Nanostructured Non-Precious Metal-based Electrocatalysts: Water Electrolysis and CO_2 Reduction

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The rapid growth of global economic and industrial activities has alarmed towards the increased energy consumption. Renewable energy powered (hydrogen) H_2 production is widely recognized as a promising energy alternative due to its high energy density and are found to be environmentally clean in nature, as its utilization results in water as the sole by-product. Conventional water electrolysis relies on high-purity water which poses a significant challenge in the context of diminishing freshwater availability. Groundwater or seawater offers can have easy accessibility. However, its practical implementation is limited by several technical challenges, which includes sluggish catalytic electrode kinetics, system degradation and economic viability. In recent years, nanostructured materials have attracted considerable attention in electrochemical energy conversion applications owing to their distinctive structural and electronic properties. Nano-structuring of electrode materials leads to an increased electrochemically active surface area, improved charge transfer characteristics, and enhanced availability of catalytic active sites. Moreover, the ability to tailor morphology, composition, and surface chemistry at the nanoscale provides opportunities to improve catalytic activity, selectivity, and stability under industrial current densities. Although notable progress has been made, stable electrodes for high current operations and their structure – electrochemical activity relations remain under progress. A systematic and fundamental understanding of these properties is essential for the rational design of next - generation electrocatalysts for water electrolysis.

In addition to water electrolysis, electrochemical CO_2 reduction into valuable products especially formic acid makes the carbon cycle complete. Formic acid is a safe, high-density H_2 source (4.4 wt.%). CO_2 reduction to into formate/formic acid remains challenging owing to the need for catalysts that perform well under reductive conditions as well as competition from HER still hinder its high yield. Although high Faradaic efficiencies of formate/formic acid (>90%) have been reported, the catalysts still suffer from limited activity and stability. New synthetic routes for robust catalysts are essential for the development of selective and durable high efficiency CO_2 reduction electrocatalysts.

The present thesis explores newer and effective ways of synthesis, characterization, and electrochemical analysis of non-precious metal-based nanostructured electrocatalysts for water splitting

and CO_2 reduction. The primary objective of this work is to develop electrocatalysts that can exhibit high catalytic activity, selectivity toward HER, OER and CO_2 reduction with long-term stable performance. The outcomes of this study are expected to contribute to the advancement of water electrolysis and CO_2 reduction technologies and support the broader goal of sustainable H_2 production for clean environment.

Chapter 1 gives a brief introduction of various type of nanostructured electrocatalysts for electrocatalytic reactions such as OER, HER and CO_2RR and their direct applications in electrochemical devices. An elaborative discussion over the importance of structure and activity relationship has been covered. Also, the chapter gives an overview of various types of electrochemical techniques and parameter for electrocatalyst evaluation as well as their characterisations.

In **Chapter 2**, we have synthesized a highly active catalyst $FeNiP_x/FeNiO_x/NF$ and demonstrated for the electro chemical OER. Dense crystalline $FeNiP_x$ – amorphous $FeNiO_x$ interfacial sites were directly grown on a NF substrate, making the catalyst robust and suitable for delivering high current density. $FeNiP_x/FeNiO_x/NF$ required only an overpotential of 220 mV to deliver an ampere-level current density with a small Tafel slope value of 42 mV dec^{-1}. It also effectively worked for seawater electrolysis. As an anode in an electrolyzer, $FeNiP_x$/ $FeNiO_x/NF$ delivered 1 A cm^{-2} current density at a low cell voltage of 1.9 V, making it one of the most efficient earth abundant catalytic anodes for water electrolysis. Spectroscopic and theoretical studies suggested strong synergy between crystalline $FeNiP_x$ nanoparticles and amorphous $FeNiO_x$ nanosheets via modulation of d-band centres. This synergy was possible as strongly coupled crystalline-amorphous interfaces can effectively tune the electronic structure of active sites and suppress the OER overpotential. In addition, studies also found that during the OER process $FeNiP_x/FeNiO_x/NF$ produces high valence Ni^{3+}/Fe^{4+} phases, while highly embedded crystalline FeNiPx nanoparticles are found quite stable for longer durations.

In **Chapter 3**, an efficient and robust bifunctional electrocatalyst, $FeNiCoP_x/FeNiCoO_x/NF$, is reported with amorphous-crystalline interfaces synthesized by integrating nanocrystalline $FeNiCoP_x$ with amorphous $FeNiCoO_x$ sheets evolved on nickel foam having two-step controlled hydrothermal-phosphidation process. The $FeNiCoP_x/FeNiCoO_x/NF$ demonstrated excellent OER and HER activity having an overpotential of ~220 and 120 mV to reach 100 mA cm^{-2} current density having small Tafel slopes of 42 and 75 mV dec^{-1}, respectively. This also adequately worked for seawater electrolysis. Bifunctional $FeNiCoP_x/FeNiCoO_x/NF$ assembled in an alkaline seawater electrolyzer, an ampere-level current density was achieved at cell potential of 2.06 V, placing it among most effective seawater electrocatalysts. Experimental and theoretical investigations revealed a strong coupling between nanocrystalline $FeNiCoP_x$ particles and amorphous $FeNiCoO_x$ nanosheets via alteration of d-band centres. The synthetic strategy and crystalline-amorphous interface regulations in this work provide directions for constructing highly efficient and stable bifunctional electrodes for commercial alkaline water electrolysis.

In **Chapter 4**, we have demonstrated a MOF-derived FeNi-NC/NF catalyst that comprises with FeNi nanoparticles embedded into N-doped carbon directly grown on nickel foam. The developed FeNi-NC/NF electrode is highly active and selective for the ethanol oxidation reaction to ethyl acetate (EOR) and HER. Specifically, FeNi-NC/NF requires only a potential of 1.5 V and 1.6 V for delivering 200 mA cm^{-2} and 500 mA cm^{-2} current densities, respectively, for EOR. The electrochemical and spectroscopic evidence suggest the EOR to be taken place via indirect pathway (HAT mechanism). Further, FeNi-NC/NF integrated EOR||HER electrolyzer exhibited a high current density of 0.5 A cm^{-2} at a cell potential of 2.0 V with electrical efficiency of ~70%. The post EOR spectroscopy revealed the retention of FeNi alloy nanoparticles with reconstructed surface layer to FeNiOOH. This work provides new opportunities in designing a very selective catalyst for building devices to produce both H_2 and high-value products from water and ethanol, respectively.

In **Chapter 5**, we have designed an electrode, Bi_2O_3@Bi-MOF-125, having uniformly embedded ultrafine Bi_2O_3 nanoparticles within Bi-MOF. Bi_2O_3@Bi-MOF-125 demonstrated selective electrochemical CO_2 reduction into formate with maintaining high faradaic efficiency (~97%) during the operations at current densities of 100 to 150 mA cm^{-2}. In flow-through cell, the electrode reached a high current density of 300 mA cm^{-2}. Spectroscopic studies suggest that Bi_2O_3@Bi-MOF-125 undergoes reconstruction and gets converted into $Bi/Bi_2O_2CO_3$ phase which are composed of Bi nanoparticles decorated into $Bi_2O_2CO_3$ nanosheets. Studies also reveal a strong synergistic interaction between Bi and $Bi_2O_2CO_3$ for high selectivity for electrochemical CO_2 conversion into formate.

In **Chapter 6**, we have derived the conclusion based upon the present studies. Important suggestions, and future scope and prospects of the work is also discussed.

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