

## Abstract

Hydrogen is one of the cleanest forms of energy which can solve several issues, including global energy crisis, environmental pollution and depletion of fossil fuels. Hydrogen evolution reaction (HER), being a carbon-neutral process can reduce the carbon footprint in the earth's atmosphere. There is a variety of processes used for hydrogen production such as cracking of petroleum, hydrocarbon reforming, steam reforming of natural gases, coal gasification, etc. but these techniques are either costly or dependent on fossil fuels with the emission of hazardous by-products. Hence, the possibility of hydrogen production through electrocatalytic water splitting makes it a potential carbon-neutral process for fulfilling energy needs. To date, platinum supported materials are mostly found efficient and resourceful electrocatalysts towards hydrogen production. However, the large scale use of such catalysts is restricted by their scarcity and high cost of the material. In order to accomplish an industrial scale hydrogen production with minimum cost, extensive research has been devoted to discovering earth-abundant materials which have similar or better activity than platinum. Among non-noble metal catalysts, molybdenum based catalysts such as molybdenum carbide ( $\text{Mo}_2\text{C}$ ), sulphide ( $\text{MoS}_2$ ), nitride ( $\text{Mo}_2\text{N}$ ), oxide ( $\text{MoO}_3$ ), phosphide ( $\text{MoP}$ ) etc. have been extensively explored for HER application. The present thesis focuses on the structural design and compositional modulation of molybdenum derivatives through an innovative in-situ synthesis route resulting in a biphasic system such as  $\text{Mo}_2\text{C}/\text{Mo}_2\text{N}$ ,  $\text{Mo}_2\text{C}/\text{MoO}_2$ ,  $\text{Mo}_2\text{C}/\text{MoP}$  etc. to enhance the catalytic activity. We have investigated the efficiency and durability of these composites for electrochemical hydrogen evolution in acidic medium. A detailed study of electrochemical hydrogen evolution revealed that the HER activity get enhanced if  $\text{Mo}_2\text{C}$  and  $\text{Mo}_2\text{N}$  nanocomposite is used as electrocatalyst instead of  $\text{Mo}_2\text{C}$ ,  $\text{Mo}_2\text{N}$  or a physical mixture of both. The catalyst exhibits an overpotential ( $\eta_{10}$ ) of 96 mV with a Tafel slope of 37 mVdec<sup>-1</sup> and durability of 1000 cycles. For the first time, we proposed that molybdenum carbide and molybdenum nitride nanoparticles if produced in-situ can led to a synergistic effect on the HER activity. Theoretical studies are also in-alignment with the experimental findings, where an appreciable charge-transfer at the interface of these nanoparticles was revealed from the charge density plots. Such charge-transfer at the interface between  $\text{Mo}_2\text{C}$  and  $\text{Mo}_2\text{N}$  further facilitate the hydrogen evolution reaction. This is also supported by the free energy calculation which is very close to commercially available Pt/C catalyst. We have extended our investigation for other biphasic systems such as,  $\text{Mo}_2\text{C}/\text{MoO}_2$ ;  $\text{Mo}_2\text{C}/\text{MoP}$  and also explored the possibility of promoter elements for further enhancing the catalytic activity. Copper nanoparticles were found to improve the catalytic activity in one of the  $\text{Mo}_2\text{C}/\text{Mo}_2\text{N}$  composites by reducing the overpotential at higher current density. The catalyst shows an enhancement in the stability (3000 cycles) and a drop in the overpotential ( $\eta_{30}$ ) from 217 mV to 112 mV for the doped one under a current density of 30 mA/cm<sup>2</sup>. Another potential composite of  $\text{Mo}_2\text{C}/\text{MoP}$  supported on mesoporous silica exhibits excellent durability of 5000 cycles and shows an overpotential of 88 mV with an onset potential of 31 mV and a Tafel slope of 37 mVdec<sup>-1</sup>. The work embodied in this thesis represents a concerted effort to continue the development of biphasic nanostructures holding great possibilities for the generation of an efficient and cost-effective catalyst for large scale production of hydrogen.