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Adsorption–degradation synergetic effects on removal of methylene blue over heterostructured $TiO_2/Co_4S_{4.23}Se_{3.77}$ composites

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ABSTRACT

Novel heterostructured $TiO_2/Co_4S_{4.23}Se_{3.77}$ composites were synthesized by a combination of solid-state and sol–gel methods, and were characterized by single-crystal X-ray diffraction, powder X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy, UV–vis diffuse reflectance spectroscopy, and photocurrent measurements. The results of photocatalytic degradation of methylene blue over the as-prepared materials indicate that photocatalytic efficiency is closely related to the composition of the materials, and the $30\%TiO_2/Co_4S_{4.23}Se_{3.77}$ catalyst exhibits the best adsorption and photodegradation efficiency under sunlight or visible-light irradiation. The adsorption capacity of $30\%TiO_2/Co_4S_{4.23}Se_{3.77}$ for methylene blue is 18.59 mg/g calculated based on the Langmuir adsorption model. Adsorption kinetics studies show that the process fits well with a pseudo-second-order rate mechanism. Recycle experiments confirm that the $30\%TiO_2/Co_4S_{4.23}Se_{3.77}$ catalyst is stable. The present work illustrates a new way for the design and syntheses of stable and high-efficiency catalysts applicable for the degradation of organic pollutants.

1. Introduction

Photocatalysis is an effective method for the harness of solar energy. The use of a TiO_2 photochemical electrode for water splitting was first reported by Fujishima and Honda in 1972 [1]. However, the wide bandgap of anatase TiO_2 (3.2 eV) restricts its photocatalytic applications in the visible-light region. In addition, it is generally observed that due to electron-hole recombination, the quantum yield is low and catalytic efficiency is poor. Efforts were put in to modify anatase TiO_2 for better performance through the doping of TiO_2 with nonmetals such as N [2–5], S [6], C [7], F [8], I [9] and B [10] or by converting TiO_2 into a heterostructured catalyst [11–13].

Transition metal sulfides, in particular CoS, CoSe and ZnS, as important chalcogenide semiconductors, have been extensively studied and applied as supercapacitor, infrared lasers in fiber optics, battery, and photocatalyst due to their unique physical and chemical properties [14–16]. And $CoS_{1-x}Se_x$ is a solid solution semiconductor with good photocatalytic activity and adjustable band structures through controlling its composition [17].

As well known, compared to single-component photocatalysts, the heterostructured counterparts exhibit superior photocatalytic activity because their band gaps can be regulated through the control of composition for efficient separation of photogenerated charges. In recent years, much attention has been given to the design and synthesis of heterostructured catalysts. However, it is uncommon to come across those that are based on solid solutions because it is not easy to prepare this kind of catalysts by conventional methods. In the literature, the methods adopted for the preparation of heterostructured photocatalysts are mainly hydrothermal (solvothermal) [18,19], coprecipitation [20], sol–gel [21] or a combination of them. In addition, it is known that solid-state synthesis is a traditional and facile approach to prepare semiconductors with uniform and adjustable composition. Especially, this method is good approach to the generation of solid-solution semiconductors with good crystallinity and high purity [22,23]. It is hence envisaged that solid-solution

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photocatalysts can be better synthesized through solid-state reactions.

During photocatalytic degradation of organic pollutants, there are adsorption and photodegradation steps. It was reported that photocatalysts, especially the heterostructured ones, are poor in adsorption activity [24–29]. It is hence desirable to prepare heterostructured photocatalysts that are synergetically effective in both adsorption and photodegradation. In view of $Co_4S_{4.23}Se_{3.77}$ with good photocatalytic performance and matching band potentials to those of TiO_2, we prepared heterostructured $TiO_2/Co_4S_{4.23}Se_{3.77}$ through a combination of solid-state and sol–gel methods because the $Co_4S_{4.23}Se_{3.77}$ solid solution can be well prepared by solid state method and then TiO_2 nanoparticales can load on the surface of $Co_4S_{4.23}Se_{3.77}$. This is the first report of such kind. For the elucidation of the related adsorption and photocatalytic mechanism, we investigated the synergetic adsorption–degradation effects on the decomposition of methylene blue (MB) under sunlight and visible-light irradiation over the as-prepared catalysts. The present work provides a new strategy for the design and synthesis of heterostructured catalysts for effective degradation of organic pollutants.

2. Experimental

2.1. Materials

In this study, cobalt (Co, ≥99.99%), selenium (Se, ≥99.99%), and sublimed sulfur (S ≥ 99.95%) were purchased from Aladdin Co., Ltd. (Shanghai, China), whereas tetrabutyl titanate ($C_{16}H_{36}O_4Ti$, CP) was supplied by Shanghai KEFENG Chemical Reagent Co., Lnc. (Shanghai, China). Nitric acid (HNO_3, AR) and ethanol (C_2H_5OH, AR) were obtained from Guangzhou Xilong Chemical Co., Ltd. (Guangzhou, China). Water was purified using a Milli-Q water system (Bedford, USA). Other chemicals were used without further purification.

