

ABSTRACT

Abstract

This thesis presents the synthesis and characterization of novel Visible-light-driven (VLD) semiconductor nanocomposites with enhanced photocatalytic properties and stability. The research work included in this thesis is divided into five chapters. The chapter wise organization of this thesis is as follows.

CHAPTER 1

Introduction

The first chapter deals with the general introduction of nanomaterials and semiconductor based nanomaterials and nanocomposites. The nanomaterials are a kind of bridge between bulk materials and atomic or molecular structures. The term nanomaterials is employed to describe a class of materials which display properties present in neither their bulk nor molecular counterparts, or “materials with structural features in between those of atoms and bulk materials, with at least one dimension in nanometer range ($1\text{nm} = 10^{-9}\text{ m}$)”. Reithmaier, a physicist while explaining the expected changes in the nanometer range expressed that “*the properties of a solid can change dramatically if its dimensions or the dimensions of the constituent phases become smaller than some critical length associated with these properties.*”

Among all nanomaterials, semiconductor nanomaterials have received considerable attention because of their unique physical, electrical and optical properties that are size dependant at nanoscale. The energy conversion and environmental accountability are two major challenges to the sustainable development of human society. Semiconductor-based photocatalysis lies at the heart of green technology, and has attracted considerable and prime attention, as one of the most promising solutions for these problems. To exploit the visible region efficiently, which overlaps the large part of solar spectrum, the development of visible-light-driven (VLD) photocatalysts has become one of the desired topics in the photocatalytic field. Although much efforts have been dedicated towards developing VLD photocatalysts and many novel VLD photocatalysts have been reported, but there are still many limitations associated with these catalysts such as high recombination rate of photogenerated electron-hole pairs, and unsatisfactory photoresponse range. Therefore, it is still necessary to devise new strategies for the design of VLD photocatalysts with improved visible light activity and enhanced visible light

absorption. One such strategy is the construction of a semiconductor heterojunction or nanocomposites. Nanocomposites (NCs) are composite materials made from combination of two or more distinct materials in which at least one of the phases show dimensions in the nanometer range ($1\text{nm}=10^{-9}\text{ m}$). In recent years, extensive efforts have been dedicated towards design and fabrication of semiconductor heterojunctions with enhanced photocatalytic activity. Although there are various categories of nanocomposites, we have carried out our work on S-S nanocomposites. In the recent past, different types of S-S heterojunctions have been reported as efficient photocatalysts.

CHAPTER 2

Ag₂S/Bi₂WO₆ nanocomposites with high photocatalytic activity and stability

Bi₂WO₆ is one of the simplest members of Aurivillius family, and has been used as one of the promising and excellent photocatalyst for water splitting and decomposition of organic pollutants under visible light. However, there are two important factors which limit the photocatalytic efficiency, and thus hinder the practical application of bare Bi₂WO₆: (1) the absorption edge of pure Bi₂WO₆ is ca, 450 nm which overlaps a small part of solar spectrum leading to the unsatisfactory photoresponse range, and (2) the recombination rate of photoinduced charge carriers is high and therefore, leads to the low quantum efficiency. Therefore, to overcome these drawbacks, and to harvest solar energy more efficiently, we synthesized novel Ag₂S/Bi₂WO₆ heterostructures *via* solvothermal route. The novel photocatalyst was synthesized by impregnating Ag₂S into Bi₂WO₆ semiconductor *via* solvothermal route without any surfactants or templates. Ag₂S is an important chalcogenide with a narrow band gap of 1.1 eV. Owing to the high chemical stability, narrow band gap, high absorption coefficient, and excellent optical limiting properties of Ag₂S, it was coupled with Bi₂WO₆ to form a heterojunction so as to extend the absorption edge of Bi₂WO₆ and simultaneously reduce electron-hole recombination. The photocatalyst was characterized with XRD, SEM, EDS, TEM, BET, XPS, and UV-vis DRS analyses. The characterization results suggest mesoporous hierarchical spherical structures with a high surface area and improved photoresponse in the visible spectrum. Compared to bare Bi₂WO₆, Ag₂S/Bi₂WO₆ exhibited much higher photocatalytic activity towards the degradation of dye Rhodamine B (RhB). The stability of the catalyst was checked by recycling experiments. Two possible reasons have been proposed for the enhanced visible light activity and stability of this novel photocatalyst: (1) broadening of the photoabsorption range, and (2) efficient separation of photoinduced charge carriers

which does not allow the photoexcited electrons to accumulate on the conduction band of Ag_2S and hence prevents the photocorrosion.

CHAPTER 3

$\text{AgBr}/\text{Ag}_2\text{CO}_3$ composites with high stability and photocatalytic activity

