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Highly efficient and stable hydrogen evolution from water with CdS as photosensitizer—A noble-metal-free system

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ABSTRACT

CdS/$Ba_{1-x}Zn_xTiO_3$ heterostructured photocatalysts were developed as a highly efficient and stable system for photocatalytic evolution of hydrogen from water splitting. In the system, CdS not only functions as photosensitizer to absorb visible light, but also participates with $Ba_{1-x}Zn_xTiO_3$ for the generation of heterojunctions that block the recombination of photogenerated electrons and holes. The photocatalysts show excellent activity and stability, giving a high H_2 production rate of 1473 μmol h^{-1} g^{-1} under the irradiation of simulated solar light in a test period of 480 h without loading any noble metal as cocatalyst or any reagents for regeneration. This study demonstrates that the development of CdS nanoparticles as photosensitizer is feasible for the photocatalytic H_2 production.

1. Introduction

Since the discovery of Fujishima and Honda on the photocatalytic splitting of water over TiO_2 electrodes [1–3], there are numerous reports on the synthesis and use of photocatalysts for water splitting, but most of them are active only under UV irradiation [4]. With respect to solar energy, only a small fraction (ca. 4%) lies in the ultraviolet region, whereas the visible light in the solar spectrum is far more abundant (ca. 46%) [5]. For better efficiency of capturing solar energy, it is desirable to develop visible-light-driven photocatalysts. One of the adopted strategies is to modify a photocatalyst of wide band gap with a photosensitizer [6], and the common photosensitizers are organic dyes [7,8]. Nonetheless, these light-absorbing molecules decompose under working conditions within hours [6]. Hence, the development of stable photosensitizers is a key issue. In the past four decades, photosensitizers based on noble metals such as $[Ru(bipy)_3]^{2+}$ were successfully used in photocatalytic hydrogen evolution [9,10,8]. However, noble metals are rare and expensive, and the mining of them is harmful to the environment [11]. It is hence desirable to develop catalytic systems that are free from noble metals.

Compared to the use of traditional organic or organometallic light-absorbing molecules, it is more economical to use semiconductor nanocrystals as photosensitizers. It is known that the semiconductor nanocrystals are photostable, and can deliver multiple electrons with minimal structural perturbation [12,13]. Recently, the nanocrystals of chalcogenides were employed as photosensitizers in photocatalytic systems [14,15], but their use for the evolution of hydrogen from water is rare [16–18]. Furthermore, the photocatalytic properties, especially long-term durability, are still needed to improve when chalcogenides are used as photosensitizers of catalysts for H_2 production due to high recombination rate of photogenerated electrons and holes and limited photostability [19–22].

We are interested in developing a noble-metal-free system that is efficient for the photocatalytic generation of hydrogen from water. It is known that the band gap of CdS nanocrystals is small and the conduction band (CB) of CdS is suitable for hydrogen production [23,24]. More importantly, CdS possesses a band structure that matches that of $Ba_{1-x}Zn_xTiO_3$ solid solution. We envisage that coupling CdS with $Ba_{1-x}Zn_xTiO_3$ would result in a high-efficient photocatalyst with good durability for H_2 evolution from water splitting. It is because CdS can act as photosensitizer for

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light-harvesting and a combination of CdS with $Ba_{1-x}Zn_xTiO_3$ would result in the formation of heterojunctions that hinder the recombination of photogenerated holes and electrons. The present work demonstrates that CdS nanocrystals photosensitizing $Ba_{1-x}Zn_xTiO_3$ is an economic and effective approach to obtain a noble-metal-free system with excellent photocatalytic activity and long-term durability for H_2 generation from water.

