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One-step in situ synthesis of CdS/SnO_2 heterostructure with excellent photocatalytic performance for Cr(VI) reduction and tetracycline degradation

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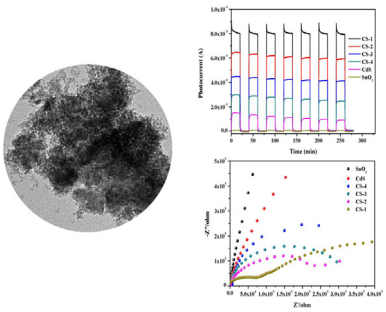
HIGHLIGHTS

- A high efficiency CdS/SnO_2 photocatalyst were fabricated.
- An intimate nanojunction was formed between CdS and SnO_2.
- Recorded, excellent photocatalytic performance on Cr(VI) reduction and TC degradation.
- The energy band alignment of CdS/SnO_2 heterostructure was proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

The heterointerface between different components of composite photocatalyst, which acts as the channel of charge transfer, is of crucial importance to photocatalytic performance. In this study, a series of tightly connected CdS/SnO_2 heterojunction photocatalysts were prepared via simple hydrothermal process containing $CdSnO_3{\cdot}3H_2O$ as templates and thiourea as sulfur source. The crystal phase, morphology, interface structure, and composition of the obtained samples were characterized by X-ray diffraction, field-emission scanning electron microscopy, and X-ray photoelectron spectroscopy. It was found that the size and morphology of CdS/SnO_2 composites can be conveniently controlled by using different $CdSnO_3{\cdot}3H_2O$ templates. The results of UV-vis diffuse reflectance spectrum (DRS), electrochemical impedance spectroscopy (EIS) and photoluminescence spectra (PL) demonstrated that the formation of ultrasmall CdS/SnO_2 heterostructure remarkable enhance visible light absorption and effectively promote the separation of photogenerated charge carriers. Moreover, the formed intimate heterointerface can maximize the superior electron conductivity of SnO_2 and thus, greatly speed up the transfer of photo-generated electron. Compared to the single CdS, the CdS/SnO_2 composites exhibited excellent photocatalytic performance towards Cr(VI) reduction and tetracycline (TC) degradation under visible light irradiation, which was ascribed to the enhanced visible light absorption and rapid separation of electrons and holes. The trapping experiments and ESR proved that $\cdot O_2^-$ and h^+ are the primary reactive species involved in the photocatalytic degradation of TC. 3D EEMs results indicated that the CdS/SnO_2 heterojuction photocatalysts owned strong mineralization ability on the TC molecules degradation. The energy band alignments of

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CdS/SnO_2 heterostructure were determined by combining DRS and XPS results. Ultimately, a possible photocatalytic mechanism was proposed.

1. Introduction

For relieving the pressure between environmental pollution and the depletion of energy, photocatalytic technology with the advantages of low consumption and environmental friendliness has been developed rapidly in recent years [1–4]. The conception that semiconductor photocatalyst absorbs light energy and converts it into chemical energy, which satisfies with the proposed requirements for green development [5]. In the past decade, cadmium sulfide (CdS) has attracted a great deal of interest in the field of photocatalytic degradation, water splitting and solar energy conversion owing to its narrow band gap (2.4 eV), appropriate band edge positions and sufficient photocatalytic activity [6–9]. Nonetheless, the fast recombination of photo-generated charge carriers and strong photocorrosion effect greatly limit its wide application [10,11]. In this context, the design and synthesis of hybrid CdS-based photocatalysts with the formation of a heterojunction has been proposed and demonstrated as a feasible route in hindering the recombination of photoelectrons and holes. To date, several CdS-based photocatalysts, such as CdS/TiO_2 [12], CdS/ZnO [13], CdS/BiOCl [14], and CdS/MoS_2 [15] are studied. But regretfully, the enhancement of photocatalytic activity is still restricted by the low migration efficiency of photogenerated charge carriers. Therefore, more appropriate materials should be further developed for designing CdS-based composite with highly efficient charge transfer.

