Abstract

The thesis entitled "*Synthesis of Electrocatalytically Active Functional Hybrid Nanomaterials for Hydrogen Evolution reaction*" describes the design and synthesis of nanostructured functional materials based on polymer, and metal carbide, metal phosphide, and chalcogenides for hydrogen evolution reaction (HER). Facile routes for the synthesis of Poly(α-terthiophene)-Pt nanoparticle-hybrid material (PolyTT-Pt), heteroatom-doped carbon encapsulated Mo_2C, MoP and OsP_2 nanostructure (Mo_2C@NC, MoP@NC, and OsP_2@NPC), and Co_9S_8-$CoSe_2$ heterostructure have been developed. The performance of these electrocatalysts towards HER has been evaluated in terms of overpotential to achieve the benchmark current density (η_{10}), turnover frequency (TOF), and durability. Although the polyyTT-Pt hybrid material contains only 2.77 wt% of Pt, it outperforms the conventional Pt/C interms of mass specific activity. The growth of Mo_2C@NC largely depends on the annealing temperature. The HER performance of Mo_2C@NC is limited only to acidic and alkaline pH. The MoP@NC and WP@NC catalysts were synthesized using supramolecular approach without using the traditional phosphidating agents. The ultrafine OsP_2@NPC catalyst was synthesized by pyrolyzing melamine and triphenylphosphine in presence of osmium-precursor. All the phosphide-based materials are HER active in acidic, neutral, and alkaline pHs. OsP_2 catalyst outperforms the MoP and WP interms of η_{10}, faradic efficiency and TOF. The encapsulation of OsP_2 with N and P-doped carbon and the possible synergistic effect between NPC and OsP_2 enhances the overall performance. The Co_9S_8-$CoSe_2$ heterostructure was synthesized by hydrothermal route and has good electrocatalytic activity toward HER and OER. Two-electrode water electrolyzer is fabricated using the Co_9S_8-$CoSe_2$, and it delivers the benchmark current density of 10 mA/cm^2 at the cell voltage of 1.66 V. It retains 85% of initial current density even for > 20 h of continuous electrolysis.

Keywords: Nanostructure; metal phosphide; carbon support; heteroatom doping; heterostructure; hydrogen evolution reaction; oxygen evolution reaction; water splitting.