ABSTRACT

In recent years, researchers have been exploring different strategies to utilize renewable energies to suppress the excessive dependence on fossil fuels to make the world greener. Water-splitting is a process where water can be decomposed to H_2 and O_2 and the former can be utilized as a fuel in fuel cell to get electricity with water as by-product. Water-splitting can be done via photocatalysis, electrocatalysis or photoelectrochemical way. Photocatalytic H_2 generation requires a semiconductor which can absorb the light and facilitates electron-hole pair generation which in turn take part in water-splitting reaction. Photoelectrochemical method is similar to the photocatalytic process and carried out by applying an external bias potential when semiconductor fails to produce enough potential to split water. In case of electrochemical water splitting, water is split-up into H_2 (HER) and O_2 (OER) at cathode and anode, respectively, in an electrochemical process. All these water-splitting and electrochemical reactions require efficient catalyst for the improved performance.

Though TiO_2 is considered as the best photocatalyst, the high band gap of TiO_2 restricts its practical uses in water-splitting reaction. In this regard, chalcogenides are promising due to their visible light active band gap. Among chalcogenides, CdS with a band gap of 2.4 eV along with suitable valance and conduction band position makes it a well explored photocatalyst. In this work, CdS with different morphologies are synthesized and their morphology-dependent photocatalytic activity is demonstrated. In particular, straight morphologies such as nanorods and nanoneedles show higher photoelectrochemical performance as compared to curved nanowires and nanobelts. To improve the CdS performance, heterostructure and solid solution of CdS are prepared with ZnS. In case of heterostructures, $(CdS)_{0.4}/(ZnS)_{0.6}$ shows the best photocatalytic and photoelectrochemical performance among other compositions. In case of solid solution, $Cd_{0.2}Zn_{0.8}S$ shows the best photocatalytic and photoelectrochemical performance among all the synthesized materials. IrO_2 and RuO_2 are generally used as standard OER catalyst but high cost makes these materials less feasible for practical application. Another chalcogenide, i.e., CuS, is synthesized and utilized as OER catalyst. The OER performance of CuS is enhanced by doping of Ni as demonstrated in this work.

In summary, this thesis focuses on the development of chalcogenide nanomaterials as photocatalyst and electrocatalyst for water-splitting reaction.

Keywords: *Solvothermal synthesis, chalcogenide, CdS, ZnS, heterostructures, solid solution, CuS, Ni-doped CuS, photocatalysis, electrocatalysis.*