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High-performance heterostructured CdS/$Ba_{1-x}Sr_xTiO_3$ system with unique synergism for photocatalytic H_2 evolution

Si-Liang Lei[a], Jian Yu[a], Shao-Kui Bao[a], Gui-sheng Zeng[a,*], Hui-Long Liu[a], Dan-Dan Wu[a], Xing-Hua Tang[a], Jian-Ping Zou[a,*], Chak-Tong Au[b]

[a] Key Laboratory of Jiangxi Province for Persistent Pollutants Control and Resources Recycle, Nanchang Hangkong University, Nanchang, Jiangxi 330063, China
[b] Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong, China

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ABSTRACT

This study demonstrates the design and synthesis of heterostructured CdS/$Ba_{1-x}Sr_xTiO_3$ composites that exhibit outstanding photocatalytic activity and long-term durability for H_2 evolution from an aqueous solution containing the sacrificial agent (Na_2S/Na_2SO_3) without loading any noble metals as cocatalysts or reagents for regeneration. The excellent performance of this heterostructured catalyst is due to the unique synergetic effect between CdS and $Ba_{1-x}Sr_xTiO_3$. In this system, CdS not only functions as a high-activity photocatalyst absorbing light to generate electrons but also acts as a cocatalyst accepting the photogenerated electrons from $Ba_{1-x}Sr_xTiO_3$ for H_2 evolution, while $Ba_{1-x}Sr_xTiO_3$ serves as captors of photoholes of CdS. In this way, the heterostructured composites can efficiently block the recombination of photogenerated electrons and holes, leading to a significant improved harvest of photogenerated electrons for H_2 evolution. In the meantime, the photocorrosion of CdS can be greatly alleviated due to fast moving photogenerated holes of CdS, contributing a long-term stability of the designed heterostructured system.

1. Introduction

Since Fujishima and Honda reported the photocatalytic splitting of water on TiO_2 electrodes in 1972 [1], the photocatalytic conversion of solar energy to hydrogen energy is considered to be promising [2–5]. Till now, tremendous efforts have been devoted to developing photocatalysts of high activity [6,7], but research on catalyst durability is far from adequate [8,9]. Photocatalysts such as GaN:ZnO and PdS/CdS are known to have a long lifetime but the former has to be regenerated using $Rh_{2-y}Cr_yO_3$ [10,11], while the latter is loaded with Pt [12]. Noble metals are rare and expensive and mining them is harmful to the environment, which limits the application of these catalysts [13–16]. Therefore, it is necessary to explore low-cost photocatalysts that are durable and highly efficient in water splitting for hydrogen evolution [17].

Titanium-based perovskite oxides such as $ATiO_3$ (A = Ba and Sr) have been investigated as a class of promising photocatalysts [18]. Attempts were made to improve the photocatalytic activity of $BaTiO_3$ and $SrTiO_3$ through doping them with metals or non-metals or creating heterojunctions [19]. However, their photocatalytic activities are still far from satisfactory due to the high recombination rate of photogenerated electrons and holes [20–23]. It is a promising method through forming solid solutions between two kinds of semiconductors with similar crystal structures, which can well control band structures of photocatalysts of solid solutions and improve their photocatalytic activity. In view of the band structures of $BaTiO_3$ and $SrTiO_3$, $Ba_{1-x}Sr_xTiO_3$ solid solution should be promising for water splitting [24–27]. Nonetheless, it is unlikely for this type of photocatalyst to excel in terms of photocatalytic activity and durability due to drawbacks such as high recombination rate of photogenerated electrons and holes and poor absorption ability of sunlight.

The use of an appropriate cocatalyst is an effective way to promote photocatalytic performance [28,29]. Compared with noble metals, CdS is cheaper and capable of absorbing visible light, which makes CdS a good cocatalyst [30]. Till now, there are a number of reports on CdS-based heterostructured catalysts or cocatalysts for H_2 evolution from water splitting. However, their photocatalytic activity and photostability are still inadequate without noble metal loading due to the photocorrosion caused by photogenerated holes.

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[*] Corresponding authors. Tel.: +86 791 83863373; fax: +86 791 83953373.
E-mail addresses: zengguisheng@hotmail.com (G.-s. Zeng), zjp_112@126.com (J.-P. Zou).

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Thus, in order to inhibit the photocorrosion of CdS, it is highly desirable to develop strategies to effectively transfer photogenerated holes on CdS to other compounds.

Interestingly, $Ba_{1-x}Sr_xTiO_3$ solid solution possesses a band structure matching that of CdS. It may effectively facilitate the separation of photogenerated electrons and holes through a combination of $Ba_{1-x}Sr_xTiO_3$ and CdS to form a heterojunction. Additionally, since the valence band (VB) of $Ba_{1-x}Sr_xTiO_3$ is more negative than that of CdS, photogenerated holes in the VB of CdS can flow into that of $Ba_{0.4}Sr_{0.6}TiO_3$ (see Scheme S1 in SI). Such a design can suppress the photocorrosion of CdS [31,32]. As a result, the present photocatalyst system can simultaneously suppress photocorrosion of CdS and accelerate the separation of photogenerated holes and electrons. Herein, we report the controlled synthesis of $Ba_{1-x}Sr_xTiO_3$ ($x = 0$, 0.2, 0.4, 0.6, 0.8, and 1.0) and heterostructured CdS/$Ba_{1-x}Sr_xTiO_3$ nanocomposites through a facile one-step solvothermal method. The optimized CdS/$Ba_{1-x}Sr_xTiO_3$ nanocomposite shows significant improvement in light-harvesting ability as well as excellent photocatalytic activity and durability. Noteworhily, the heterostructured photocatalyst exhibits excellent photocatalytic activity and long-term durability for H_2 production without loading any noble metals as cocatalyst or reagents for regeneration.

