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Hydrothermal synthesis of SnO_2/ZnS nanocomposite as a photocatalyst for degradation of Rhodamine B under simulated and natural sunlight

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ABSTRACT

A novel nanocomposite, SnO_2/ZnS, was successfully synthesized via a one-step hydrothermal method. The composite was characterized by several techniques such as XRD, SEM, TEM, XPS and UV–vis spectrum, and utilized for photocatalytic degradation of refractory dye Rhodamine B (RhB) under simulated and natural sunlight. It was found that the composite prepared at the molar ratio of $n(SnCl_4{\cdot}5H_2O)/n(Zn(NO_3)_2{\cdot}6H_2O) = 1.5$ and hydrothermal temperature of 180 °C showed the highest photocatalytic activity. The photocatalytic degradation of RhB reached the maximum of 95% at the 1 g/L SnO_2/ZnS dosage, 10 mg/L initial RhB concentration, 4.59 initial solution pH and 23 °C. The RhB photocatalytic degradation fitted well to the first-order kinetics model, and the increased SnO_2/ZnS dosage, decreased initial RhB concentration and optimal initial solution pH were responsible for the increase of RhB photocatalytic degradation rate. The composite also displayed stable performance during 5 runs of reuse. Quenching tests demonstrated that the dominant active species generated in SnO_2/ZnS-RhB-H_2O-simulated sunlight system was $O_2^{\bullet-}$; nevertheless, h^+ and $^\bullet OH$ also contributed to RhB degradation. The formation mechanism of the SnO_2/ZnS nanosphere and RhB photocatalytic degradation mechanism were proposed. Moreover, the composite has proved to have the high efficiency for the degradation of RhB under natural sunlight irradiation.

1. Introduction

Over the past decades, the design and synthesis of highly efficient visible-light photocatalysts have attracted considerable attention due to their potential applications in environmental remediation and solar-energy conversion. Many efforts have been concentrated on developing novel visible-light photocatalysts such as oxides (Bi_2O_3, Cu_2O, Fe_2O_3) [1–3], sulfides (CdS, SnS_2, Sb_2S_3) [4–6], nitrides (g-C_3N_4) [7,8], oxynitrides ($Ti_{1-x}Nb_xON$, ZnGaNO) [9,10], composite metal oxides (Bi_2WO_6, $Bi_{12}TiO_{20}$, $LaNiO_3$, $Pb_2Nb_2O_7$) [11–14], Ag-based compounds (Ag@AgX, Ag_3PO_4, Ag_2S, Ag/$AgVO_3$, $AgSbO_3$) [15–20], and bismuth oxyhalides (BiOX (X = Cl, Br and I)) [21–22]. Among them, semiconductor photocatalysts have drawn much attention because of their optical and electronic properties, strong oxidizing power, inexpensiveness, non-toxicity, long-term stability, and resistance to photo-corrosion and chemical corrosion [23–25]. Moreover, in comparison with the synthesized single semiconductor, the combination of different semiconductors has proved to be successful in developing better performance photocatalysts. It has been found that coupling two semiconductors with different band-gap width to form a hierarchical nanostructure would improve the photocatalytic activity, because such configuration can not only suppress the recombination of electron–hole pairs but also extend the energy range of photoexcitation [26,27]. Several research teams have investigated the photocatalytic activity of various semiconductor coupled system such as CdS/TiO_2, TiO_2/ZnS, ZnO–ZnS, SnO_2/SnS_2 and Fe_3O_4/SnO_2 [28–32].

Tin dioxide (SnO_2), an n-type semiconductor with the band gap energy (Eg) of 3.6 eV is known to have higher electron mobility than TiO_2 nanocrystals [33]. It has been widely used for photocatalytic processes due to its excellent transparency, high photosensitivity, suitable band gap, low cost and environmental friendliness. Zinc sulfide (ZnS) as an important II–VI semiconductor with a wide band gap of 3.5–3.7 eV is one of efficient photocatalysts, due to its rapid generation of electron–hole pairs and highly negative redox potentials of excited electrons [34]. However, the photocatalytic

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performance of above two semiconductors under visible light was restricted due to their wide band gap and intrinsic defects. Ling et al. [35] developed a two-step thermal evaporation method to produce SnO_2–ZnS nanocomb hierarchical heterostructure with the improved photocatalytic performance under UV irradiation. In the SnO_2–ZnS, the ZnS nanorods were grown on the SnO_2 core nanowires/ribbons, while ZnS were just decorated at the two sides of SnO_2, which reduced the electric field on the interface between SnO_2 and ZnS, and could decrease the charges transfer and separation efficiency of SnO_2–ZnS composite. Accordingly, the efficient efforts are still desired to improve the photocatalytic properties of SnO_2/ZnS composites under visible light via promoting the electron transfer and broadening the light absorption range.

It is known that the size and morphology of semiconductor materials have the significant effect on their properties and applications. However, the size and morphology depend on the synthesis methods and conditions [34]. Up to now, many synthesis methods such as sol–gel, situ chemical solution, solid-state, hydrothermal and precipitation methods have been successfully applied to fabricate semiconductor photocatalysts. Among these methods, hydrothermal method as a "soft solution chemical process" facilitates the control of grain size, particle morphology, microstructure, phase composition, and surface chemical properties by adjusting the hydrothermal reaction conditions [36].