2. Experimental

2.1. Materials and measurement

All chemicals were analytically pure and used without further purification. The crystalline phases of samples were investigated by X-ray diffraction (Bruker D8 ADVANCE) using graphite monochromatized Cu $K\alpha$ ($\lambda = 1.5406$ Å) radiation. The XRD data for indexing and cell-parameter calculations were collected in a scan mode with a scanning speed of 2°/min in the 2θ range between 10° and 70°. The morphology of samples was studied with a scanning electron microscope (SEM, FEI, Holand) and a transmission electron microscope (TEM). 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). X-ray photoelectron spectroscopy (XPS) measurements were taken with a VG Escalab 250 spectrometer equipped with an Al anode (Al $K\alpha = 1486.7$ eV). UV–vis diffuse reflectance spectra were measured with a PE Lambda 900 UV/Vis spectrophotometer at room temperature. Photoluminescence recording was performed on a fluorescence spectrometer (F-7000, Hitachi, Japan).

Electrochemical measurements were performed on a CHI 660D electrochemical workstation (Shanghai Chenhua, China) using a standard three-electrode cell with a working electrode, a graphite electrode as counter electrode, and a standard calomel electrode in saturated KCl as reference electrode. The working electrodes were prepared by dip-coating: 20 mg of photocatalyst was suspended in 5 mL ethanol to produce slurry that was then dip-coated onto a 2 cm × 0.5 cm fluorine-tin oxide (FTO) glass electrode. After drying under ambient condition, the films were sintered at 300 °C for 1 h. The electrolyte (Na_2S/Na_2SO_3: Na_2S 0.35 M, Na_2SO_3 0.25 M) was purged with nitrogen. As for photocurrent measurements, a 300 W xenon lamp was used to generate simulated sunlight and the other conditions were similar to those of electrochemical measurements.

2.2. Syntheses

2.2.1. Syntheses of $Ba_{1-x}Zn_xTiO_3$ solid solutions

The $Ba_{1-x}Zn_xTiO_3$ ($x = 0$, 0.05, 0.1, 0.15, and 0.2) solid solutions were synthesized by a hydrothermal-gel method. In a typical procedure, solution A was prepared by dissolving stoichiometric amounts of barium acetate (0.01–0.01x mol) and zinc acetate (0.01x mol) in 10 mL 36% acetic acid solution. Solution B was prepared by dissolving 3.4 mL of tetrabutyltitanate (0.01 mol) in 5 mL isopropanol and then 1.5 mL of acetic acid was added. Solution B was slowly added to solution A and the resulted mixture was magnetically stirred for 30 min. Then the mixture was hydrothermally treated in a 25 mL Teflon-lined stainless steel autoclave at 100 °C for 2 h. The resulting gel was calcined at 900 °C for 10 h. The as-synthesized products with $x = 0$, 0.05, 0.1, 0.15, and 0.2 are designated as $BaTiO_3$, $Ba_{0.95}Zn_{0.05}TiO_3$, $Ba_{0.9}Zn_{0.1}TiO_3$, $Ba_{0.85}Zn_{0.15}TiO_3$, and $Ba_{0.8}Zn_{0.2}TiO_3$, respectively.

2.2.2. Syntheses of heterostructured $CdS/Ba_{1-x}Zn_xTiO_3$

The heterostructured composites $CdS/Ba_{1-x}Zn_xTiO_3$ ($x = 0$, 0.05, 0.1, 0.15, and 0.2) with different CdS loadings (based on initial molar ratio of Cd/Ti) were synthesized by solvothermal method. Typically, the as-synthesized $Ba_{1-x}Zn_xTiO_3$ solid solution was dispersed in 30 mL deionized water under magnetic stirring. Then under ultrasonic treatment, stoichiometric cadmium acetate solution and thiourea solution was added in a span of 15 min. Finally, the mixture was hydrothermally treated in a 100 mL Teflon-lined stainless steel autoclave at 150 °C for 10 h. The resulting samples were separated by filtration, washed several times with deionized water and alcohol and then dried at 90 °C for 12 h. Hereinafter, the heterostructured $CdS/Ba_{0.9}Zn_{0.1}TiO_3$ containing 10%, 20%, 30% and 40% (atom%) CdS are denoted hereinafter as 10CBZTO, 20CBZTO, 30CBZTO and 40CBZTO, respectively.