2. Experimental

2.1. Materials and measurement

All chemicals were AR grade and used without further purification. The crystalline phases of samples were investigated by X-ray diffraction (Bruker D8 ADVANCE) using graphite monochromatized Cu-*Ka* ($\lambda = 1.5406$ Å) radiation. The XRD data for indexing and cell-parameter calculations were collected in a scanning mode with a scanning speed of 2°/min in the 2θ range of 10–70°. The morphology of samples was studied with a scanning electron microscope (SEM, FEI, Holland) and a transmission electron microscope (TEM). Composition analyses on several randomly selected samples of as-prepared catalysts were performed on a field-emission scanning electron microscope equipped with an energy dispersive X-ray spectroscope (EDS). The elemental analyses of as-prepared samples were also determined based on the data collected over an inductively coupled plasma atomic emission spectrometer (ICP-AES; Vista-MPX, VARIAN). 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 a slurry that was then dip-coated onto a 2 cm × 0.5 cm fluorine-tin oxide (FTO) glass electrode with a sheet resistance of 15 Ω. 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 as the source of simulated solar irradiation and the other conditions were similar to those of electrochemical measurements.

2.2. Syntheses

2.2.1. Syntheses of $Ba_{1-x}Sr_xTiO_3$ solid solution

$Ba_{1-x}Sr_xTiO_3$ ($x = 0$, 0.2, 0.4, 0.6, 0.8, and 1.0) solid solution were synthesized by a solvothermal method. In a typical procedure, stoichiometric amounts of barium nitrate ($0.01 \times (1 - x)$ mol; $x = 0$, 0.2, 0.4, 0.6, 0.8, and 1.0) and strontium nitrate ($0.01 \times x$ mol; $x = 0$, 0.2, 0.4, 0.6, 0.8, and 1.0) were add to 25 mL 2 mol/L sodium hydroxide solution under magnetic stirring within a period of 30 min. Then a mixture of tetrabutyltitanate (3.4 mL, 0.01 mol) and alcohol (5 mL) was added to the above solution. After being stirred under cooling on an ice-water bath for 30 min, the mixture was hydrothermally treated in a 50 mL Teflon-lined stainless steel autoclave at 200 °C for 4 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. Finally, the obtained samples were calcined at 200 °C for 6 h. The resulting products with $x = 0$, 0.2, 0.4, 0.6, 0.8, and 1.0 were designated as $BaTiO_3$, $Ba_{0.8}Sr_{0.2}TiO_3$, $Ba_{0.6}Sr_{0.4}TiO_3$, $Ba_{0.4}Sr_{0.6}TiO_3$, $Ba_{0.2}Sr_{0.8}TiO_3$ and, $SrTiO_3$ respectively.

2.2.2. Syntheses of heterostructured CdS/$Ba_{1-x}Sr_xTiO_3$

The heterostructured composites CdS/$Ba_{1-x}Sr_xTiO_3$ ($x = 0$, 0.2, 0.4, 0.6, 0.8, and 1.0) with different CdS loadings (based on initial molar ratio of Cd/Ti) were synthesized by a one-step solvothermal method. Typically stoichiometric amounts of barium nitrate and strontium nitrate were added to 25 mL 2 M sodium hydroxide solution under magnetic stirring for 30 min, and then a mixture of tetrabutyltitanate (3.4 mL, 0.01 mol) and alcohol (5 mL) was added to the above solution. After being stirred under cooling on an ice-water bath for 30 min, the solution was subject to ultrasonic treatment for 15 min. After that, stoichiometric amounts of cadmium acetate solution and sodium sulfide were added to the above solution under ultrasonic treatment for 15 min. Then a procedure similar to that for the preparation of $Ba_{1-x}Sr_xTiO_3$ was followed to obtain the heterostructured photocatalysts CdS/$Ba_{1-x}Sr_xTiO_3$. Finally, the obtained samples were calcined at 200 °C for 6 h. Here after, the heterostructured CdS/$Ba_{0.4}Sr_{0.6}TiO_3$ containing 10%, 20%, 30%, 40%, 50%, and 60% (at.%) CdS are denoted as 10CBSTO, 20CBSTO, 30CBSTO, 40CBSTO, 50CBSTO, and 60CBSTO, respectively.

The as-prepared powder of $Ba_{1-x}Sr_xTiO_3$ solid solution and CdS/$Ba_{1-x}Sr_xTiO_3$ were purified in a 36% acetic acid solution for 1 h, then filtered out and soaked in pure water until a pH value of the solution was about 7, and cleaned by pure water and air-dried at 90 °C for 12 h. ICP analyses show that the Ba/Sr/Ti, Cd/S and Cd/Ti ratios fit reasonably well with the nominal values described above (Table S1).

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. A 300 W Xe lamp (Wavelength Range: $320\ \text{nm} \le \lambda \le 780\ \text{nm}$, light intensity: 160 mW/cm^2) was used as the simulated solar source. H_2 production was achieved by dispersing 50 mg of catalysts 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. Noteworthily, in order to well compare the photocatalytic performance of $Ba_{1-x}Sr_xTiO_3$ with that of CdS/$Ba_{1-x}Sr_xTiO_3$, Na_2S/Na_2SO_3 was selected as the sacrificial reagent for the both kinds of catalysts. 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 flow of cooling water during the reaction. The evolved gases were in situ analyzed by gas chromatography equipped with a thermal conductivity detector (TCD) and a 5 Å molecular sieve column, using argon as the carrier gas.