Ag_2CO_3 is an important narrow band gap semiconductor with plane triangular structure. Ag_2CO_3 has a band gap of 2.46 eV, and has been recognised as one of the most promising visible-light-driven (VLD) photocatalyst for its excellent and efficient photooxidative capabilities. However, Ag_2CO_3 is unstable. The recycle experiments suggested that Ag_2CO_3 was not stable and displayed photocorrosion which seriously deactivates the photocatalyst. It is therefore, necessary to fabricate the original Ag_2CO_3 , so as to improve its stability, and to further enhance its photocatalytic efficiency. Therefore, we synthesized $\text{AgBr}/\text{Ag}_2\text{CO}_3$ hybrids with different contents of AgBr by *in situ* exchange method. This novel system can easily transform into plasmonic $\text{Ag}@\text{AgBr}/\text{Ag}_2\text{CO}_3@$ Ag system in the early stages of photocatalytic reaction. The as prepared $\text{AgBr}/\text{Ag}_2\text{CO}_3$ hybrids exhibited wide absorption in the visible light region and displayed efficient and higher photocatalytic activities towards the degradation of dye molecules (Ponceau BS) as compared to pure AgBr and Ag_2CO_3 samples under visible light irradiation. The stability of the catalyst was investigated and it was found that after the formation of heterojunction with AgBr, the stability of the catalyst improved significantly. The improved visible light activity and stability of the catalyst was related to efficient separation of electron-hole pairs derived from matching band potentials between AgBr and Ag_2CO_3 , as well as the good electron trapping role of Ag nanoparticles *in situ* formed on the surface of AgBr and Ag_2CO_3 particles during photocatalytic oxidation process.

CHAPTER 4

$\text{Ag}_3\text{PO}_4/\text{BiOBr}$ heterojunctions with high photocatalytic activity and stability

BiOBr is an important V-VI-VII ternary compound, and belongs to the family of main group multicomponent metal oxyhalides. It is known to exhibit good photocatalytic activity due to the hybridization between O 2p and Bi 6s states. However, the band gap of BiOBr has been reported around (2.9 eV) which limits its absorption above 430 nm, and to further enhance the photocatalytic activity of BiOBr for practical applications, it is important to decrease the electron-hole recombination to a higher rate.

Ag_3PO_4 is a visible light responsive photocatalyst, and exhibits extremely high photooxidative capability for O_2 evolution from water, and decomposition of organic

dyes. Ag_3PO_4 has a band gap of around 2.36-2.40 eV which enables it to absorb visible light up to 540 nm, and therefore could act as a sensitizer, and enhance the visible light absorption. Considering the extended photoresponse range and the unique photo oxidative ability of Ag_3PO_4 , we coupled it with BiOBr so as to enhance the visible light absorption and photocatalytic activity of BiOBr. The as synthesized $\text{Ag}_3\text{PO}_4/\text{BiOBr}$ microspheres were characterized with transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), X-ray diffraction (XRD) and UV-vis. diffuse reflectance spectroscopy (DRS). The new $\text{Ag}_3\text{PO}_4/\text{BiOBr}$ heterojunctions exhibited wide absorption in the visible-light region and compared to pure BiOBr and Ag_3PO_4 samples displayed exceptionally high photocatalytic activity for the degradation of typical organic pollutants such as Rhodamine B (RhB) and phenol. The optimal Ag/Bi weight ratio in $\text{Ag}_3\text{PO}_4/\text{BiOBr}$ microsphere (AB7) was found to be 0.7. The enhanced photocatalytic activity was related to the efficient separation of electron-hole pairs at interface. Moreover, the synthesized samples exhibited good stability and did not show significant loss of activity in repetition experiments.

CHAPTER 5

$\text{Fe}_2\text{O}_3/\text{BiOI}$ nanocomposites with high activity and stability

BiOI is an attractive p-type semiconductor having a band gap of 1.78 eV, which makes it to exhibit strong photoresponse in visible light region. The coupling of p-type semiconductors with n-type semiconductors is believed to improve the separation efficiency of photogenerated charges because an internal electric field is generated when junction is formed between them. Therefore, to facilitate the separation of photoinduced charge carriers in BiOI, it is extremely fit to couple it with a n-type semiconductor which will result in the generation of internal electric field, with the direction from n-type semiconductor to p-type semiconductor. BiOI has been previously coupled with many n-type semiconductors to improve its catalytic ability such as n-type TiO_2 , $\text{ZnSn}(\text{OH})_6$, ZnTiO_3 , ZnO , Zn_2SnO_4 .

Fe_2O_3 is an n-type semiconductor and its energy band can well match with that of BiOI which will favour the transfer of photogenerated charges. Further, coupling of n-type Fe_2O_3 with p-type BiOI results in the formation of a stable heterojunction which favours the separation of photogenerated charge carriers due to the generation of internal electric field, and hence effectively facilitates the separation of photogenerated electron-hole pairs. In the present work, novel p-n heterojunction between nanostructured p-type BiOI and n-type Fe_2O_3 were fabricated to overcome the draw backs of low quantum

efficiency. The $\text{Fe}_2\text{O}_3/\text{BiOI}$ composites were synthesized by a simple *in situ* hydrolysis method under solvothermal conditions. The as synthesized nanocomposites were studied using several characterization tools including X-ray diffraction (XRD), scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), Fourier transform infrared (FTIR), N_2 adsorption-desorption isotherms (BET) and UV-visible diffuse reflectance spectroscopy (UV-DRS). The photodegradation performances of the $x\text{Fe}/y\text{Bi}$ samples were investigated using aqueous solution of Rhodamine B (RhB) dye. The $x\text{Fe}/y\text{Bi}$ composites displayed much higher photocatalytic efficiencies for RhB degradation than the single BiOI under visible light ($\lambda > 400 \text{ nm}$). The novel $\text{Fe}_2\text{O}_3/\text{BiOI}$ heterojunction was found to be highly stable in cyclic experiments. The enhanced photocatalytic efficiency can be mainly ascribed to the formation of stable p-n heterojunction between Fe_2O_3 and BiOI, which facilitates the transfer and separation of photogenerated electron-hole pairs.