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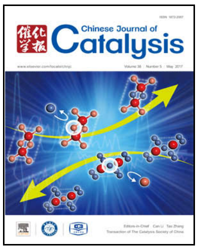

Article

Facile synthesis of S-doped reduced TiO_{2-x} with enhanced visible-light photocatalytic performance

Zhenyu Huang [a], Zhenggang Gao [a], Shanmin Gao [a,b,*], Qingyao Wang [a], Zeyan Wang [b], Baibiao Huang [b], Ying Dai [b]

[a] *College of Chemistry and Materials Science, Ludong University, Yantai 264025, Shandong, China*
[b] *State Key Lab of Crystal Materials, Shandong University, Jinan 250100, Shandong, China*

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ABSTRACT

A different approach to synthesize visible-light-active sulfur (S)-doped reduced titania (S-TiO_{2-x}) using thiourea dioxide as both the S source and reductant was developed. The structure, morphology, and optical and electronic properties of the as-prepared S-TiO_{2-x} samples were examined by multiple techniques, such as X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy, ultraviolet-visible diffuse reflectance spectroscopy, Brunauer-Emmett-Teller and photocurrent measurements, and electrochemical impedance spectroscopy. The photocatalytic activity of S-TiO_{2-x} was evaluated by photodegradation of organic Rhodamine B under visible-light irradiation. The degradation rate of Rhodamine B by S-TiO_{2-x} obtained by calcination was about 31, 2.5, and 3.6 times higher than those of pure TiO_2, pristine TiO_{2-x}, and S-doped TiO_2, respectively. In addition, the as-prepared S-TiO_{2-x} exhibited long-term stable photocatalytic performance in the degradation of Rhodamine B under visible-light illumination. This report reveals a new approach to prepare stable and highly efficient solar light-driven photocatalysts for water purification.

1. Introduction

Since the discovery of photocatalytic water splitting on titania (TiO_2) single-crystal electrodes by Fujishima et al. in 1972 [1], photodegradation of toxic organic pollutants in wastewater using solar light as an energy source has been considered to be one of the most promising directions to solve global environmental problems. Although numerous novel compounds with various photocatalytic activities have been developed, TiO_2 has remained a leading catalyst in the photocatalytic degradation of organic pollutants because it is effective, photo and chemically stable, non-toxic, and readily available [2]. However, the wide band gap and quick recombination of photogenerated electron-hole pairs of TiO_2 impede its practical applications. Therefore, band-gap engineering of TiO_2 is needed to use it as a high-efficiency photocatalyst under visible-light illumination for antibacterial applications [3,4].

Nonmetal-doped TiO_2 has received much attention because the incorporation of nonmetals into TiO_2 can extend its photoresponse from the ultraviolet (UV) to the visible region [5–8]. The introduction of doping agents as anions or cations to substitute Ti or/and O in the lattice of TiO_2 could narrow the TiO_2 electronic band gap or create localized electronic states in the band gap, which could improve its visible-light absorption and result in high visible-light photocatalytic activity. Among nonmetal dopants, sulfur (S) has received particular attention be-

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* Corresponding author. Tel: +86-535-6672176; Fax: +86-535-6693096; E-mail: gaosm@ustc.edu

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cause of its high thermal stability and ability to enhance visible-light photocatalytic activity. S-doped TiO_2 photocatalysts have been prepared using S-based compounds including TiS_2, thiourea, elemental S, CS_2, and dimethyl sulfoxide as the S source [9–13]. However, these precursors are either expensive or highly toxic. Therefore, it is worth seeking safe and cheap S sources for use in S-doped TiO_2 photocatalysts.

Recently, Ti^{3+} self-doping of TiO_2 (TiO_{2-x}) has emerged as an effective approach to trigger the visible-light activity of TiO_2 [14,15]. In TiO_{2-x}, electronic transitions originating from the Ti^{3+}-induced states in the band gap are known to contribute to its photoabsorption. Meanwhile, Ti^{3+} endows TiO_2 with good electronic conductivity, which is important to improve its photoelectric conversion efficiency [16,17], and enhance its visible-light photocatalytic activity [18,19]. Various attempts have been made to synthesize TiO_{2-x} photocatalysts [20–24], but most methods involve complicated experimental conditions and multistep processing. In situ reduction treatment using a short processing time and mild conditions to prepare TiO_{2-x} photocatalysts with high photocatalytic and photoelectrochemical performance is still challenging [18]. In our previous work, we used an oxidation-based method to prepare TiO_{2-x} nanomaterials in aqueous solution using the water- and air-stable industrial raw material TiH_2 as the Ti source [25,26]. Hydrogen peroxide was used as an oxidizing agent to give different states of precursor gels, after which different treatment methods were used to produce TiO_{2-x} nanoparticles.

