Abstract

Palladium (Pd) and copper (Cu) based nanoparticles (NPs) have received great attention because of their proficient exploitation in various field of catalysis such as catalytic reforming, organic transformations, chemical synthesis, biological, environmental and energy related reactions etc. Formation of hybrid catalysts of Pd and Cu with various metals, metal oxides and carbon-materials further enhance the activity and selectivity of Pd- and Cu-based catalysts. Therefore, the present thesis aims at the development of Pd- and Cu-based NPs for their different energy and environmental related applications such as fuel cell (FC) reactions and harmful nitroaromatic reductions. Especial emphasis has been paid toward application of catalysts toward fuel cells oxygen reduction reaction (ORR; for energy related issues) and various nitroaromatic reduction reactions (for chemical and pharmaceuticals).

Because of the increasing population and rapid industrialization, the fossil-fuel resources are decreasing day by day, hence there is a critical need for the use of non-fossil-fuel resources. Sustainable alternative, such as wind, solar, wave energy power, geothermal, and FCs are being explored. Along with other such alternatives, FCs are actively developed for the purpose as they have several advantages like zero emissions, high power density, high efficiency, noiseless operation etc. Among all the existing FCs, the proton exchange membrane fuel cell (PEMFC) has been actively developed for use in vehicles, portable electronics systems due to its simplicity, high power density, quick start-up and low working temperature. However PEMFC faces several difficulties, primarily the sluggish kinetics of the ORR, and thermodynamic instability of cathodes under unsympathetic electrochemical conditions. On the other hand, the catalytic reduction of organic substrates such as nitroaromatic**s** is considered as most significant reactions in chemical industry as these are key step in various industrially important organic transformations. Metal NPs involving elements such as Cu, Ni, Pd, Ru, and Pt have been extensively studied as catalysts for a variety of non-identical reduction reactions.

This thesis is broadly categorized in to two major parts. The first part discusses the application of hybrid Pd-based NPs and Cu/MOx-based interfacial catalysts (MOx = $CuFe_2O_4$ or $CuCo_2O_4$) toward ORR in FCs. The second part elaborates the applications of Cu-based NPs for the reduction reactions of various nitroaromatics that are most important in chemical and pharmaceutical applications.

ORR is a multi-electron reaction that proceeds via several elementary steps involving various intermediates and suitable mechanisms on the cathode surface of FCs. In acidic medium, O_2 reduction proceeds as follows:

(i) A direct four-electron reduction pathway where O_2 is converted into H_2O.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

(ii) A partial two-electron reduction pathway that involves formation of H_2O_2 as intermediate.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$

Similarly, O_2 reduction in alkaline medium also proceeds via four-electron pathway to give OH^- as follows:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Or, by a two-electron pathway to give HO_2^- as intermediate and then OH^- as shown below:

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$$

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$$

The slow kinetics of the ORR is among the most limiting factors in the energy conversion efficiency of FCs. For these reason the Pt based catalysts have been extensively used for the desired ORR. However, the high-ceilinged price and low abundance of Pt in resources leads to its high cost of its corresponding devices. Moreover, when Pt is used as cathode catalyst kinetic limitations of the ORR, as well as the low alcohol tolerance in direct alcohol fuel cells become pertinent obstacles in the commercialization of low-temperature fuel cells. Therefore it is an urgent necessity to develop non-platinum based ORR catalysts with low cost, superior efficiency and high alcohol tolerance.

On the other hand, the growing world populations with their intensification of agricultural and industrial activities are responsible for the contamination of air, soils and aquatic ecosystems and also for global climate change. Therefore environmental issues are becoming a major focus of academic and industrial attention. Currently, a global effort have promulgated to understand the impact of human activities on the environment and to develop new technologies that mitigates the health and environmental effects. Among the other strategies to address these persistent challenges of human health and environment, contemporary developments in the field of material sciences have prompted increased interest in using the unique properties of Cu-based catalytic materials for such environmental applications.

The contents of the thesis are broadly divided into seven chapters. **Chapter 1** includes the introduction part and **Chapter 2** summarizes the details of experimental procedures, materials used and the characterization techniques. **Chapter 3**, **Chapter 4**, **Chapter 5 and Chapter 6** include the results and discussion of the present investigation. Conclusions and future scopes of this thesis are presented in **Chapter 7**.

