Abstract

Hydrogen (H_2) is an excellent energy server and a clean fuel source, but at present fossil fuel covers the major supply of H_2. We are all aware of the fact that fossil fuel won't last forever and produces a large amount of harmful CO_2. Hence, it is a major concern to search for an alternate H_2 production method. An effective method of H_2 evolution is via electrocatalytic water splitting. Electrochemical water splitting can be powered by renewable energy sources (solar energy, wind energy etc.) which is a means of storing sustainable energy in the form of chemical energy (H_2 molecule). However, numerous research challenges regarding cost-effective and efficient catalyst material, preparation method, corrosion prevention strategies, etc. need to be addressed for widespread implementation of electrocatalytic Hydrogen Evolution Reaction (HER). The present investigation focuses on the development of cost-effective electrocatalyst materials via easy synthesis routes. Our research primarily condensed on the study of the electrocatalytic efficiency of the synthesized materials towards HER. Apart from HER another means to store solar energy is the use of storage device. Batteries and supercapacitors are two major energy storage devices. Batteries take a long time in the charging and discharging process and this time-consuming process generates heat that degrades the material. Compared to batteries supercapacitors possess longer cycle life with no short circuit problem, shorter charge-discharge times, and thus deliberate more power very quickly which is beneficial for applications where high-power uptake and delivery are required. In one of the chapters, we have explored the application possibility of our synthesized material as supercapacitor, along with HER application of the same material. Chapter-wise summary of this doctoral thesis is given below.

Chapter 1: General Introduction

This chapter introduces the motivation of our investigation to carry out the research work. Starting with a brief description of the importance of Hydrogen fuel and the dire need of Hydrogen Evolution Reaction (HER) this chapter emphasizes on the alternate earth abundant and cost effective electrocatalyst to replace Pt, the best HER catalyst till now. Regarding efficiency transition metal phosphides, transition metal chalcogenides, and transition metal selenides are the most explored HER catalysts. Here we try to give a brief overview of the experimental findings behind the best activity of these catalysts and how the research community try to modify it. We address numerous

factors that still need to be overcome by catalysts for its viable commercial implication along with a list of strategies adopted by the researchers for engineering the catalytic activity. Along with HER catalytic activity, the importance of Supercapacitors is also discussed in these advanced technological eras.

Chapter 2: Modulation of the electronic structure of carbon by Cu-doped Co_2P for efficient Hydrogen Evolution Reaction (HER) in acidic medium.

Metal phosphide is one of the most explored HER catalysts. P atom serves as the dopant atom in metal clusters and has a significant role in enhancing catalytic efficiency. However, increasing P content sometimes inhibits the electron delocalisation resulting decrease in charge transfer. Keeping this in mind we targeted to explore the effect of Co_2P nanoparticles on C atom. In this chapter, we have tried to modulate the catalytic activity of expanded graphite by doping Cu-Co_2P multifaceted nanoparticles. To draw the maximum catalytic efficiency, we first tune the Cu content in Co_2P structure and the best catalytic activity was obtained with 0.005 wt% Cu-Co_2P@EG. Our experimental findings provide strong evidence that the multifaceted Cu doped Co_2P could work in concert with carbon atoms of the expanded graphite (EG) that leads in the changing of the energy states of nearby carbon atoms of the metal phosphide particle which is also in well agreement of our theoretical calculation. The lower contact electrical resistance of EG has a significant impact in endowing fast electron transfer to the catalytic active sites and the aid of catalytic performance. The specific morphology of the catalyst hints at increased surface area and overall exposed active sites to bestow the catalytic performance. The study suggests that the energetically modulated carbon atoms can act as a fine active site for HER.

Chapter 3: Fe-doped TiO_2/MWCNT nanocomposite as a robust electrocatalyst for hydrogen evolution reaction.

Except for metal oxides and metal hydroxides all other metal-based efficient HER catalysts do involve harmful chemicals. But study reveals that without modification the oxide-based catalysts do not act as an efficient HER catalyst. In this chapter, we have discussed the electrocatalytic effect of modified metal oxide nanoparticles on MWCNT towards HER. The catalyst is prepared using *in situ* sol-gel method. This method generates a well-defined nanocomposite with individual MWCNTs decorated with active

Fe-doped titania particles. The performance enhancement of Fe-doped TiO_2/MWCNT can be attributed specifically to the increased electric conductivity by MWCNTs. The catalytic activity rises with increasing MWCNT content (from wt% 0.35 to 0.50). MWCNTs provides well channel for mass and charge transfer along with overall increase in the number of active sites in the final composite.

Chapter 4: Fe doped TiO_2/PANI composite as an efficient electrocatalyst for hydrogen evolution reaction in acidic medium.

PANI is known for its good electrical conductivity, high corrosion resistance property and high adsorption of reaction intermediate, but its unsuitable. ΔG_{Hads} value makes it useless for HER. In this chapter, we discuss the change of electrical properties as well as monitor the electrocatalytic activity of PANI after the incorporation of modified TiO_2 nanoparticles into its structure. The nanocomposite was synthesized via in situ polymerization of aniline monomer in presence of Fe-doped TiO_2 particles. However, a unique balance of PANI content is maintained to draw the maximum efficiency from the conjuncture of active Fe-doped TiO_2 particles and PANI. The interfacial electronic coupling of PANI with Fe-doped TiO_2 transfers electrons to the antibonding states of the N atom of PANI enhancing the rapid desorption of H_2 and thus augmenting HER activity to acquire at an overpotential value of 0. V.

Chapter 5: Hierarchically porous N, P co-doped reduced graphene oxide aerogel as a symmetric supercapacitor material and a hydrogen evolution reaction electrocatalyst.

The literature survey reveals that poor-conducting metal catalysts are often accompanied by high-conductive carbon nanomaterials. In an urge to understand the intrinsic role of carbon in these catalysts, here in this chapter, we try to monitor the activity of graphitic carbon atoms whose structure is modified by N and P dual doping in supercapacitor application and HER. Here, we present a hierarchically porous nitrogen and phosphorous co-doped graphitic carbon synthesized *via* an easy multi-step route. The performance of the material is optimized by elemental doping and carbonization temperature variation. The porous N, P co-doped graphitic carbon pyrolyzed at 800°C displays a specific surface area of 613 $m^2\ g^{-1}$ which is significantly enhanced after P doping. P atom sticks out of the graphene plane due to its large size compared to N and C

atom increasing the separation between the graphene layers and consequently, the surface area. The material effectively exploits its unique properties to operate at a high cell voltage of 2 V as well as deliver high energy (84 W h kg^{-1}) and power density (33.6 kW kg^{-1}). The material also performs well at different operating temperatures. The composite not only performs as an excellent supercapacitor but also carries out HER effectively at an overpotential value of 0.351 V to achieve the benchmark current density of 10 mA cm^{-2} coupled with remarkable long-term stability for 17 h.

Chapter 6: Conclusion and future scope

The chapter-wise concluding remarks and future scope of this thesis work are summarized in this chapter. We have carried out a limited study and focused mainly on the electrocatalytic efficiency of our synthesized materials towards HER. However, theoretical studies need to be carried out to gain the proper insight into the catalytic activity of these materials. These carbon-based nanocomposites further can be explored in other energy-related applications, e.g., in OER, ORR, Methanol fuel cell, etc.