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Hierarchical architectures of $ZnS–In_2S_3$ solid solution onto TiO_2 nanofibers with high visible-light photocatalytic activity

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ABSTRACT

A unique hierarchical architecture of $ZnS–In_2S_3$ solid solution nanostructures onto TiO_2 nanofibers (TiO_2@$ZnS–In_2S_3$) has been successfully fabricated by simple hydrothermal method. The $ZnS–In_2S_3$ solid solution nanostructures exhibit a diversity of morphologies: nanosheet, nanorod and nanoparticle. The porous TiO_2 nanofiber templates effectively inhibit the aggregation growth of $ZnS–In_2S_3$ solid solution. The formation of $ZnS–In_2S_3$ solid solution is proved by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) and the intimate contact between TiO_2 nanofibers and $ZnS–In_2S_3$ solid solution favors fast transfer of photogenerated electrons. The trinary TiO_2@$ZnS–In_2S_3$ heterostructures exhibit high adsorption capacity and visible light photocatalytic activity for the degradation of rhodamine B dye (RhB), remarkably superior to pure TiO_2 nanofibers or binary structures (ZnS/TiO_2 nanofibers, In_2S_3/TiO_2 nanofibers and $ZnS–In_2S_3$ solid solution). Under visible light irradiation the RhB photocatalytic degradation rate over TiO_2@$ZnS–In_2S_3$ heterostructures is about 16.7, 12.5, 6.3, 5.9, and 2.2 times that over pure TiO_2 nanofibers, ZnS nanoparticles, In_2S_3/TiO_2 nanofibers, ZnS/TiO_2 nanofibers, and ZnS-In_2S_3 solid solution, respectively. Furthermore, the TiO_2@$ZnS–In_2S_3$ heterostructures show highly stable recycling performance.

1. Introduction

Dye wastewater is characterized by large amounts of discharge, high concentration, complicated composition and high chroma. Especially various pollutants composed of synthetic textile dyes and other industrial dyestuffs, which are harmful to human health, arouse great attention [1]. Most of dyes are difficult to degrade by natural ways. The oxidization process employing TiO_2 photocatalyst has attracted great attention because of nontoxic, abundant and easily available [2–4]. However, the application of TiO_2 is limited due to its nature drawbacks of poor visible light utilization and high recombination of photogenerated electron–hole pairs. To overcome the obstacles, numerous strategies have been adopted, including doping with noble metal [5], modification with graphene [6], metal oxides or sulfides [7,8].

Sulfide semiconductor-based photocatalysts have attracted great attention due to their remarkable visible light absorption and high energy conversion efficiency [9]. However, most of the metal sulfides are known for their instability during photocatalytic process. Forming a sulfide solid solution, such as $In_{2x}Zn_{3(1-x)}S_3$ [9], $Zn_{1-x}Cd_xS$ [10,11], and ZnS–CuS [12], is regarded as a viable method to solve the problem. The properties of sulfide solid solution can be optimized by regulating their band gaps and morphologies [9–14].

Moreover, the structure and morphology of photocatalytic materials is one of the most important factors to determine their photocatalytic activities [15,16]. As we well know, the three-dimensional (3-D) hierarchical structure is an ideal morphology which can expose as many active sites as possible and make it use light better though strong light scatterings [17]. In general, the formation of such a nanostructure based on semiconductor materials can be achieved through solution growth model [18]. However, sulfide solid solution nanostructures built by solution growth model tend to aggregate [19,20], which might dramatically reduce their photocatalytic efficiencies. How to control the growth of sulfide solid solution nanostructures is crucial. Recently, electrospun TiO_2 nanofibers have attracted great attention for the following advantages: (1) the one-dimensional (1D) nanostructure could provide quick charge transfer channels, leading to the high

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separation efficiency of electron–hole pairs; (2) electrospun TiO_2 nanofibers can serve as excellent substrates for the assembly of secondary nanostructures with high density without aggregation, etc. [21]. To the best of our knowledge, there has no report on hierarchical heterostructures of ZnS–In_2S_3 solid solution-TiO_2 nanofibers, which might possess high photocatalytic activity and favorable recycling characteristics.