Here, for the first time, the nanocomposite SnO_2/ZnS was prepared by a simple and cost-effective hydrothermal method, and the formation mechanism of the composites was proposed. The photocatalytic activity and stability of SnO_2/ZnS composite were evaluated using the degradation of RhB as a model reaction, and the RhB photocatalytic degradation kinetics and mechanism were investigated.

2. Experimental

2.1. Materials

Tintetrachloride pentahydrate ($SnCl_4{\cdot}5H_2O$), zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), Thiourea (CN_2H_4S), *Tert* butyl alcohol (TBA), *p*-benzoquinone (BQ) and Ethylene Diamine Tetraacetie Acid (EDTA) were purchased by Sinopharm Chemical Reagent Co. Deionized water was used throughout this investigation. Other commercial chemicals used were of analytical reagent grade without further purification.

2.2. Hydrothermal synthesis of SnO_2/ZnS composite

The SnO_2/ZnS composite was prepared from $SnCl_4{\cdot}5H_2O$, CN_2H_4S and $Zn(NO_3)_2{\cdot}6H_2O$ by hydrolysis under basic conditions. A typical synthesis could be described as follows: 3 mmol $SnCl_4{\cdot}5H_2O$, 2 mmol $Zn(NO_3)_2{\cdot}6H_2O$ and 8 mmol CN_2H_4S were dissolved in 40 mL of deionized water, and then the mixture was subjected to ultrasonic treatment for several minutes to become a transparent solution. Later, the mixed solution was transferred into a 50 mL Teflon-lined stainless steel autoclave. It was sealed, maintained at 180 °C for 16 h and then cooled to room temperature. The product was centrifuged and washed several times with deionized water and absolute ethanol, and then dried in a vacuum at 60 °C for 5 h.

For comparison, by changing the dosage of $SnCl_4{\cdot}5H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$, 4SnO_2/ZnS composite samples with the different Sn/Zn molar ratios were obtained, marked as Sn_2Zn, Sn_3Zn_2, Sn_4Zn_3 and SnZn, in which the subscript numbers are the molar number of Sn or Zn. Meanwhile, the single SnO_2, ZnS and SnS_2 as the control samples were also synthesized.

2.3. Characterization

XRD patterns of all the samples prepared were obtained on a Rigaku D/Max-2200X powder X-ray diffractometer using Cu Kα radiation source of wavelength 1.54056 Å at 40 kV and 40 mA. The wide-angle data were collected from 10° to 80° (2θ) with a scan speed of 5°/min. The external morphology of the sample was observed on a JSM-6700F scanning electron microscope (SEM) equipped with an energy dispersion X-ray spectrometer (EDS). The internal structure of the sample prepared was characterized by a JEM-2010F (JEOL) high resolution transmission electron microscope (HRTEM) with field emission gun at 200 kV. The surface element compositions and their chemical states in the samples were analyzed by an X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi), using 300 W Al Kα radiation. The optical absorption spectra of the samples were obtained by UV–vis (TECHCOMP U-3010) spectrophotometer equipped with a diffuse reflectance accessory, with $BaSO_4$ as the reflectance standard reference.

2.4. Measurement of photocatalytic activity

The photocatalytic activities of the as-fabricated SnO_2/ZnS composite were evaluated by the RhB degradation under simulated sunlight irradiation at 23 °C. Typically, 0.5 g the as-fabricated photocatalysts were suspended into 500 mL of an aqueous solution of RhB with an initial concentration of 10 mg/L. Prior to irradiation, the suspensions were stirred in the dark condition for 1 h to obtain a good dispersion and establish adsorption–desorption equilibrium. The tests were carried out using a quartz sleeve photoreactor (ID = 4 cm) equipped with an circulating water device and magnetic stirrer to maintain the photocatalyst suspended in the aqueous solution. The light source with a 500 W Xe lamp ($\lambda > 400$ nm) was immersed in the quartz sleeve placed in the middle of the reactor. During the simulated sunlight irradiation, 5 mL of the reaction solution were sampled at the given time intervals, centrifuged to remove the catalysts and then analyzed by a UV–vis spectrophotometer (UV-5300PC, Shanghai) at 552 nm. The UV–vis spectra were obtained using a UV–vis spectrophotometer (UV-5300PC, Shanghai) at different reaction time, with the spectrum scanned from 200 to 800 nm. The main degradation products of RhB were detected by GC–MS, with an Agilent 7890A gas chromatograph equipped with a DB-5 capillary column (30 mm × 0.25 mm × 0.18 mm) combined with an Agilent 5975C mass spectroscopy equipment employed.

To identify the active species in RhB photocatalytic degradation, TBA, BQ or EDTA was added into the RhB degradation system as a quencher of hydroxyl radicals ($^{\bullet}OH$), superoxide radicals ($O_2^{\bullet-}$) and holes (h^+), respectively.

Generally, the tests were conducted in duplicate and the errors of the experimental results were below 3%.

3. Results and discussion

3.1. Synthesized sample characterization

3.1.1. XRD

The XRD spectra of as-synthesized SnO_2/ZnS composites are shown in Fig. 1. All relevant XRD peaks were identified and indexed based on the available JCPDS (Joint Committee for Powder Diffraction Studies) data. The diffraction peaks of the curve (g) can be assigned to hexagonal ZnS (JCPDS No. 03-1093), and no impurity peaks are observed. From the XRD diffraction curves of SnO_2/ZnS composites (Fig. 1(c)–(f)), we can see 3 major peaks (2θ = 28.990°, 47.281° and 56.564°) corresponding to the ZnS (0 0 2, 1 1 0 and