Tin oxide (SnO_2) is an important research topic and is widely applied in the field of energy storage, gas sensors and solar cells [16–19]. Owing to the excellent electrical conductivity and relatively positive conduction band position ($E_{CB} = -0.07$ eV), SnO_2 is often used as co-catalyst to enhance electron transfer efficiency of other photocatalyst via the formation of heterojunction. So far, a lot of hybrid SnO_2 photocatalysts have been reported, such as $g\text{-}C_3N_4/SnO_2$ [20], $BiOI/SnO_2$ [21], Ag_3PO_4/SnO_2 [22] and SnS_2/SnO_2 [23], exhibiting much faster charge carrier separation and higher photocatalytic activity than single photocatalysts. Considering these great merits of SnO_2-based hybrid photocatalysts, coupling CdS with SnO_2 may be an effective strategy to enhance migration efficiency of photoelectron and reduce the recombination rate of charge carriers of CdS. Currently, the existing synthesis method of complex photocatalysts is commonly involved in multi-step reaction or physical mixing. Unfortunately, the intimate contact and strong interaction between different semiconductors are difficult to be achieved. The heterointerface between different components of composite photocatalyst, which acts as the channel of charge transfer, is of crucial importance. Therefore, the charge migration and separation in composite photocatalysts cannot be effectively promoted. In-situ chemical solution method is often used for fabricating composite nanomaterials because it can achieve the efficient chemical transformation from one material to another with adjustable composition, controlled crystal phase and size [24–26]. The fast interface chemical reaction process not only can guarantee the formation of tight heterointerface but also reduce the agglomeration of different components to generate nanosized particles during the crystal growth. In general, the migration distance of the photogenerated charge carriers will be greatly shorted when the size of photocatalyst decreases to nanoscale, which contributes to the rapid separation of electron and hole [27,28]. Besides, a great lattice mismatch will be generated between the interface regions of the two phases, which can enhance the interface contact areas [29].

In view of advantage of in-situ chemical solution method on the fabrication of composite materials with strong interaction and controlled nanosized structure, in this paper, we developed a facile procedure to prepare CdS/SnO_2 composite by synthesizing $CdSnO_3{\cdot}3H_2O$ nanocube and further reacting with thiourea. The size and structure of obtained CdS/SnO_2 composite could be controlled by using different $CdSnO_3{\cdot}3H_2O$ templates. The photocatalytic activity of prepared CdS/SnO_2 samples were evaluated by Cr(VI) reduction and TC degradation under visible light irradiation. The influence factors on photocatalytic reaction were investigated in detail. 3D EEMs technology was used to analyze the TC degradation process. The enhancements of light harvesting and charge transfer efficiency were reflected by the results of UV–vis diffuse reflectance spectrum (DRS), electrochemical impedance spectroscopy (EIS), transient photocurrents and photoluminescence (PL) spectrum. Trapping experiments and electron spin resonance (ESR) analysis were carried out to determine the main active species on TC degradation. The energy band alignment of CdS/SnO_2 heterostructure was proposed. This work expects to provide a facile method to fabricate composite photocatalyst with intimate heterointerface and small nanostructure.

2. Experimental

2.1. Materials and reagents

Cadmium acetate dihydrate ($Cd(CH_3COO)_2{\cdot}2H_2O$), stannic chloride pentahydrate ($SnCl_4{\cdot}5H_2O$), thiourea (CH_4N_2S), potassium dichromate ($K_2Cr_2O_7$), tetracycline (TC), diphenylcarbazide (DPC), ammonium formate, EDTA-2Na, methyl alcohol, sodium sulfite (Na_2SO_3), ammonium oxalate ($(NH_4)_2C_2O_4$), potassium persulfate ($K_2S_2O_8$), polyvinyl alcohol (PVA), sodium hydroxide (NaOH), sodium sulfate (Na_2SO_4) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were of analytical reagent grade without further purification.

2.2. Synthesis of $CdSnO_3{\cdot}3H_2O$

The $CdSnO_3{\cdot}3H_2O$ was prepared by homogenous precipitation according to our previous reports [30]. In a typical synthesis process, 1.2 g of sodium hydroxide was added to 75 mL 0.1 M $SnCl_4{\cdot}5H_2O$ aqueous solution with mechanical agitation. Then 75 mL 0.1 M $Cd(CH_3COO)_2{\cdot}2H_2O$ solution was dropwise added into above solution to form white precipitation. The pH of mixture solution was finally adjusted to 8.0 by adding NaOH (0.1 M). After agitation at room temperature for 1 h, the white slurry products were collected by vacuum filtration and washed with water several times until the filtrate was neutral. Finally, the solid power was dried at 60 °C overnight. For obtaining $CdSnO_3$ samples with different size, the pH value of reaction solution was adjusted to 10.0, 12.0, and 14.0, respectively.

2.3. Fabrication of CdS/SnO_2 nanoparticles

CdS/SnO_2 nanoparticles were synthesized via simple hydrothermal process with the reaction between $CdSnO_3{\cdot}3H_2O$ and thiourea. Firstly, 1.0 mmol of $CdSnO_3{\cdot}3H_2O$ prepared under pH = 8.0 were uniformly dispersed in 120 mL water with continuous ultrasonic. And then 1.0 mmol of thiourea was added into above solution with stirring constantly 10 min, followed by transferring together into a Teflon-lined autoclave with reaction 12 h at 180 °C. After the autoclave cooled down, the yellow products were washed with ethanol and water and collected by filtering. Finally, CdS/SnO_2 nanoparticles (denoted as CS-1) were obtained after drying at 60 °C overnight. The other samples were prepared by using different $CdSnO_3$ solid under the same condition, which were denoted as CS-2, CS-3 and CS-4, respectively. For