Thiourea dioxide is an organosulfur compound that is used in reductive bleaching in textiles and as an antioxidant in organic synthesis [27]. Thiourea dioxide is a strong reductant and has high thermal stability. In addition, compared to other S sources, thiourea dioxide is cheap and easy to use. We were therefore inspired to explore a facile, effective, and environmentally friendly route to synthesize S-doped TiO_{2-x} using thiourea dioxide as both the S source and reductant. In this study, pristine TiO_{2-x} and S-doped TiO_{2-x} are prepared by a hydrothermal or calcination method using thiourea dioxide as the S source and reductant. The relationship between the structure and photocatalytic performance of the products obtained from different methods are studied in detail. Rhodamine B (RhB) dye is used as a model pollutant to evaluate the photocatalytic activity of the samples.

2. Experimental

2.1. Sample preparation

All chemicals were reagent grade from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without further purification. Double-distilled water was used throughout the experiments.

The precursor gel preparation process was similar to that described in our preliminary study, except that yellow precursor gel was obtained by controlling the oxidation time [25,26]. To obtain the pristine TiO_{2-x}-H, the wet gel was hydrothermally treated at 180 °C for 20 h. To prepare the S-doped TiO_{2-x} photocatalyst, thiourea dioxide (0.2 g) was added to the precursor gel and its pH was adjusted to 8 using NaOH solution. The mixture was then hydrothermally treated at 180 °C for 20 h. The obtained bluish-gray sample was denoted as S-TiO_{2-x}-H. Half of the precursor gel was dried in air, mixed with thiourea dioxide (0.2 g), and then calcined at 500 °C for 3 h. The obtained gray-blue sample was denoted as S-TiO_{2-x}-T (Fig. 1). For comparison, pristine S-doped TiO_2 (denoted S-TiO_2-T) nanoparticles were prepared according to ref. [10].

2.2. Characterization

An X-ray diffractometer (XRD; Rigaku, D/max-2500VPC) was employed to characterize the crystalline phases of the final products using Ni-filtered Cu-K_α radiation from 20° to 70° at a scan rate of 0.02° s^{-1}. A transmission electron microscope (TEM; JEOL-2100) was used to observe the morphologies of the products. An X-ray photoelectron spectrometer (XPS; ESCA 3000) with a monochromatic Al K_α X-ray source (1486.6-eV photons) was used to characterize the chemical state of elements in the as-prepared samples. The C 1*s* signal at a binding energy of 284.6 eV was used as a reference. UV-Vis diffuse reflection spectra (DRS) were recorded on a Shimadzu UV-2550 UV-Vis spectrophotometer at room temperature from 200 to 800 nm. Fine $BaSO_4$ was used as the reflectance standard. The Brunauer-Emmett-Teller (BET) specific surface areas of the powders were determined by nitrogen adsorption-desorption measurements at 77 K in a Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA). Mass spectra (MS) were collected on an electrospray ionization mass spectrometer (Bruker ESQUIRE 3000). The total organic carbon (TOC) content of the samples after degradation for different times was measured with a Shimadzu TOC-VCPH analyzer. Fourier transform infrared (FT-IR) spectra were recorded on a MAGNA 550 FT infrared spectrometer for samples embedded in KBr pellets.

2.3. Photoelectrochemical measurements

The transient photocurrent responses of the samples were performed with a standard three-electrode setup using a CHI 660E electrochemical station (Chenhua Instrumental Co., China). Each photoelectrode was prepared by spin coating a mixture of sample (0.01 g) in ethanol Nafion solution (5 wt%, 0.05 mL) on a 1.0 cm^2 fluorine-doped tin oxide glass substrate and drying at 100 °C for 2 h. The as-prepared photoelectrodes were used as working electrodes; Ag/AgCl and platinum wire were

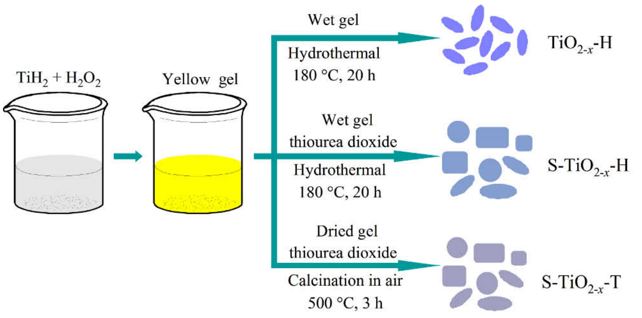

Fig. 1. Overview of the formation of different samples.