPs and AuNPs prepared from AEC were more stable, smaller, spherical, and large in number as compared to AgNPs and AuNPs obtained from AEX. Therefore, the AgNPs and AuNPs obtained from AEC were further utilized for the preparation of AgNPs-rGO-PANI and AuNPs@RGO nanocomposite which showed enhanced electrochemical detection of hydrogen peroxide and cholesterol respectively. The current thesis is divided into following eight chapters.

Chapter 1 The current chapter deals with the exhaustive literature survey related to green and economical route for the AgNPs and AuNPs synthesis. This chapter described the various types of nanomaterials, and their synthesis approaches briefly. This chapter also discussed an overview and history of AgNPs and AuNPs. The green synthesis of AgNPs and AuNPs using bacteria, fungi, algae, actinomycetes, and yeasts are discussed in detail. The green synthesis of AgNPs and AuNPs using plants extracts were focused and elaborated thoroughly using the published reports so far. The present chapter also discussed the properties and application of AgNPs and AuNPs, selection of the plant source as well as objective of the current thesis work.

Chapter 2 furnishes the materials and the protocols used in the present thesis work. This chapter provides the list of chemical which have been used up throughout the experiments. The detail procedures of the preparation of leaf extracts, determination of polyphenolic compounds including the confirmation and quantification of polyphenolic present in AEX and AEC is discussed in the current chapter. The procedure of the synthesis of AgNPs and AuNPs, GO, rGO, AgNPs-rGO-PANI, and AgNPs@rGO nanocomposites used in this study is also given in this work. The current chapter also covers the detailed experimental processes of various applications done in this chapter such as antibacterial, antileishmanial, antioxidant, detection of iron (III), H_2O_2, GSH and Cholesterol.

Chapter 3 explains the photoinduced synthesis of stable AgNPs using aqueous extract of AEX which was eco-friendly and economical. The present chapter presented the rapid synthesis of AuNPs in the presence of sunlight. The presence of SPR band at λ_{max} of 436 nm confirmed the synthesis of AgNPs which was confirmed by UV–visible spectrophotometer. The factors affecting the synthesis process were optimized using one

parameter at a time approach where 30 min of sunlight exposure time, 3.0% (v/v) of AEX inoculum dose and 3.5 mM $AgNO_3$ concentration were found to be optimum. The current chapter discussed the characterization of AgNPs by TEM, SAED, FE-SEM, EDX, XRD, AFM, and FTIR. The present chapter also focused on the investigation of biological application of AgNPs such as antibacterial and antileishmanial activity.

Chapter 4 The present study corroborated the selective colorimetric detection of Fe^{3+} using AEC synthesized AgNPs. Primarily, the synthesis of AgNPs was confirmed by the appearance of a single SPR band at λ_{max} 436 nm after 40 sec and 428 nm after 30 min of sunlight exposure. This chapter also aimed at the optimization of process variables where 30 min sunlight exposure time, 5.0% (v/v) AEC inoculum dose and 4 mM $AgNO_3$ concentration were optimum.. The size and shape of AgNPs were determined by FE-SEM and HR-TEM and the average size of AgNPs were found to be 19.4 nm. The XRD and SAED pattern confirmed the crystalline nature of AgNPs. The chemical and elemental compositions were determined by FTIR and EDX respectively. The surface topography was studied by AFM analysis which represented the lateral and 3D topological characteristics of AgNPs with average roughness 4.84 nm. The XPS analysis revealed the presence of two individual peaks at 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. On the basis of results and facts, a probable mechanism was also proposed to explore the possible route of AgNPs synthesis, colorimetric detection of Fe^{3+}, antibacterial and antioxidant activity.