2.3. Photocatalytic activity for water splitting

Photocatalytic reactions were carried in a Pyrex top-irradiation reaction vessel with a capacity of 100 mL connected to a glass closed gas system (PerfectLight). A 300 W Xe lamp (PerfectLight, wavelength Range: 320 nm $\leq \lambda \leq$ 780 nm, light intensity: 160 mW cm^{-2}) was used to generate simulated sunlight and visible light (cutoff filter applied for the latter, $\lambda > 420$ nm). H_2 production was performed by dispersing 25 mg of catalyst in an aqueous solution (80 mL) containing Na_2S/Na_2SO_3 (Na_2S 0.35 M, Na_2SO_3 0.25 M) as sacrificial reagents. The reaction solution was evacuated several times to remove air completely prior to irradiation. The temperature of the reaction solution was maintained at 6 °C by a continuous flow of cold water (constant temperature device XODC-0506, Nanjing Shunliu, China) during the reaction. The evolved gases were in situ analyzed by gas chromatography equipped with a thermal conductive detector (TCD) and a 5 Å molecular sieve column, using argon as the carrier gas.

3. Results and discussion

3.1. Characterization of materials

The XRD patterns of $Ba_{1-x}Zn_xTiO_3$ ($x = 0$, 0.1 and 0.2) are shown in Fig. 1a. It is clear that the patterns of $Ba_{1-x}Zn_xTiO_3$ ($x = 0$, 0.1, and 0.2) are similar to that of cubic $BaTiO_3$ (JCPDS No. 01-075-0461). The doping of Zn^{2+} does not obviously change the crystalline structure of $BaTiO_3$. A careful comparison of the (1 1 0) diffraction peaks in the 2θ range of 31–32.5° (the inset of Fig. 1a) shows that with the increase of Zn^{2+} doping, the XRD peak positions shift to slightly higher angles. The result indicates that there is partial substitution of Ba^{2+} by Zn^{2+} because the ionic radius of Zn^{2+} (0.074 nm) is smaller than that of Ba^{2+} (0.135 nm) but larger than that of Ti^{4+} (0.0605 nm). Based on similar results of XRD analysis reported in the literature [2,25,26], one can accept that our $Ba_{1-x}Zn_xTiO_3$ are solid solutions rather than mixtures of $BaTiO_3$ and $ZnTiO_3$.

Fig. 1b shows the XRD patterns of $CdS/Ba_{0.9}Zn_{0.1}TiO_3$ loaded with different amounts of CdS (10CBZTO, 20CBZTO, 30CBZTO and 40CBZTO). The diffraction profiles indicate a mixture of $Ba_{0.9}Zn_{0.1}TiO_3$ and hexagonal CdS (JCPDS No. 00-002-0549), and there is no detection of impurity phase. As the amount of CdS increases from 10% to 40%, the peaks of hexagonal CdS intensify and there is no change of position of the major $Ba_{0.9}Zn_{0.1}TiO_3$ peaks. The results indicate that the loading of CdS does not change of $Ba_{0.9}Zn_{0.1}TiO_3$ crystal structure.

The UV–vis absorption spectra of $BaTiO_3$, $Ba_{0.9}Zn_{0.1}TiO_3$, CdS, 10CBZTO, 20CBZTO, 30CBZTO and 40CBZTO are shown in Fig. 2. Compared to $BaTiO_3$, $Ba_{0.9}Zn_{0.1}TiO_3$ exhibits an absorption edge that is slightly red-shifted, but light absorption is still in the UV region with a band edge of approximately 3.1 eV. After CdS sensitization, there is clear absorption of visible light. And with increase of CdS loading (from 10% to 40%), there is continuous red shift of