Summary

The thesis entitled "**Studies on Coordination Polymers of 2–Mercapto–1,3,4–thiadiazole and their Application in Drug Sensing"** personified the designing of coordination polymers of 2–Mercapto–1,3,4–thiadiazole derivatives with gold and silver to accomplish the electrochemical detection of drugs. The research in the area of nano–porous coordination polymers and nano–crystalline coordination polymers is not well explored. Here, the ligand plays a crucial role in the fabrication of coordination assembly. In this aspect DMTD and AMT have promising functionality and active sites for the development of nanocoordination building blocks. Further, the designing of novel synthetic routes for nanocoordination polymers is challenging and creative architecture is needed to attain valuable applications of these nanoscale materials. Significant work needs to be executed in order to expand the scope of the applications for nanocrystalline coordination polymers for practical applications. This inspired us to explore the development of nano coordination polymers using DMTD and AMT as linkers for Ag and Au metal ions. This is the focal point of this thesis. The Ag and Au form prominent and fascinating networks with DMTD and AMT and thus formed nanocoordination polymers have tremendous implications in the drug sensing. The developed frameworks are applicable in voltammetric assay of atropine sulphate and ciprofloxacin hydrochloride and their pharmaceutical formulations. It is worth to mention that it is for the first time to report the electrochemical applications of these assemblies in drug sensing.

This thesis is systematically organized based on the structural network, architecture of the developed coordination assemblies and their application in the sensing of various drugs. The chapter wise summary of the thesis is described below.

Chapter 1 deals with the Introduction and literature survey about the use of mercapto–thiadiazole system derived ligands 2,5–dimercapto–1,3,4–thiadiazole (DMTD) and 2–amino–5–mercapto–1,3,4–thiadiazole (AMT). The chapter also describes the structural features of gold and silver coordination polymers on the basis of different characterization techniques. It also narrate my own research efforts, rationale and ideas behind the synthesis of some new coordination polymers of gold and silver with interesting morphology and excellent electrokinetics and their potential use as sensing materials. The synthesized coordination networks have been fully characterized by various physico–chemical and spectral techniques (FT–IR and UV–Vis). Based on several investigations, the structural network of these materials has also been proposed. Further, the proficient electron transfer kinetics of proposed networks has also been explored in the electrochemical detection of drugs.

After giving a brief introduction to the formation of one dimensional infinitely arrayed coordination polymers, pertinent literature on the nitrogen, oxygen and sulphur donor coordination complexes have been discussed. The applications of these compounds in various fields *viz.* as luminescent and magnetic material, as sensing material, conductivity, catalyst, gas storage, optical devices and analytical devices etc. have also been described in this chapter. An attempt has been made to make an up–to–date survey of the literature related to nanoporous coordination polymers.

Chapter 2 deals with the one pot synthesis of coordination polymer 2,5–dimercapto–1,3,4–thiadiazole–gold and its application in voltammetric sensing of resorcinol. The synthesis, characterization and sensing properties of the coordination polymer derived from 2,5–dimercapto–1,3,4–thiadiazole with $AuCl_3$ precursors has been reported. The synthesized material was characterized by FT–IR, NMR, Raman, XPS, X–ray diffraction, UV–Vis and TGA. The architecture of infinite arrayed coordination polymer (DMTD–Au) has been investigated by indexing with Dicvol software which provides tetragonal arrangement of the polymeric network. The X–ray photoelectron spectroscopy reveals the oxidation state of Au(I) and Raman studies explores the metal-ligand linkage. The DMTD–Au is thermally stable up to 260 ºC. The electro–chemical studies of DMTD–Au explore the ultra-trace detection of resorcinol using differential pulse voltammetry. It provides a good sensitivity of 0.019 µA nM^{-1} with limit of detection as 29.77 nM.

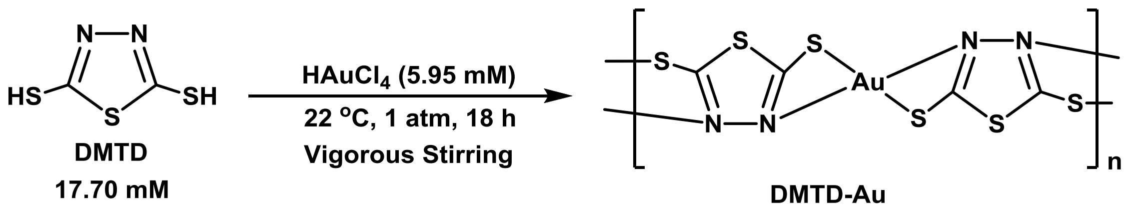

Figure 5.1 Scheme for DMTD–Au synthesis.

