

Summary and Future Work

8.1 Summary

The Present chapter summarizes the findings of thesis and potential proposals for the extension of this work. The focus of present experimental investigations is to design metal nanomaterials such as MoS₂-QDs, WS₂-QDs, AuNPs@MoS₂-QDs composite, AuNPs@WS₂-QDs composite, silver nanoparticles and nano coordination polymers of 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (AHMT) with silver and palladium to develop efficient catalyst and sensors for early and accurate detection of biomolecules, drugs and hazardous molecules. These materials showed enormous potential towards to use as active material for catalysis and sensing applications. Among these research in the area of bio-mimic catalysts and sensing using artificial enzymes are less explored and reported in the literature. Here, nanomaterials and coordination polymers play crucial role in catalysis with promising functionality and active sites for the development of efficient sensors.

Further, the designing of stable biomimic metal nanomaterials and nanocoordination polymers as efficient sensor materials is challenging and there is a need to fabricate a simple, sensitive and portable sensor for the onsite measurement of biomolecules. So that, one can monitors the concentration of analytes in real sample. This inspired us to explore the designing of stable biomimic metal nanomaterials and nano coordination polymers which are applicable in colorimetric assay of biomolecules (glucose, choline), hazardous molecule (picric acid) and electrochemical detection of anticancer drug 6-mercaptopurine and their pharmaceutical formulations. It is for the first time to report the colorimetric and electrochemical applications of such assemblies.

This thesis is thoroughly organized based on the synthesis of the metal nanomaterials, coordination polymers and their application in the catalysis and sensing. The chapter wise summary of the thesis is described below.

Chapter 1 gives basic concepts about sensors, components, types of sensors, importance of nanomaterials, their composites, coordination polymers and metal nanomaterials for catalysis and sensing. Nanomaterials and coordination polymers are used as artificial enzyme which substitutes natural enzymes to develop sensitive and selective sensor for detection of biomolecules, hazardous molecules, life saving drugs and their portability. Review of literature presents a detailed survey related to the work.

Chapter 3 involves one step synthesis of AuNPs@MoS₂-QDs composite peroxidase-mimetic for instant unaided eye detection of glucose in serum, saliva and tear. AuNPs@MoS₂-QDs composite synthesized successfully which showed a robust peroxidase mimetic activity towards peroxidase substrates to produce colored product in the presence of H₂O₂. The AuNPs@MoS₂-QDs composite ideally follows the enzyme kinetics i.e. Michaelis–Menten kinetics with peroxidase mimetic activity against wide range of pH and temperature. The composite system is utilized for successful detection of glucose in buffer solution with excellent selectivity and sensitivity. The proposed method further is used to develop a portable test kit which is simple, inexpensive for the detection of glucose in human biological fluids (serum, saliva and tear). The designed bio-sensor is cable for non invasive determination of glucose in tear and saliva. The developed colorimetric system based on peroxidase mimetic activity can be applicable in biotechnology and clinical diagnoses field.

Chapter 4 In this chapter, we have designed nanoporous palladium(II) bridged coordination polymer (AHMT-Pd) acting as a peroxidase mimic for visual detection of

glucose. Extended π conjugated system and high surface area of nanoporous coordination polymer AHMT-Pd facilitate fast electron transfer. It shows peroxidase-like activity to obey Michaelis–Menten kinetics. It catalyzes oxidation of TMB in presence of H_2O_2 to produce noticeable green blue color. The catalytic proficiency of AHMT-Pd depends on the concentration of H_2O_2 , temperature, and pH. Based on these results, a sensitive glucose test was worked out at 652 nm which get intensify if the greenish-blue product is related to the actual concentration of glucose, a portable test kit is also formulated for visual analysis of blood glucose level in the serum. The noticeable color change was observed from colorless to yellow–green for a normal range of glucose and blue–green indicated a diabetic person. The sensing platform is highly sensitive and showed linear response toward glucose additions with 47 nM limit of detection. The designed biosensing system is also able to determine glucose levels both in tear and saliva as a non-invasive assay. Moreover, the assay has potential to directly correlate color with the concentration of glucose in sample by colorimetry test but the scheme can be used in biomedical application to monitor the environment.