In this work, a unique hierarchical heterostructure of TiO_2-sulfide solid solution (TiO_2@ZnS–In_2S_3) has been successfully prepared through fabricating ZnS–In_2S_3 solid solution nanostructures onto porous TiO_2 nanofiber templates by simple hydrothermal method. The ZnS–In_2S_3 solid solution nanostructures uniformly grow on the surface of TiO_2 nanofibers and exhibit a diversity of morphologies: nanosheets, nanorods and nanoparticles. The rough and porous surface of TiO_2 nanofiber templates effectively inhibit the accumulation growth of ZnS–In_2S_3 solid solution and endow the heterojunction with high structural stability. The 3-D TiO_2@ZnS–In_2S_3 hierarchical heterostructures show strong visible light response and effective separation of photogenerated carriers. The TiO_2@ZnS–In_2S_3 heterostructures display highly efficient and stable photocatalytic activity for rhodamine B degradation (RhB). RhB is selected as a model pollutant because it is one of the most important commercial dyes.

2. Experimental

2.1. Materials

Poly (vinylpyrrolidone) (PVP, Mw = 1,300,000) was purchased from Alfa Aesar. Titanium tetraisopropoxide and thioacetamide were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. Rhodamine B was purchased from Tianjin Guangfu Fine Chemical Research Institute. $ZnCl_2$ was obtained from Sinopharm Chemical Reagent Co., Ltd and $InCl_3{\cdot}4H_2O$ was purchased from Shanghai Aladdin Industrial Corporation. All other reagents of analytical grade were used without further purification. Deionized water was used for preparation of all aqueous solutions.

2.2. Preparation of TiO_2 nanofibers

Firstly, 1.5 g of titanium tetraisopropoxide ($Ti(O_iPr)_4$) was dissolved in a mixture solution containing 3 mL acetic acid and 6 mL absolute ethanol under stirring for 1 h. Then, 0.45 g PVP was added into the above solution and the mixture was vigorously stirred for 6 h to form a homogeneous precursor solution. Subsequently, the precursor solution was transferred into a syringe for electrospinning. The positive voltage of 10 kV was applied and the distance between needle tip and aluminum foil collector was 15 cm. The precursor solution was ejected at a rate of 0.5 mL/h, resulting in electrospun nanofibers. The as-collected nanofibers were calcined at 450 °C for 3 h to get porous TiO_2 nanofibers.

2.3. Fabrication of TiO_2@ZnS–In_2S_3 heterostructures

TiO_2@ZnS–In_2S_3 heterostructures were prepared by hydrothermal method. In a typical procedure, 0.5 mmol $ZnCl_2$, 0.1 mmol $InCl_3{\cdot}4H_2O$ and 3 mmol thioacetamide (TAA) were dissolved in 20 mL deionized water. Then 50 mg TiO_2 nanofibers were added to the above solution and the mixture was further stirred for 1 h. The resulting mixture was transferred into a 40 mL Teflon-lined stainless steel autoclave and maintained at 80 °C for 12 h. After hydrothermal reaction, the autoclave was cooled down to room temperature in air. The yellow products were collected, washed with ethanol and deionized water for several times, and dried at 60 °C for 12 h to obtain the final product (TiO_2@ZnS–In_2S_3). For comparison, ZnS/TiO_2 nanofibers and In_2S_3/TiO_2 nanofibers were synthesized under similar process. Meanwhile, ZnS–In_2S_3 solid solution and ZnS nanoparticles were prepared by the same hydrothermal conditions in the absence of TiO_2 nanofibers.

2.4. Characterization

The morphologies of all as-prepared samples were observed by S-4800 field-emission scanning electron microscopy (FESEM, Hitachi, Japan) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F). The energy dispersive X-ray spectrometer (EDX) mapping images were captured on a Tecnai G2 F20 S-TWIN atomic resolution analytical microscope. The crystal phases of the samples were collected on an X-ray diffractometer with Cu Kα radiation (XRD, M21X, MAC Science Ltd., Japan). The UV–vis diffuse reflectance spectra (DRS) were performed on a UV–vis spectrophotometer (Cary 300, USA) with an integrating sphere. The X-ray photoelectron spectroscopy (XPS, K-Alpha 1063, Thermo Fisher Scientific, England) was used to determine the binding energies of S, Zn, In, Ti and O of the heterostructures. The BET specific surface areas were measured on Belsorp-Mini II analyser (Japan). The photoluminescence (PL) spectra were recorded with Hitachi F-2500 fluorescence spectrophotometer at an excitation wavelength of 275 nm.