Chapter 1: Introduction

A general introduction to nanotechnology, importance and their emerging applications in diverse areas as catalyst is described in the chapter 1. The present chapter includes an overview on the history, background and use of nanoparticles in catalysis as well as the importance of various nanoparticles in various fields. Furthermore, the chapter describes extensive literature reviews on the applications of Pd-based nanoparticles for electrocatalytic oxygen reduction reaction and Cu-based nanoparticles for the reduction reactions. At the end of this chapter, the final objectives for the present investigation are highlighted.

Chapter 2: Experimental Section

This chapter provides the details of the materials that are used in the entire work. All the experimental methods for the synthesis of nanoparticles and the reaction procedures to evaluate the catalytic activities are described herein. Moreover, the present chapter also contains the details of the different analytical tools and techniques that have been used to characterize the synthesized nanoparticles.

Chapter 3: Synthesis and Characterization of $Pd_{4-x}Fe_x$/C (x = 1-3) and $Pd_3Fe_{0.5}Cu_{0.5}$/C Nanoparticles: Robust Non-Platinum Electrocatalysts for Enhanced Oxygen Reduction Reaction

In the Chapter 3 we have discussed synthesis of different compositions of $Pd_{4-x}Fe_x$/C NPs (x = 1–3) and $Pd_3Fe_{0.5}Cu_{0.5}$/C NPs, via a solvothermal route without adding any surfactant. The synthesized NPs were characterized by different analytical and spectroscopic techniques, for instance, XRD, ICP-OES, TGA, EDX, BET surface area, TEM, XPS etc. The catalytic activities were evaluated towards ORR in both alkaline and acidic media. Furthermore, we have also investigated how the incorporation of small amount of Cu on optimized composition of PdFe/C NPs improve the electrocatalytic ORR activity in all respects as compared to that of the standard Pd/C, Pt/C and other compositions of PdFe/C NPs.

Chapter 4: Synthesis and Characterization of $Pd_3Cu_{0.5}Ni_{0.5}$/C and Pd_2CuCo/C Nanoparticles and Their Oxygen Reduction Reaction Activity

Chapter 4 describes the synthesis and characterization $Pd_3Cu_{0.5}Ni_{0.5}$/C and Pd_2CuCo/C NPs and their ORR activity. Depending on the structure of the NPs this chapter has been divided into two sections as described below.

Section 4A: Synthesis and Characterization of $Pd_3Cu_{0.5}Ni_{0.5}$/C Nanoparticles and Their Oxygen Reduction Reaction Activity

This section contains the synthesis and characterization of $Pd_3Cu_{0.5}Ni_{0.5}$/C NPs by simple one step solvothermal method using hydrazine hydrate ($NH_2NH_2 \cdot H_2O$) as reducing agent. Synthesized $Pd_3Cu_{0.5}Ni_{0.5}$/C NPs were characterized by thermogravimetric analysis, X-ray diffraction, transmission electron microscopy, Brunauer-Emmett-Teller surface area analyses and X-ray photoelectron spectroscopy etc. To evaluate the electrocatalytic ORR properties of $Pd_3Cu_{0.5}Ni_{0.5}$/C, the cyclic voltametry (CV), linear sweep voltametry (LSV) and chronoamperometry (CA) test were empolyed.

Section 4B: Tuning the Electrocatalytic Activity of Pd_2CuCo/C towards Fuel Cell Oxygen Reduction Reaction

In this section, Pd_2CuCo/C (PCCC NFs) flower like NPs were synthesized via facile one step solvothermal process using hydrazine hydrate as a reducing agent and studied their electrocatalytic activity for ORR in both acidic and alkaline media. Experimental results showed that PCCC NFs exhibit superior electrochemical performance for ORR than commercial Pd/C and Pt/C. The highly active (111) exposed facet, multiple twin defects and lattice strain along with synergetic effects are the key factors for enhancement of electrocatalytic activity.

Chapter 5: Synthesis and Characterization of Noble Metal-Free Nanoparticles for Enhanced Oxygen Reduction Electrocatalysis

This chapter describes the synthesis and characterization of carbon (Vulcan XC-72R) supported Cu-$CuFe_2O_4$ and CuCo/CuO-Co_3O_4 NPs and their applications for ORR in fuel cells. The chapter has been divided into two sections, viz., Section 5A, Section 5B as described below.

