Preface

Selectivity in sensing process has been one of the major requisite, lack of which has restricted the practical implementation and subsequent commercialization of many chemical sensors. Chemical sensor is a device which consists of a chemically selective layer either closely related or integrated within physico-chemical transducer and has received a great attention because it provides an inexpensive, portable, and simple to operate analytical tool for identification and quantification of the specific analytes in the areas of food technology, medical engineering, environmental engineering and pollution monitoring. The use of catalytic material as chemically sensitive layer has boosted the development of chemical sensor technology and the role of nanomaterials during such development received great attention since, metal nanotubes, nanocomposites, nanorods, nanostructured polymers, nanoparticles, nanowire, different allotropes of carbons like carbon nanotubes, graphene and others lead to enhance the catalytic efficiency and selectivity during sensing process. Nanoparticles provide advantages because of their high surface to volume ratio as compared to bulk materials and has directed for specific attentions during chemical sensing as a replacement of biocatalyst during chemical sensor design.

One of the potentially explored biocatalyst is peroxidase enzyme, being used in many bioassay kits in healthcare. The susceptibility of peroxidase activity on environmental conditions directed the attention of world scientists for its replacement and the role of Prussian blue, an artificial peroxidase, has gained attention and directed for precise investigations on transition metal hexacyanoferrate. Transition metal hexacyanoferrates are the important class of extremely stable co-ordination compounds which have been used in the field like display technology, solid state batteries, hydrogen storage, cesium remediation and sensor fabrication. Amongst the transition metal hexacyanoferrates, Prussian blue is most studied, inorganic crystalline substance which have been used in various analytical applications and investigated extensively due to its electrochemical, magnetic, photophysical and electrochromic properties. However, many potential applications, specifically as a replacement of peroxidase, are restricted due to non-processability of such crystalline material in various solvents. Accordingly the findings on the synthesis of processable Prussian blue nanoparticles have been one of requirement that constitute the theme of present research program.

The finding demonstrated that non-processability of Prussian blue and its mixed metal analogues are mainly due to uncontrolled nucleation during the synthesis of the same and directed to control the nucleation process through the participation of organic reagents. Accordingly, the synthesis of Prussian blue nanoparticles and its mixed metal hexacyanoferrate has been reported through the use of 3-aminopropyltrimethoxysinae and cyclohexanone followed by subsequent innovative development involving tetrahydrofuran hydroperoxide. These findings encouraged us to undertake the research program from the following angles: (1) Organic reagent mediated controlled synthesis of PBNPs, (2) Stabilization of PBNPs in the reaction medium itself, (3) Synthesis of PBNPs-AuNPs nanocomposite, (4) Organic reagent mediated controlled synthesis of mixed metal hexacyanoferrates of variable stoichiometric ratio of hetero transition metal ions, (5) analytical applications of Prussian blue nanoparticles and its mixed metal nanoparticles in both homogenous and heterogeneous catalysis.

The finding on ~~thesis~~ these lines have been undertaken in the present thesis programme with specific detail given below : (1) General Introduction, (2) THF and H_2O_2 mediated synthesis of nanocrystalline PBNPs and its analytical applications, (3) THF and H_2O_2 mediated synthesis of nanocrystalline Ni-Fe hexacyanoferrates nanoparticles and its analytical applications, (4) Polyethylenimine (PEI) mediated synthesis of nanocrystalline PBNPs and its analytical applications, (5) PEI mediated synthesis of nanocrystalline mixed metal analogue nanoparticles and its analytical applications.

Chapter 1 starts with the general introduction including the results of earlier studies done on the metal hexacyanoferrates with the special attention to the Prussian blue and their application in chemical sensing.

Chapter 2 describes tetrahydrofuran (THF) and hydrogen peroxide (H_2O_2) mediated synthesis of nanocrystalline Prussian blue nanoparticles (PBNPs) and its application in hydrogen peroxide sensing. It has been found that THF in the presence of H_2O_2 allow controlled synthesis of PBNPs at 60 °C in 20 minutes under optimum ratio of reacting components. The as generated nanoparticles have been characterized through UV-Vis spectroscopy, Fourier Transformation Infrared Spectroscopy, X-Ray Diffraction analysis, Energy Dispersive Spectroscopy and Transmission Electron Microscopy. The typical application of as made nanomaterial in H_2O_2 sensing and its use as peroxidase mimetic is reported.

Chapter 3 describes THF and H_2O_2 mediated synthesis of nanocrystalline Nickel-iron hexacyanoferrates (Ni-Fe HCFs) and its application in the electrochemical oxidation study of hydrazine. It has been found that optimum concentration of $K_3[Fe(CN)_6]$, THF, H_2O_2 and $NiSO_4$ leads to the synthesis of Ni-Fe HCFs at 60 °C within 30 minutes. The as synthesized Ni-Fe HCFs have been characterized through UV-Vis spectroscopy, Fourier Transformation Infrared Spectroscopy, X-Ray Diffraction analysis, Energy Dispersive Spectroscopy, Scanning Electron Microscopy and Transmission Electron Microscopy. The effect of nickel ions on the electrochemical behaviour is also discussed. This chapter ends with the potential application of as synthesized Ni-Fe HCFs as peroxidase mimetic activity.

Chapter 4 describes polyethylenimine (PEI) mediated controlled synthesis of nanocrystalline PBNPs. It has been found that single precursors, $K_3[Fe(CN)_6]$ efficiently converts into stable, well dispersed PBNPs having excellent electrocatalytic activity. As synthesized PBNPs have been used for the synthesis of AuNPs assembled PBNPs. PBNPs and AuNPs assembled PBNPs is characterized through UV-Vis spectroscopy, X-Ray Diffraction analysis, and Transmission Electron Microscopy. These nanomaterials have been explored in both homogeneous and heterogeneous detection of H_2O_2.

Chapter-5 deals the PEI mediated synthesis of copper-iron hexacyanoferrate (Cu-Fe HCFs) and nickel-iron hexacyanoferrates (Ni-Fe HCFs) nanoparticles. As synthesized nanocrystalline Cu- Fe hexacyanoferrates and Ni-Fe hexacyanoferrates have been characterized through XRD and TEM analysis. The effect of other transition metal ion on the electrochemical behaviour has also been investigated. These nanomaterials have been used in both homogeneous and heterogeneous catalysis for sensing of H_2O_2, hydrazine and dopamine.

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