2.5. Adsorption and photocatalytic degradation of rhodamine B (RhB)

The adsorption experiments were carried out in a quartz beaker containing 50 mL 10 mg L^{-1} RhB and 10 mg photocatalyst samples. The mixture was stirred in the dark for 30 min to achieve adsorption/desorption equilibrium. The RhB concentration change was determined by a UV–vis spectrophotometer (Varian Cary 500).

The photocatalytic activities of all samples were evaluated by the degradation of RhB in an aqueous solution under visible light irradiations. The catalytic activity experiments were carried out in a quartz beaker containing 50 mL 10 mg L^{-1} RhB and 10 mg photocatalyst samples. A 500 W xenon arc lamp (CHF–XQ–500 W, Beijing Changtuo Co., Ltd.) with 100 mW cm^{-2} photon flux served as the visible light source using a UV-cutoff filter $\geqslant$420 nm. Before the irradiation, the system was maintained in the dark for 30 min to reach complete adsorption–desorption equilibrium, so that the decreased concentration of RhB with irradiation time could fully reflect the photocatalytic activity of the catalysts. The real-time concentration of RhB was determined by the characteristic maximum UV–vis absorption using a UV–vis spectrophotometer (Cary 300, USA).

3. Results and discussion

3.1. Morphology and structure characterization

Fig. 1 shows the FESEM and TEM images of the samples. Compared to raw electrospun TiO_2 nanofibers without calcination (inset of Fig. 1a), the surfaces of the calcined electrospun TiO_2 nanofibers become highly rough and porous due to the removal of PVP porogenic agents by calcination (Fig. 1a). Without using TiO_2 nanofibers as growth templates, both ZnS nanoparticles and ZnS–In_2S_3 solid solution are clustered to form large agglomerates (Fig. 1b and c, respectively). Meanwhile, the surfaces of In_2S_3/TiO_2 nanofibers and ZnS/TiO_2 nanofibers are smooth and decorated with some scattered In_2S_3 or ZnS nanoparticles (Fig. 1d and e, respectively). In contrast, after hydrothermal reaction of TiO_2 nanofibers with the sulfide precursors, bush-like ZnS–In_2S_3 solid solution grew on the surface of TiO_2 nanofibers, expanding the diameter from 130 nm of the bare TiO_2 nanofiber (Fig. 1a) to about 200 nm of the coaxial TiO_2@ZnS–In_2S_3 heterostructures (Fig. 1f). The TEM images of TiO_2@ZnS–In_2S_3 heterostructures clearly show that the ZnS–In_2S_3 solid solution on the surface of TiO_2 nanofibers exhibits bush-like porous structure built with large numbers of nanoparticles, nanorods and nanosheets, indicative of a variety of crystal growth model (Fig. 1g and h). The use of the rough and porous TiO_2 nanofiber templates effectively inhibits the aggregation growth of ZnS–In_2S_3 solid solution.

3.2. HRTEM and formation mechanism

In order to investigate the formation mechanism of ZnS–In_2S_3 solid solution on TiO_2 nanofibers, a detailed structural characterization was further performed by HRTEM. The HRTEM image of TiO_2@ZnS–In_2S_3 heterostructures shows the (1 0 1) plane of anatase (d = 0.35 nm) [22] and the (1 1 1) plane of cubic ZnS (d = 0.31 nm) [21] (Fig. 2a). The selected-area electron diffraction (SAED) pattern of ZnS–In_2S_3 solid solution can be further indexed to the cubic lattices of ZnS with (1 1 1), (2 2 0) and (3 1 1) reflections (Fig. 2b). Fig. 2c clearly displays that the interplanar distance between two neighboring fringes is 0.31 nm corresponding to (1 1 1) plane of cubic ZnS. The (1 1 1) lattice plane has low surface-free energy and hence is formed favorably [23]. The reconstructed lattice image from the outlined area in Fig. 2c clearly shows the existence of an edge dislocation (Fig. 2d) where the nanorods are composed of a number of nanocrystals which connect with each other in series. The formation of such a nanostructure based on semiconductor