Chapter 7

Conclusions and Future Scopes

7.1 Conclusions

This is the concluding chapter of the thesis which combines conclusions drawn from each chapter. The major objectives of the present work were to synthesize, characterize and evaluate the catalytic activity of Pd- and Cu-based NPs. As discussed in the earlier chapter the use of costly platinum (Pt) and its sluggish ORR kinetics are the main drawback for commercialization of PEMFCs. In this present investigation, considerable effort has been made to overcome this issue by developing Pd-based and Cu-based NPs. From the present investigation, it was concluded that Pd-based trimetallic nanocatalyst shows superior activity in all respect than the commercial Pt/C. Moreover, the noble metal-free catalyst also shows good electrocatalytic activity in terms of current density, stability and followed similar mechanism like that of commercial Pt/C. Moreover, Cu/Fe_2O_3 and CuNi also showed very good catalytic activity for reduction of nitroaromatics compounds.

The **Chapter 1** and **Chapter 2** contain general information. **Chapter 1** provides overview on NPs and their catalytic applications specifically ORR and reduction of nitroaromatics. **Chapter 2** of the thesis describes all experimental procedures with the details of materials and characterization techniques that we have used during the whole thesis work. **Chapter 3, 4, 5 and 6** mainly contain the experimental findings during the thesis work to address difficulties observed for ORR and reduction of nitroaromatics. This chapter of the thesis also comprises the future scopes of synthesized NPs in various energy and environment related applications.

Chapter 3: This chapter describes the facile synthesis of various compositions of PdFe/C and $Pd_3Fe_{0.5}Cu_{0.5}$/C NPs that exhibited remarkably enhanced catalytic activity towards ORR. Some major findings from the chapter are highlighted below:

- The Cu incorporated Pd_3Fe/C NPs modified the lattice constrain and d-band center of the $Pd_3Fe_{0.5}Cu_{0.5}$/C.
- This impressively displayed superior activity and long term stability when used as a cathode electrocatalyst towards ORR.
- The nanoalloy with surface defects, for instance; vacancy, dislocation and low-coordinate atomic steps offer numerous energetic sites accessible to catalyze the ORR.

Therefore, the present investigation offers new possibilities for the development of sustainable energy conversion and related technologies with superior activity, favorable kinetics and long term durability in relatively low cost.

Chapter 4: This chapter discussed about the synthesis, characterization and activity of $Pd_3Cu_{0.5}Ni_{0.5}/C$ and Pd_2CuCo/C NPs for ORR. The chapter is divied into two sections. Some major findings from the chapter are highlighted below:

- In Section A of chapter 4, $Pd_3Cu_{0.5}Ni_{0.5}/C$ has been synthesized successfully using surfactant free solvothermal methods and characterized thoroughly.
- The unique nanowire structure of the nanoalloy offers stable electronic coupling between the carbon matrix and $Pd_3Cu_{0.5}Ni_{0.5}$.
- The trimetallic $Pd_3Cu_{0.5}Ni_{0.5}/C$ shows the better electrocatalyic ORR activity than the bimetallic Pd_3Cu/C, Pd_3Ni/C commercial Pd/C and Pt/C.
- Section B of chapter 4 presents a new strategy one-pot surfactant free synthesis of Pd_2CuCo/C (PCCC NFs) with superior electrochemical performance for the ORR.
- The preferential exposure of (111) phase, multiple twin defects and lattice strain along with synergetic effects are the key factors for enhanced ORR activity.
- The hierarchical PCCC NFs would have great potential in the real field of electrocatalysis because of the advantages of unique architectures, alloy composition of nanomaterial and simplistic synthetic procedure, which could provide a new approach for the development of practical catalysts in electrochemical fields.

Chapter 5: This chapter describes the synthesis and characterization of carbon (Vulcan XC-72R) supported $Cu\text{-}CuFe_2O_4$ and $CuCo/CuO\text{-}Co_3O_4$ NPs and their applications for ORR in fuel cells. The chapter has been divided into two sections. Some of the major findings of this chapter describe bellow:

- In Section A of chapter 5, the $Cu\text{-}CuFe_2O_4/C$ cathode materials for superior ORR have been successfully prepared by a facile one-step solvothermal approach.

- The well-defined Cu-$CuFe_2O_4$ NPs are uniformly dispersed on the carbon matrix and result in the enhancement of ORR performance.
- The Cu-$CuFe_2O_4$/C, shows a high limiting current density than physically mixed Cu-$CuFe_2O_4$ + C, bare Cu-$CuFe_2O_4$ and Vulcan carbon.
- In particular, the facile fabricated Cu-$CuFe_2O_4$/C electrode can deliver high limiting current density (0.54 mA/cm^2) and electrochemical stability than state of the art 20wt% Pt/C.