Chapter 3 deals with the nano-porous network of DMTD–Ag coordination polymer for the ultra–trace detection of anticholinergic drug. The reaction of 2,5–dimercapto–1,3,4–thiadiazole with silver results DMTD–Ag nanoporous coordination polymer at room temperature without using any initiator. The infinite arrayed coordination polymer, DMTD–Ag is thoroughly investigated for the metal–ligand linkage and oxidation state of metal by FT–IR, Raman spectroscopy and XPS;

confirming the presence of Ag(I) in the polymeric matrix. The coordination polymer designed using Ag(I) exhibits nanoporous morphology examined by FE–SEM and TEM micrograph also the amorphous architecture of DMTD–Ag is scrutinized by X–ray diffraction and SAED pattern corresponding to TEM images.

In the light of various studies, the structural network of DMTD–Ag has been proposed and that is in consistent with the results. The derived network explores the excellent electron channeling through the nano porous veins. The efficient electro–activity of DMTD–Ag is exploited for the modification of electrode in the voltammetric detection of anticholinergic drug, Atropine sulphate. The analyte interacts with the modified electrode through inter molecular hydrogen bonding and responds to the electrode.

Further the proof of concept is demonstrated with the assay of drug in a pharmaceutical formulation, i.e. atropine sulfate detection in an eye drops with a sensitivity of 0.02 μA/μM, and limit of detection as 72.50 nM.

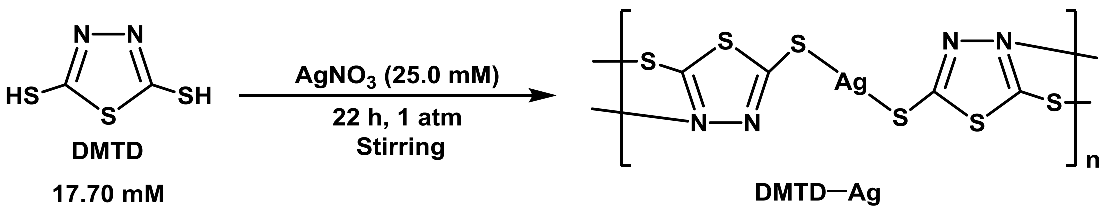

Figure 5.2 Scheme for DMTD–Ag synthesis.

Chapter 4 explores nanocrystalline coordination polymer of AMT–Ag for an effective detection of Ciprofloxacin hydrochloride in pharmaceutical formulation and biological fluid. This chapter explores the organization of nano–crystalline coordination polymer (AMT–Ag) derived from 2–amino–5–mercapto–1,3,4–thiadiazole with silver (AMT–Ag). The interaction of Ag(I) with ligand is investigated using various spectroscopic techniques (FT–IR, XPS and UV–Vis) and the nano–crystalline architecture of AMT–Ag is investigated by X–ray diffraction, FE–SEM and TEM analysis. The indexing of diffraction pattern reveals the Pm monoclinic organization of AMT–Ag. The structural assembly of AMT–Ag is proposed based on the various investigations and molecular modeling.

The developed polymeric assembly is highly electro–active as examined by ferri–ferro (Fe^{+3}–Fe^{+2}) redox couple. The effective redox activity of AMT–Ag is utilized for electrode modification in the electrochemical detection of ciprofloxacin hydrochloride up to nano molar level of concentration. The practical utility of concept is successfully proved by the trace level electro–detection of Ciprofloxacin hydrochloride in pharmaceutical formulation and biological fluid.

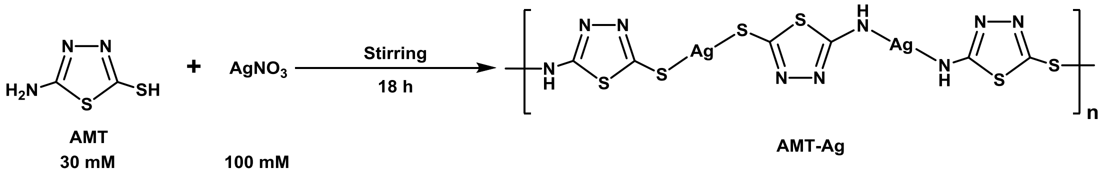

Figure 5.3 Scheme for AMT–Ag synthesis.