2.2. Syntheses

2.2.1. Synthesis of pure $Co_4S_{4.23}Se_{3.77}$

The $Co_4S_{4.23}Se_{3.77}$ (CSS) solid solution was prepared by solid-state reaction of a mixture of Co (4 mmol, 235.7 mg), S (4 mmol, 128 mg) and Se (4 mmol, 316 mg) at 850 °C. The starting materials were ground to fine powders and pressed into a pellet. The pellet was loaded into a Pyrex tube which then was evacuated to 1×10^{-2} Pa and flame-sealed. The tube was placed into a computer-controlled furnace, heated from the room temperature (RT) to 850 °C at a rate of 25 °C/h, kept at 850 °C for 72 h, and slowly cooled down to 50 °C at a rate of 2 °C/h. Then it was finally cooled down to RT over a period of 1 h and a crop of black CCS crystals that was stable in air was collected. Semiquantitative microscope element analysis on several grains of the as-obtained single crystals over a field-emission scanning electron microscope equipped with an energy dispersive X-ray spectroscope confirmed that Co, S and Se were present in an approximate molar ratio of 4.0:4.15:3.85 (see Table S1 in Supplementary information), and there was no detection of any other elements. Based on the preliminary results and followed similar procedures, we obtained a light-red crystalline CCS sample with the exact composition through reaction of a mixture of Co/S/Se in a molar ratio of 4/4.23/3.77 at 850 °C for 72 h. The purity of the as-prepared crystalline sample was confirmed by XRD powder diffraction.

2.2.2. Syntheses of heterostructured $TiO_2/Co_4S_{4.23}Se_{3.77}$ composite

The heterostructured $TiO_2/Co_4S_{4.23}Se_{3.77}$ composite was prepared by a sol–gel method. The typical procedure for the preparation of $TiO_2/Co_4S_{4.23}Se_{3.77}$ with a designated TiO_2 to $Co_4S_{4.23}Se_{3.77}$ weight ratio is as followed: With stirring tetrabutyl titanate (0.75 mL, CP) was dissolved in a mixture of ethanol (2.0 mL) and glacial acetic (0.075 mL) at 80 °C. Then a mixed solution of HNO_3 (0.15 mL, AR), distilled water (0.1 mL) and ethanol (1 mL) was added slowly into it under stirring. At this stage, a calculated amount of $Co_4S_{4.23}Se_{3.77}$ (0.1667–0.8335 g) prepared by the solid-state method was added into the as-obtained solution. For example, heterostructured 30%$TiO_2/Co_4S_{4.23}Se_{3.77}$ (weight ratio of TiO_2 to $Co_4S_{4.23}Se_{3.77}$ = 3:10) was prepared by using 0.5 g $Co_4S_{4.23}Se_{3.77}$ and 0.75 mL tetrabutyl titanate. Finally, the obtained sample was vacuum dried at 120 °C for 5 h and then calcined at 400 °C for 2 h. Hereinafter, the $Co_4S_{4.23}Se_{3.77}$ loaded with 10%, 20%, 30%, 40% and 50% TiO_2 are denoted as 1TCSS, 2TCSS, 3TCSS, 4TCSS and 5TCSS, respectively.

2.3. Characterization

The crystal phases of powder samples were identified by X-ray diffraction (XRD, Bruker D8 ADVANCE, Germany) using graphite monochromatized Cu-Kα (λ = 1.5406 Å) radiation. The XRD data for indexing and cell-parameter calculations were collected in a scan mode with scanning speed of 2°/min in the 2θ range between 20° and 70°. The morphology of samples was observed with a scanning electron microscope (SEM, FEI SIRION, Holand) and a transmission electron microscope (TEM, JEOL JEM-200CX, Japan). Composition analyses on several randomly selected samples of the as-prepared catalysts were performed on a field-emission scanning electron microscope equipped with an energy dispersive X-ray spectroscope (EDS). The Co/Ti molar ratio of the as-prepared samples was also determined based on data collected over an inductively coupled plasma atomic emission spectrometer (ICP-AES; Vista-MPX, VARIAN). X-ray photoelectron spectroscopy (XPS, ESCALAB 250, ThermoFisher SCIENTIFIC, China) measurements were taken with a VG Escalab 250 spectrometer equipped with an Al anode (Al-Kα = 1486.7 eV). UV–vis diffuse reflectance spectra were measured with a PE Lambda 900 UV/Vis spectrophotometer at room temperature. The finely ground sample powder was coated on a $BaSO_4$ plate which was also used as a reference. The absorbance spectra were converted by the Kubelka–Munk method. Raman measurements were performed using a JY LabRam HR800 spectrometer equipped with a microscope, and laser radiation of λ = 514.5 nm (at 5 mV) was used as excitation source. Photoluminescence analyses were performed on a fluorescence spectrometer (F-7000, Hitachi, Japan). The Brunauer–Emmett–Teller (BET) surface area of samples were measured by means of N_2 adsorption over a NOVA 2000e (Quantachrome) equipment.

X-ray diffraction patterns of $Co_4S_{4.23}Se_{3.77}$ single crystal (black in color) were collected at 293 K over a SMART APEX CCD diffractometer equipped with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The intensity data were all collected with ω scan technique and corrected for *LP* factors as well as for absorption by the multiscan method. The structure of CSS was solved by direct methods and refined on F^2 with full-matrix least-squares techniques using Siemens SHELXTL™ version 5.1 package of crystallographic software [30]. We conducted final refinements on anisotropic displacement parameters (for all atoms) with secondary extinction correction. The crystallographic data of CSS are listed in Table S2. Further details of the crystal structures can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number ICSD-424304.

Electrochemical measurements were performed on a CHI 660D electrochemical workstation (Shanghai Chenhua, China) using a standard three-electrode cell having a working electrode, a platinum wire as counter electrode, and a standard calomel electrode in