Section 5A: Synthesis and Characterization of Cu-$CuFe_2O_4$/C Nanoparticles for Enhanced Oxygen Reduction Electrocatalysis

In this section of chapter 5 we have synthesised Cu-$CuFe_2O_4$ onto hetero-atom free Vulcan carbon along with high performing conductive Cu metal through a one-step solvothermal approach at 120 ^oC. In this approach we used inexpensive $CuCl_2 \cdot 2H_2O$, $FeCl_2 \cdot 4H_2O$ as metal precursors and hydrazine hydrate as reducing agent. The as-synthesised catalysts showed very good activity towards ORR in alkaline media. The morphological and the structural propertied of the synthesized NPs were investigated by powder XRD, BET surface area, TEM and HRTEM and XPS analyses. Thus, the present work reports a new way for enhancing the catalytic activity of noble metal free NPs towards ORR in alkaline media.

Section 5B: Synthesis and Characterization of CuCo/CuO-Co_3O_4/C Nanoparticles and Their Electrochemical Oxygen Reduction Reaction Activity

In the section 5B, CuCo/CuO-Co_3O_4/C NPs were synthesized via solvothermal method and characterized by various spectroscopic and analytical techniques. The electrocatalytic activities of the as-synthesized NPs were evaluated for ORR in alkaline media. The CuCo/CuO-Co_3O_4/C exhibited enhanced electrocatalytic activity toward ORR and the reaction proceeds via $4e^-$ pathway. Thus, the synthesized carbon supported CuCo/CuO-Co_3O_4 NPs can be accepted as a noble metal free potential candidate for the application in fuel cell reactions.

Chapter 6: Synthesis and Characterization of Cu-Fe_2O_3 and CuNi Nanoparticles and their Catalytic Activity for the Reduction of Nitroaromatics Compounds

Bimetallic NPs have renewed interest in different fields like magnetic, optical and catalytic application. Their catalytic activity, composition, selectivity are clearly different from mono metallic counterparts. Due to the combination of two metals, bimetallic NPs have additional degrees of freedom which give rise to synergism when used as catalysts. But bimetallic heterogeneous catalyst, especially those non precious, abundant, low cost and synthesise with facile and relatively green method are always be demanded for every time for practical application. In addition magnetically separable NPs have several advantages compared to the traditional heterogeneous catalyst including conservation of energy, cheaper and greener chemical procedure. Moreover electron transfer of the catalyst system also enhances due to the presence of magnetic phase (e.g. iron oxide) which can ultimately increase the efficiency of the catalyst system. In the Chapter 6, we have discussed about the synthesis and characterization of Cu-Fe_2O_3 and CuNi NPs and their catalytic activity for the reduction of different nitroaromatics. This chapter is divided into two sections.

Section 6A: **Facile Synthesis of Embedded Cu/Fe_2O_3 as Magnetically Recoverable Nanoparticles for Efficient Reduction of Nitroaromatics in Aqueous Medium at Room Temperature**

In this section of chapter 6 we have discussed about the synthesis of embedded Cu/Fe_2O_3 as magnetically recoverable NPs and characterized by different analytical techniques. The as-synthesized Cu/Fe_2O_3 NPs lead to mild and selective catalytic reductions of nitro aromatics in water at room temperature, in presence of $NaBH_4$ serve as source of cost-effective hydride.

Section 6B: **Non-precious Magnetically Retrievable CuNi Alloy Catalyst: Transfer Hydrogenation of Nitroaromatics in 2-Propanol**

In the section 6B we demonstrate a heterogeneous magnetically retrievable copper-nickel catalysts system, which were employed for the reduction of nitroaromatics through transfer hydrogenation using 2-propanol as both solvent and hydrogen donor. The CuNi NPs was prepared by facile hydrothermal method without used of any surfactant and structure directing agent. The CuNi NPs system exhibited unique catalytic activity for the reduction of various substituted nitroaromatics to the corresponding valued product due to the synergistic effect of metal Cu and Ni species, giving excellent yields of >95%.

Chapter 7: Conclusions and Future Scopes

This chapter describes the overall conclusions and also the summary of the major findings of the experiments with the significance of the work. The future scopes of the present investigation are also highlighted in this chapter.