ELECTRO-CATALYTIC AND PHOTO-ELECTROCHEMICAL WATER SPLITTING BY GRAPHITIC CARBON NITRIDE-BASED NANO-HETEROSTRUCTURES

By

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ABSTRACT

The recent challenge for our society is to tackle the present energy crises by moving towards the clean environment and availability of sufficient energy. Interestingly, among the various sources of renewable energy such as solar, biomass, biofuel, geothermal, wind, tidal, solar energy has gained a lot of attention as it is the largest and one of the most promising source for sustainable development without having any compromise with the quality of environment. The generation of hydrogen and oxygen through electrochemical water splitting especially the light assisted i.e. photo-electrochemical (PEC) water splitting reaction is an attractive solution towards sustainable and clean sources of energy. Eventually, it has become one of the prime technologies to answer the sporadic storage problem related to solar energy. The thesis is aimed to synthesize and characterize various nano and nanoheterostructured materials by simple methods such as in-situ heating and hydrothermal for application in photoelectrochemical (PEC) water splitting and hydrogen evolution reaction catalyst. These two areas have immense potential to meet the future energy demands and solve the present energy crises scenario. Transition metal based catalysts are studied due to their many advantages over other metals, such as cost effective features, easy modification of electronic structure, easy synthesis, versatile activity and stability under broad range of pH value.

The thesis deals with the metal oxide nanostructure and nanoheterostructure of metal oxide and graphitic carbon nitride (g-C_3N_4). Photoelectrocatalytic activity for Oxygen evolution reaction and Electro catalytic for Hydrogen evolution reaction were investigated. Synthesis of 2D/2D interfaces between nickel/nickel oxide (Ni/NiO) hexagonal nanosheets with graphitic-carbon nitride (g-C_3N_4) using an in-situ solid-state heat treatment was done, which results in higher electrochemical and PEC water splitting activity of 2D/2D interface depicting a maximum OER photocurrent

density of 20 mA cm^{-2} at an over potential of 190 mV. Varying the ratio of precursors effect for NiO to that of g-C_3N_4 viz. 1:1, 1:8, and 1:16 was also studied. Among which, the highest ratio of NiO to g-C_3N_4 nanosheets (i.e. 1:1) was noted to demonstrate the best performance towards electrochemical (HER) hydrogen evolution reaction showing dramatically reduced over potential to 26 mV to drive a current density of 10 mA cm^{-2} and 1:8 for OER. The enhanced results may be due to the more intimate contact between 2D sheets of NiO with g-C_3N_4. Next Nickel Incorporated Graphitic Carbon Nitride Supported Copper Sulfide reported for Efficient Noble-Metal-Free Photo-electrochemical Water Splitting. These copper sulfides supported on nickel-incorporated graphitic carbon nitride (Ni/g-C_3N_4@CuS) sheets improved the PEC activity due to the formation of p-n junction. The Ni/g-C_3N_4@CuS nanohybrids depicts almost three-fold enhancement in current density under light illumination reaching to 15.5 mA cm^{-2} at an over potential of ca. 600 mV than in the dark and almost fifteen-fold enhancement as compared to its parent materials, CuS and g-C_3N_4. Further work is done on the in-Situ solid-state synthesis combination of hexagonal sheets and tubes a composite of MoO_3/g-C_3N_4 for enhanced photo-electrochemical water splitting. The effect of the composition of g-C_3N_4 sheets to MoO_3 viz. 1:1, 8:1, and 16:1 has been studied. Among these, the 8:1 (i.e. 8 parts g-C_3N_4 and 1 part MoO_3) have been found to be the best for the PEC activity. The said heterojunction leads to improvement in PEC activity by having the photocurrent density of 4.96 mA cm^{-2} at an over potential of 190 mV. Next we tried to study the ternary nanoheterostructures composed of two metal oxides Ni/NiO and Co_3O_4 with graphitic carbon nitride forming 2D/3D interfaces. This formation of ternary nanoheterostrutures leads to the enhanced PEC response, g-C_3N_4/NiNiO/Co_3O_4 was noted to be 2.5 times g-C_3N_4/NiNiO and 5.8 times g-C_3N_4/Co_3O_4 higher than the individual composites. Besides, doing the study on heterojunctions for HER and OER we also tried to develop a catalyst for the study of methanol oxidation and methanol assisted electrochemical water splitting. We tried to decorate the Ag nanoparticles on the surface of dendritic hematite. We observed the enhanced electro catalytic activity for water splitting with the increase in the addition methanol amount which could be attributed to the synergistic effect of hematite dendrites, larger surface area of dendrite structure leading to higher loading of Ag NPs. Following the chapters in details, the thesis present conclusion and future scope where we plan to modify the g-C_3N_4 by making heterostructures with metal oxide and suggesting new materials to have efficient PEC results and optimizing the charge-transfer process at the interface.