The thesis entitled, "Synthesis of Metal Nanomaterials and Coordination Polymers for Catalytic and Sensing Applications" consist of the development of Transition Metal Dichalcogenides (TMDCs) nanomaterials e.g. Molybdenum disulfide quantum dots (MoS_2-QDs), Tungsten disulfide quantum dots (WS_2-QDs) and their composites e.g. gold nanoparticles (AuNPs) decorated over MoS_2 quantum dots (AuNPs@MoS_2-QDs), gold nanoparticles (AuNPs) decorated over WS_2 quantum dots (AuNPs@WS_2-QDs), synthesis of silver nanoparticles and nano coordination polymers of 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (AHMT) with silver and palladium metal.

The role of nanomaterials is very important due to the fact that they possess large surface area to volume ratio, ease of functionalization, fast electron transfer kinetics, catalytic activity and biocompatibility and also selectivity and specificity. Additionally, nano-coordination polymers with interesting morphologies and high specific surface areas are remarkably promising for both technological and scientific applications as they explore growing interest in establishing advance materials with novel building blocks.

With the advent of nanotechnology, its application in catalysis and sensing is entering to a new era for the development of advanced sensors that can detect low level concentration of analytes using a portable sensor device which was hardly possible earlier. Sensors have fascinated much attention in recent times because of the potential applications of these devices in the clinical diagnosis, environmental monitoring, pharmaceuticals and food processing industries etc.

DEFINITION OF THE PROBLEM

Nanomaterials and coordination polymers are a good substitution candidate of the natural enzymes and act as a catalyst in catalysis and sensing. However, bio-mimic catalysts and sensing using artificial enzymes are less explored and reported in the literature for development of stable and low cost sensors. Currently, optical, electrochemical, mass sensitive sensors are being used for detection of different biomolecules. Though, these techniques suffer from the lack of stability, poor detection limit and requiring high amount of analytes.

Colorimetric detection based on nanomaterials and coordination polymer is showing potential for screening large number of samples. Fast and low cost sensors for toxic chemicals and biologically important analytes have massive demand. Considering these facts and futuristic applications of nanomaterials and coordination polymers in bio-mimic and sensors, the major focus of the thesis are as follows.

Broad Objectives of the work:

- To synthesize metal nanomaterials, nanocomposites and nanocoordination polymers for simple and low cost biomimic catalysts and sensors and their characterization by using various techniques.
- To explore the outstanding physical, chemical and catalytic properties of nanomaterials and nano-coordination polymers for catalysis and sensing of biomolecules (glucose, choline), hazardous analytes (picric acid) and drug (6-mercaptopurine) and developing portable sensing kits for early and accurate detection of different analytes of interest.Based on above objectives, this thesis is divided into eight chapters with brief conclusive remarks:

Chapter 1 gives a general idea and an introduction to some 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 used as artificial enzyme which substitute natural enzymes, need to develop sensitive and selective sensor for detection of analytes of interest. Review of literature presents a detailed survey related to the proposed research topic.

Chapter 2 describes different experimental techniques which have been used for the characterizations of developed materials. The main techniques which have been employed characterizations are Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), X-ray Diffractometer (XRD), Energy Dispersive Spectroscopy (EDX), Atomic Force Microscope (AFM), X-ray photoelectron spectroscopy (XPS), Zeta potential and Fourier Transform Infrared Spectroscopy (FTIR) used for the morphological and structural investigation. UV-Visible spectrometer has been used for spectroscopic characterizations and optical sensing of different analytes. Cyclic voltammetry (CV) and Differential cyclic voltammetry (DPV) setup has been used for electrochemical characterization.

Chapter 3 deals with the one step synthesis of gold nanoparticles (AuNPs) decorated over MoS_2 quantum dots (AuNPs@MoS_2-QDs) composite as a robust peroxidase-mimetic for instant unaided eye detection of glucose in serum, saliva and tear. The composite instantly catalyzed the peroxidase substrate 3,3 ,5,5 –tetramethylbenzidine (TMB) in presence of H_2O_2 to produce bluish-green color and is stable in harsh conditions such as high or low temperature and pH. Further, AuNPs@MoS_2–QDs composite is used to detect H_2O_2 and glucose by using colorimetric method. The developed sensing system executes excellent selectivity, reproducibility and stability towards glucose sensing and shows an excellent detection in dynamic ranges from 1 to 400 µM (R^2~0.996) with detection limit of 0.068 µM in PBS buffer solution. Low *Km* value (0.06 mM) and high *Vmax* value (10.6×10^{-6} Ms^{-1}) shows strong binding affinity towards substrates and greater catalytic reaction rate. Further portable test kit was developed for detection of glucose in blood serum, tear and saliva which shows an excellent response towards glucose detection.

