Abstract

A green energy-dependent sustainable future can be promised by converting and storing renewable energies in terms of chemical fuels like hydrogen through electrochemical water splitting. However, the requirements of high overpotential to overcome the energy barriers of both hydrogen and oxygen evolution reactions (HER & OER) restrict the overall efficiency of hydrogen generation by electrocatalysis of water. Noble metal based electrocatalysts (platinum, iridium, ruthenium) have been believed as ideal electrocatalysts due to their high activity, selectivity and optimal adsorption ability for HER, OER reaction intermediates. However, their high cost and scarcity compelled scientists to search for new, cost-effective and simple strategies for the development of efficient electrocatalysts. In this regard, rational design of heterostructures and anchoring single-atom catalysts (SAC) on adequate support are the two successful strategies to lower the overpotentials for HER and OER processes. Though substantial work has been presented in the literature based on efficient heterostructure and SAC development, the used conventional methods are extremely time-consuming, energy inefficient and complex. In addition, high quality atomistic interfacing in heterostructure development is difficult to realize due to the multi-step process requirement of the conventional strategies. Stabilization of SACs over a proper support is also very challenging yet important to synergistically enhance catalytic activity of the system specially in the dynamic OER environment where usually reconstruction of the catalyst happens. These challenges drastically reduce the efficiency of the catalysts and increase the required overpotential for HER and OER and thus realization of catalysts with high current density for practical application become very difficult. Therefore, for practical adaptation of these catalysts we need to focus not only on the optimization of performances but also in new technologies to do the processing of the catalyst at low cost. The current thesis thoroughly addresses the described challenges by inventing radically new processes for the development of heterostructures and SACs and by providing theoretical understanding of synergistic electronic coupling for the enhancement of catalytic activity. For instance, atomic interfacing between molybdenum selenide ($MoSe_2$) and nickel cobalt selenide ($NiCo_2Se_4$) has been achieved by selenization induced dealloying process. This results in vertical orientation of inter-spaced $MoSe_2$ on conducting $NiCo_2Se_4$ support which drastically enhances the HER catalytic activity due to its unique structural configuration and synergistic heterostructure formation as confirmed from density functional theory (DFT) thus requires only overpotential of 89 mV to get a current density 10 mA cm^{-2}, and a Tafel slope of 65 mV dec^{-1}. Further, interfacing between crystalline and amorphous structure has been presented here to achieve an advanced crystalline-amorphous core-shell heterostructure of amorphous molybdenum sulfide (a-MoS_x) and crystalline molybdenum tungsten oxide (MoWO) via microwave induced rapid surface amorphization process. From the DFT analysis we found that the core not only provides sufficient conductivity and increases the HER activity of the active site of amorphous a-MoS_x but also substantially increases the number of HER active sites. This results in excellent catalytic activity for HER and exhibits an overpotential of 136 mV at 10 mA cm^{-2} in the acid electrolyte, which is much lower than the overpotential of parent oxide (356 mV) and its fully sulfurized crystalline counterpart (163 mV), and the same catalyst can be extended to operate in various pH conditions as well. In addition, we have realized a rapid and energy efficient recrystallization strategy based on microwave irradiation for the universal development of nickel-iron based chalcogenide and phosphides. This strategy results in biphasic structure of iron doped Ni_3S_2/NiS which shows exceptionally high OER activity requiring only 187 mV for 10 mA cm^{-2} and commercial level current density of 500 mA cm^{-2} at 289 mV. The comprehensive analysis indicates the phase evolution of NiS to amorphous Ni-(oxy)hydroxide during OER process to generate iron doped Ni_3S_2/NiOOH heterostructure is the reason for its high activity. Furthermore, single atom iridium has been photochemically decorated on the surface of $MoSe_2$@$NiCo_2Se_4$ heterostructure which on electrochemical surface reconstruction displays outstanding OER activity, requiring only 200 mV overpotentials for 10 mA cm^{-2}. A series of post-OER characterizations have been done to understand how iridium single atoms stabilize over the surface of base material and the structure realized from these findings has been used in DFT to understand the origin of high activity of this catalyst. We believe, this present thesis work will provide a new direction for the development of electrocatalysts via new efficient strategies and lay the platform for the development of highly active practical electrocatalysts not only in water electrolysis application but also in diverse fields like sea water splitting, fuel cell and metal-air batteries.