Titanium Dioxide Based Heterojunction Nanomaterials for Solar-to-Chemical Energy Conversion and Selective Oxidation of Organic Substances

ABSTRACT

In recent years, generation of a greener fuel, i.e., hydrogen (H_2), on the semiconductor surface using solar energy in a single step photochemical (PC) or photoelectrochemical (PEC) water splitting has attracted great attention of the scientific community to make a carbon free society. The PC/PEC water splitting requires a semiconductor which absorbs maximum solar energy with minimum recombination of charge carriers. Another prospect of photocatalysis is to produce value-added organic chemicals by the oxidation of different organic precursor materials using solar energy. Therefore, the major concern in this field is controlling of the semiconducting properties of the photocatalyst material which regulate the light absorption and creation for photoexcited charge carriers for the catalytic reaction. TiO_2 is considered as an excellent photocatalyst for overall water splitting and for organic transformation reaction. However, the major limiting factors with TiO_2 involve poor visible light absorption ability of anatase TiO_2, low charge separation and low quantum efficiency. Therefore, the best possible way to enhance its performance is by forming homojunction or heterojunction with different phases of TiO_2 or with a different semiconductor material. Here, we demonstrate synthesis of mixed phase (anatase+rutile) TiO_2 that forms a type-II homojunction and several heterojunctions such as CuS/TiO_2, ZnS/TiO_2 and $g\text{-}C_3N_4/TiO_2$ using facile solution chemistry routes, i.e., either hydrothermal/solvothermal and/or chemical precipitation. The anatase to rutile ratio of 41:59 in the mixed phase TiO_2 shows the best H_2 generation performance among other compositions. The CuS/TiO_2 forms a type-II band alignment that enhances the charge separation and migration as confirmed from different characterization techniques leading to enhanced PC and PEC H_2 generation activity. Interestingly, sulfur vacancy induced ZnS/TiO_2 heterojunction forms a Z-scheme band alignment with more negative conduction band potential and more positive valence band potential, which substantially enhances the PC and PEC water splitting performance of TiO_2. Moreover, this heterojunction is employed to oxidize benzyl alcohol in situ water splitting. Another heterojunction ($g\text{-}C_3N_4/TiO_2$) is further demonstrated to enhance the performance of TiO_2 for PC water splitting and oxidation of benzylamine which is supported by theoretical analysis. In summary this thesis focuses on the development of TiO_2 based homojunction/heterojunction photocatalysts for PC and PEC water splitting as well as for the synthesis of value-added organic chemicals.

Keywords: *Solvothermal synthesis, wet chemical synthesis, homojunction, heterojunction, anatase and rutile TiO_2, CuS, ZnS, g-C_3N_4, photocatalysis, photoelectrocatalysis, organic transformation.*