Chapter 4 deals with the nanoporous palladium(II) bridged coordination polymer acting as a peroxidase mimic in a method for visual detection of glucose. A nanoporous coordination polymer (NPCP) was prepared from palladium(II) chloride and 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole. AHMT–Pd NPCP was synthesized under optimal conditions at room temperature in the absence of any extra additives. The Pd(II) ions coordinated to the sulphur and nitrogen atoms of organic ligand afford outstanding capacity intended for molecular-level modification of the internal pore architecture and the cavities of AHMT–Pd NPCP can generate biomimic active centers. Therefore, NPCP act as a peroxidase mimetic. It can catalyze the oxidation of 3,3′,5,5′-tetramethylbenzidine (TMB) by H_2O_2 which is formed on enzymatic oxidation of glucose by glucose oxidase. Based on these findings, 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. Figures of merit include (a) rather low Km value (30 µM) (b) high v(max) (8.5 $M \cdot s^{-1}$), (c) 47 nM detection limit, (d) lifetime of a month, (e) wide working pH range (2–10), and (f) 25–80 °C temperature range. The assay was applied to non-invasive determination of glucose assay in tear, saliva where the detection limits are found to be 61 and 91 nM, respectively in tear and saliva.

Chapter 5 Represents facile and sensitive colorimetric assay of choline based on gold nanoparticles (AuNPs) decorated over WS_2 quantum dots (AuNPs@WS_2-QDs) as a peroxidase mimetic. AuNps@WS_2-QDs exhibit strong enzyme like catalytic activity in the oxidation reaction of peroxidase substrate of 3,3′,5,5′-tetramethylbenzidine(TMB) in presence of H_2O_2 to produce a blue color product. The peroxidase mimicking properties of AuNps@WS_2-QDs depend on temperature, H_2O_2 concentration and pH value. Choline is an important precursor for the synthesis of the neurotransmitter acetylcholine. Choline oxidase oxidizes the choline into betaine and H_2O_2 in presence of oxygen (O_2).The TMB is oxidized in presence of hydrogen peroxide (H_2O_2) to generate blue colored product. Absorbance spectra applied for detection of choline best at 652 nm as colorimetrically detected. The technique applied in the concentration range of 1 to 150 µM choline with a 0.086 µM detection limit. This assay is selective, rapid and simple. It was further used for detection of the choline in serum and milk.

Chapter 6 describe the Colorimetric detection of picric acid using silver nanoparticles modified with 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole. We have established a simple and sensitive colorimetric technique for the assay of picric acid using spherical FCC silver nanoparticles modified with 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole (AHMT). In this context, highly stable AHMT capped silver nanoparticles (Ag@AHMT) are developed and optimized *via* UV–vis, IR and zeta potential. The designed Ag@AHMT nanoparticles of 4–10 nm size range are symmetrically distributed, regularly arranged and utilized for the ultra-trace assay of picric acid. It is found that picric acid encourages the aggregation of modified Ag nanoparticles through charge transfer complex formation; leading to color varies from light yellow to brownish yellow. This variation can be visualized by naked eyes and further examined through UV–vis spectra with detection limit of 0.13 nM and sensitivity 0.045 ng/mL.

The new approach lightens scope for fabrication of naked eye sensing devices of environmental pollutants.

Chapter 7 includes Nano network of coordination polymer AHMT-Ag for the effective and broad spectrum detection of 6-mercaptopurine in urine and blood serum. In this report, significantly stable infinite arrayed coordination polymeric network was self-assembled *via* metal with efficient organic tecton 4-amino-3-hydrazino-5-mercapto-1,2,4,-triazole (AHMT) in which silver (I) ions are coordinated by AHMT *via* hydrazino and exocyclic thiol linkage to form AHMT–Ag NCCP. An efficient and highly sensitive detection of 6-MP is attained owing to eminent electron channelling *via* polymeric nano-crystallite pores. An effective charge transfer leads at interface of the AHMT–Ag nano–pores and electrolyte anchored electrode *via* π–π electron coupling and hydrophobic interaction. The voltammogram exposes acute redox behaviour of 6-MP and discloses an impeccable illustration for the AHMT–Ag facilitated oxidation 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 μA/μM, 0.058 μA/μM and 0.036 μA/μM and the detection limit 87 nM, 97 nM and 37 nM respectively. Thus, the prepared AHMT–Ag NCCP can provide a valuable platform for fabrication of highly sensitive electrochemical devices to assay biologically essential drug molecules.

Chapter 8 includes the conclusive remarks and future prospects of the thesis.