Chapter 5 In this chapter AuNPs@WS₂-QDs composite has been synthesized which shows the peroxidase mimetic activity towards the TMB substrate applied for facile and sensitive colorimetric assay of choline. TMB oxidation is catalyzed by AuNPs@WS₂-QDs composite in presence of H_2O_2 and formed blue color of the TMB oxidation product which confirmed peroxidase mimetic activity. The intrinsic peroxidase like catalytic activity of AuNPs@WS₂-QDs composite also follows Michaelis-Menten kinetics. The stability and catalytic activity of AuNPs@WS₂-QDs composite considerably shows over broad range of pH from 1.5 – 10.0 and temperature 25°C – 70°C. Proposed sensing system is very sensitive and selective towards the colorimetric detection for H_2O_2 and choline based on choline oxidase (ChOx) and AuNPs@WS₂-

QDs composite. The reaction system is calorimetrically detected, at 652 nm and applied in the range of 1 to 150 μM in PBS of choline concentration with the 0.086 μM limit of detection. For the development of visual platform, inexpensive, simple paper based test strip was fabricated for detection of the choline in blood serum and milk samples. Additionally the designed scheme has potential to be applied on field and color shade directly comparable with amount of choline present in the real samples. Hence, cost effective choline assay strip have been fabricated and Match with color detection wheel to detect desired choline concentration in the real sample. It is projected that result can support application of the peroxidase mimetic activity of AuNPs@WS₂-QDs composite in field of food industry, clinical analysis, biological sciences and other fields.

Chapter 6 is based on the synthesis of highly stable and homogenously distributed 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (AHMT) capped silver nanoparticles (Ag@AHMT). The key point for success of synthesis and stabilization of Ag@AHMT nanoparticles is strong interaction between Ag and S atoms of AHMT which is in consistent with the various results of this article. The developed Ag@AHMT is explored for the highly sensitive ultra-trace detection of hazardous environmental pollutant picric acid. The sensing platform exhibits instant response toward variation in picric acid concentration through change in color from light yellow to brownish yellow and can be visualized *via* naked eye. Herein, the highly sensitive assay is possible in the light of strong H-bonding and charge transfer complex formation which affect catalytically the surface plasmon resonance of Ag@AHMT Nps and shows linear response towards picric acid concentration with the sensitivity 0.045 ng/mL and limit of detection 0.13 nm. This approach suggests a highly sensitive, enzymeless, mediatorless colorimetric assay and will open nano avenues in the area of naked eye sensing device fabrication.

Chapter 7 This chapter involves the development of an elegant nanocrystalline polymeric network of AHMT-Ag which provide a geometrically and symmetrically feasible highly sensitive platform for the ultra-trace and whole spectrum systematic and potential quantification of 6-MP. The effective electron channelling through nanocrystalline architecture is essential for facile production of feature centred events. The complete experimentation depicted that serendipitous use of the AHMT-Ag is crucial for generating distinctive current pattern in characteristic events. This feature endows highly sensitive assay at ultra-trace level. The key success of sensing methodology is the feasible and faster electron channelling through the nanocrystalline polymeric platform. The potential of the study is enzyme-less, cost effective and complete spectrum ultra-trace detection of 6-MP. This unique signature was applied in voltammetric detection of 6-MP in blood serum, human urine and pharmaceutical formulation (tablet) by considerably high sensitivity of $0.074 \mu\text{A}/\mu\text{M}$, $0.058 \mu\text{A}/\mu\text{M}$ and $0.036 \mu\text{A}/\mu\text{M}$ and the detection limit 87 nM , 97 nM and 37 nM respectively. This strategy can be explored in the commercial portable device fabrication for a variety of anticancer drugs.