Such outstanding electrochemical performances make the copper ferrites promising materials for the energy-related devices.

Also in the Section B of the chapter,

- CuCo/CuO-Co_3O_4/C NPs were synthesized by facile one-step solvothermal method using hydrazine hydrate as reducing agent.
- The NPs showed very efficient electrocatalytic activity toward ORR in alkaline media.
- The CuCo/CuO-Co_3O_4/C electrode shows high limiting current density than the monometallic Cu/C, Co/C, physically mixed CuCo/CuO-Co_3O_4+C, bare CuCo/CuO-Co_3O_4.
- Moreover, the integration of metallic Cu and Co with CuO-Co_3O_4 NPs can accelerate the transportation of electrons/ion and the chemical interaction of the carbon with CuCo/CuO-Co_3O_4 NPs resulting in the enhancement of ORR performance.

Thus, the present investigation provides a remarkable application of CuCo/CuO-Co_3O_4/C NPs in the fields of fuel cell ORR.

Chapter 6: This chapter describes about the synthesis and characterization of Cu-Fe_2O_3 and CuNi NPs and their catalytic activity for the reduction of different nitroaromatics compounds. This chapter is divided into two sections. Some of the major findings are highlighted below:

In Section A, the fabrication and characterization of the embedded Cu/Fe_2O_3 bimetallic along with two monometaliic NPs for the reduction of nitroaromatics compounds in water at room temperature, in the presence of $NaBH_4$ (as hydrogen donor).

- The catalysts are highly capable and quantitatively reduce a variety of functionalized nitroaromatics compounds to the corresponding amines in > 99% selectivity and conversion, due to the synergistic effect of metal Cu and Fe_2O_3.
- It was seen that *m*-substituted halogen nitro-compounds showed less reactivity compared to their *p*-substituted counterpart. The halogen (F, Cl, Br)-substituted nitro-compounds also reduced to their corresponding amines with no discernible dehalogenation.
- The catalyst is highly stable and can be reused up to 6th cycle without significant loss of catalytic activity. This work can highly motivate in developing new non-precious catalysts for other industrially and academically important reduction reactions.

In Section B, we have synthesised the CuNi NPs using facile hydrothermal method without using any surfactant and harmful organic structure directing agent.

- We describe an efficient approach for synthesis of various high valued compounds from corresponding nitroarenes using CuNi bimetallic alloy NPs.
- Additionally the catalyst can be easily separated by filtration as well as by an external magnet.
- The use of 2-propanol as both solvent and reducing agent instead of other harmful and risky reducing agent makes the process very efficient in industrial manufacture of value added product.

The replacement of precious metal catalysts with less-expensive transition metal in reduction reactions will be of great significance due to the less availability and high cost of noble metals.

7.2 Future Scopes

The present study represents systemic and inclusive study on Pd- and Cu-based NPs with their catalytic activity in the two different energy and environmental related reaction. The increasing energy demand at the same time shrink of fossil fuels and diverse environmental effects of fossil fuel-based technologies are big challenges to the researcher to introduce alternative energy conversion systems for future energy applications. Thus, the fuel cells, solar cells, and batteries are attaining plenty of attention of the researchers due to their independence on fossil fuels and it's greener nature. So, there are numerous opportunities left to introduce these technologies to work in the practical field. Although in the present investigation we have discussed several possibilities of Pd- and Cu-based NPs, but there remain much more scopes for future studies in this area. The following effort may be made for future works.

- The electrocatalytic performance of the carbon supported Pd-based NPs may be explored for hydrogen evolution reaction (HER), oxygen evolution reaction (OER), methanol/ethanol oxidation, formic acid oxidation etc.
- The carbon supported Cu- based NPs may be studied for the electrochemical CO_2 reduction. The analyses of various reduced products of CO_2.
- By controlling different parameters, nanomaterial size and shape can be modified, with their modified size and shape activities needs more investigation.
- Different 0D, 1D and 2D carboneous supports may be also used to enhance the catalytic properties of the above-mentioned catalytic system.
- Mixed metal/metal oxide spinel compounds with various composition and structure can be synthesized by using different methods and may be employed the possible new contributions in the various research domain.
- In detail study is needed to understand the reaction mechanisms of ORR and nitroaromatics reductions and study can be extended to degradation of various organic pollutants. Theoretical calculation/ investigation can also be attempted understanding the details ORR mechanism.