Chapter 5 depicts the photoinduced green synthesis of AuNPs using AEX with tuned size and shape. The change in color of the reaction mixture containing AEX and $HAuCl_4.xH_2O$ from yellowish to purple primarily confirmed the synthesis of AuNPs. The optimization of process parameters affecting the synthesis of AuNPs such as sunlight exposure time, AEX inoculum dose and $HAuCl_4.xH_2O$ concentration were carried out using one factor at a time approach which were 30 min, 3%, and 1.2 mM respectively. The optimized AuNPs was characterized through several characterizing techniques such as HR-TEM, XRD, FTIR, XPS etc. The current study was also focused on the size dependent synthesis of AuNPs using different concentration of $HAuCl_4.xH_2O$ from 0.4 mM to 3.2 mM. The crystallalinity of the green synthesized AuNPs from 0.4 mM to 3.2 mM confirmed by XRD having 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 important role played by phytochemicals in the synthesis and stabilization was confirmed by FTIR analysis by comparing the FTIR spectra of pure tannic acid, AEX, pre and post-annealed AuNPs. The XPS analysis 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 depicted excellent peroxidase-like mimicking activity which was utilized for the colorimetric detection of hydrogen peroxide.

Chapter 6 covered the eco-friendly and zero cost approach for synthesis of more stable AuNPs using AEC. The sunlight exposed reaction mixture of AEC and $HAuCl_4.xH_2O$ turned purple from yellowish which primarily confirmed the synthesis of AuNPs. The synthesis of AuNPs 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 also optimized and it was observed that 24 min of sunlight exposure time, 4.0% (v/v) of AEC inoculum dose and 1.6 mM $HAuCl_4.xH_2O$ concentration were the optimum conditions. This chapter was also focused on the shape and size dependent synthesis of AuNPs at different $HAuCl_4.xH_2O$ concentrations from 0.4 mM to 3.2 mM. The XRD analysis of AuNPs synthesized from 0.4 mM to 3.2 mM confirmed their crystalline nature. 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 acitivity 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 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 aims at the development of an electrochemical sensor for the sensitive and selective detection of H_2O_2. For this purpose AgNPs-rGO-PANI-GCE was fabricated. The 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. 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 µM to 1000 µM (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 µA mM^{-1} cm^{-2} which indicated that it has significant potential as a non-enzymatic H_2O_2 sensor.

Chapter 8 describes the fabrication of AuNPs@rGO nanocomposite using negatively charged AuNPs synthesized from AEC. Thus, the fabricated AuNPs@rGO nanocomposite showed the peroxidase like-mimetic activity. The utilization of negatively charged AuNPs synthesized from plant extracts has not been reported yet for the fabrication of AuNPs@rGO for peroxidase-like mimetic activity. The fabrication of AuNPs@rGO was confirmed by several characterizing techniques such as UV-visible spectroscopy, FTIR, XRD, and TEM. The peroxidase-like activity was influenced by change in pH, and temperature. The other variables affecting the catalytic activity of the AuNPs@rGO like 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 ºC temperatures which was used in the colorimetric detection of H_2O_2 and cholesterol in human blood serum. In current investigation, the typical limit of detection for H_2O_2 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.

After the exhaustive literature survey related to the synthesis of AgNPs and AuNPs and completion of the present thesis work, following suggestion might be helpful for the photoinduced potential synthesis of these nanoparticles and their application in future.

- The pants *Xanthium strumarium* and *Croton bonplandianum* are weed plants which possessed great amount of secondary metabolites having important medicinal value which synthesized biocompatible AgNPs and AuNPs. Therefore, these biocompatible AgNPs and AuNPs can be investigated in various biological applications.
- The AgNPs synthesized in this study showed several potent applications such as antibacterial antileishmanial, antioxidant, detection of H_2O_2 and Iron (III) which could be utilized for the development of antimicrobial and biological sensors.
- The AuNPs obtained in this work showed peroxidase-like mimetic activity. Such a novel property could be helpful for the medical diagnosis and biochemistry based applications.
- The photoinduced synthesis of AgNPs and AuNPs using AEX and AEC was very rapid which started the synthesis processes within seconds. The in situ TEM analysis can enlighten the fact of growth of these nanoparticles.
- Since, the photoinduced synthesis was very rapid, the in situ TEM analysis and UV-visible spectra can relate the actual development of surface plasmon bands and the formation of different shaped AgNPs and AuNPs using plant extracts.