Abstract

The rising importance of photocatalysis and electrocatalysis as clean energy technologies has created massive interest in material sciences and nanotechnology for development of nanocatalysts with optimal characteristics for maximum catalytic performance. This work aims to address this scope in clean energy catalysis by presenting a detailed understanding of the design and characterization of five different grades of novel nanostructures for applications in photocatalytic wastewater treatment and electrochemical / photoelectrochemical water splitting. The materials have been designed in particular nano-architectures and their morphology has been tailored to achieve maximum electronic activity. The developed samples have been applied in visible light photodegradation of different organic compounds, especially pharmaceuticals and in water splitting experiments. Thus dual catalytic applications have been studied to establish the immense value of each sample as an energy material.

The first phase of work discusses the influence of cerium dopants on the evolution of the morphological and optoelectronic properties of indium sulphide (In_2S_3) nanosheets. The insertion of cerium into pristine In_2S_3 microflowers resulted in formation of distinct nanosheets with higher crystallinity. The doped samples achieved above 90% photodegradation of complex fluoroquinolone compound ciprofloxacin. The second phase of work demonstrates the excellent dual catalytic properties of cobalt oxalate (CoC_2O_4) nanorods and also explores their morphological tunability for enhancing catalytic performance. The samples have been developed in nanorods of different dimensions by solvent mediated coprecipiation techniques. The nanorods developed in tetrahydrofuran revealed consistent nanoscale dimensions and achieved robust electrocatalytic oxygen evolution generating a current density of 10 mA/cm^2 at a remarkably low overpotential of 240 mV. These samples also achieved 97% degradation of organic complex ofloxacin within 90 min. The third phase of work establishes the excellent photocatalytic activity of potassium vanadate ($K_2V_3O_8$) nanorods. The nanorod morphology was tailored by surfactant assisted techniques to enhance catalytic performance. The enhanced charge transfer along the tailored surfaces resulted in 93% degradation of complex pharmaceutical levofloxacin and a robust photocurrent density of 0.7 mA/cm^2 at 1.23 V vs RHE. The fourth phase of work establishes the synergistic influence of niobium and vanadium atoms in vanadium pentoxide (V_2O_5) nanorods for enhanced photocatalytic performance. Niobium dopants have improved the structural and optoelectronic properties of V_2O_5 nanorods, resulting in enhanced charge kinetics for photocatalytic and photoelectrochemical activity. The optimally doped samples achieved a maximum degradation of 91% caffeine. The boosted charge kinetics also resulted in a maximum photocurrent generation of 0.97 mA/cm^2 at 1.4 V vs RHE in a photoelectrochemical cell. The fifth and final phase of research work establishes the controlled morphological growth of gadolinium molybdate (Gd_2MoO_6) nanoflakes and demonstrates their robust electrocatalytic oxygen evolution activity. Nanostructuring the nanoflake surfaces has had a profound influence on their electrochemical performances. The samples containing nanoflakes with superior morphological and structural properties achieved oxygen evolution with much lower overpotential and Tafel slope.

In all the samples, structural tuning has had strong influence on optoelectronic properties, resulting in modified band gaps and lesser electron hole recombination tendencies. These properties have been studied by various crystallographic, microscopic and spectroscopic characterization techniques. DFT calculations have been performed to theoretically verify the experimental results. The correlations between different properties have thus been understood and this understanding has been applied in developing nanocatalysts with optimum activity. The optimal samples in each of the studies achieved catalytic activity comparable with, or even better than most state-of-the-art catalysts for photodegradation or water splitting. Thus this thesis provides novel insights into the rational design and analysis of novel nanostructures belonging to five different grades of materials for application in clean energy catalysis.

Keywords: Nanomaterials, Photocatalysis, Electrocatalysis, Photoelectrochemical water splitting, Photocatalytic wastewater treatment, Doping, Nanostructuring, Transition metal sulphides/ oxides, Spectroscopic study, Reactor Setup, DFT study