Applied Catalysis B: Environmental 217 (2017) 30–36

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Self-optimizing bifunctional CdS/Cu_2S with coexistence of light-reduced Cu^0 for highly efficient photocatalytic H_2 generation under visible-light irradiation

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ARTICLE INFO

Article history:
Received 2 April 2017
Received in revised form 22 May 2017
Accepted 25 May 2017
Available online 26 May 2017

Keywords:
Self-optimizing
Bifunctional
CdS/Cu_2S
Hydrogen evolution
Photocatalysis

ABSTRACT

A self-optimizing bifunctional core-shell CdS/Cu_2S heterojunction with high activity and superb stability for the photocatalytic hydrogen evolution under visible light irradiation was synthesized by a simple two-step solvothermal method. Compared with pure CdS, the photocatalytic activity of the hybrid is significantly enhanced by almost 25 times. The sample CdS/Cu_2S-30 has shown a maximum H_2 evolution rate of 14.4 mmol h^{-1} g^{-1} with an apparent quantum yield of 19.5% at 420 nm. The surface of single-crystalline CdS nanorod is fully covered by Cu_2S, observed via SEM and TEM, which benefits the activity of catalyst by shorting radial transfer path of charge carriers and increasing the surface area for reaction. This photocatalyst features both bifunction and self-optimizing. During photo reaction, part of Cu_2S is reduced to Cu^0 by irradiation on the surface between CdS core and Cu_2S shell, while the rest of Cu_2S offers plenty of active sites for hydrogen evolution reaction (HER). These generated Cu^0 retard the charge carrier recombination process by forming multi-heterojunction. Meanwhile, the self-optimizing of this photocatalyst is realized by Cu/Cu_2S ratio on the surface of catalyst varying automatically to the optimal value to adapt to the corresponding reaction condition. Based on all these benefits, hydrogen evolution reaction is facilitated.

1. Introduction

Light-driving catalyst-assisted water reducing reaction (LCWR) is considered to be a promising method to tack the global energy and environment crisis [1]. Since Fujushima et al. firstly developed a TiO_2 photocatalyst for hydrogen evolution reaction (HER) from water splitting in 1972 [2], many semiconductor photocatalysts have been studied. Due to the low catalytic activity caused by poor solar spectral responding and high rate recombination of charge carriers in those photocatalysts [3], the practical application of HER is blocked.

Cadmium sulfide (CdS) is a promising semiconductor for HER with a 2.4 eV band gap which matches well with solar spectral [4]. This material was widely studied as a photocatalyst for LCWR [3]. However, the fast recombination of charge carriers consisting of both bulk recombination and surface recombination [5], is the vital factor that results in low catalytic activity and severe photocorrosion. Different morphologies of CdS nanostructures have been explored to reduce the bulk recombination, such as microspheres, nanopatrticles, nanorods and microsheets [3,5]. The nanorods have been extensively studied because they can benefit the activity of catalyst by shortening radial transfer path of charge carriers and increasing the surface area for reaction [3,5]. Several methods have been developed to reduce the surface recombination, such as cocatalyst loading, heterojunction construction and surface defect modification. Noble metals such as Pt [6], Pd [7], Ru [8], Au [9] et al., have been loaded on CdS as cocatalysts, which was proved to be an effective way. However, its application is limited by the high cost of noble metals. Therefore, nowadays much more attention is focused on exploring non-noble metal and semiconductor as cocatalyst to overcome these drawbacks. Duel cocatalysts, also known as bifunctional cocatalysts, which include one material helping the separation of charge carriers and another offering active sites for HER, have also been applied in photocatalytic HER to enhance its catalytic activity [10].

The potential of Cu_2S conduction band(CB) edge is slightly more negative than the reduction potential of H^+/H_2, making it feasible for HER [11]. Its excellent property in surface reaction of HER

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http://dx.doi.org/10.1016/j.apcatb.2017.05.074
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has been noticed and applied to electrocatalytic hydrogen evolution [12]. Meanwhile, under irradiation, Cu^+ in Cu_2S can be easily reduced to Cu^0 [13] which retard the charge carrier recombination process by forming multi-heterojunction [10]. Both excellent characters of Cu_2S make it possible to become an ideal bifunctional cocatalyst in LCWR. Furthermore, the coexistence of Cu_2S and Cu^0 reduced from Cu^+ may exhibit potential function of self-optimizing, which can balance the separation of charge carriers and active sites for HER via varying Cu/Cu_2S ratio on the surface of catalyst.

To the best of our knowledge, there are few papers that have investigated the self-optimizing strategy of photocatalyst in HER [14]. Furthermore, there is no open literature that has reported the application of self-optimizing combined with bifunctional strategy of photocatalyst in HER. In this study, a self-optimizing bifunctional binary core-shell heterostructured CdS/Cu_2S photocatalyst with high activity and superb stability was synthesized for hydrogen evolution via water splitting under visible light. The novel CdS/Cu_2S nanohybrid was synthesized by a simple two-step solvothermal method and characterized to present its crystallography, morphology, spectral features and composition. Furthermore, the bifunctional and self-optimizing features of this material are illustrated for its superiority in catalytic activity and stability.

2. Experimental details

2.1. Chemicals and reagents

All materials are commercial available and used without further purification. Cadmium nitrate tetrahydrate ($Cd(NO_3)_2$, AR, 99%, Sigma-Aldrich Co., Ltd), thiourea (CH_4N_2S, AR, 99%, Sigma-Aldrich Co., Ltd), cuprous chloride(CuCl, AR, 99%, Sigma-Aldrich Co., Ltd), polyvinylpyrrolidone($(C_6H_9NO)_n$, K30, AR, Macklin Co., Ltd), ethylenediamine($C_2H_8N_2$, AR, 99%, Kermal Co., Ltd), ethanol(C_2H_5OH, AR, 99%, Kermal Co., Ltd), glycerol($C_3H_8O_3$, AR, 99%, Kermal Co., Ltd), ethylene glycol($(CH_2OH)_2$, AR, 99%, Kermal Co., Ltd) and distilled water.

2.2. Synthesis

2.2.1. Synthesis of single-crystalline CdS nanorods

Pure CdS nanorods were prepared by a modified one-step solvothermal method [15]. In a typical procedure, 2.28 g of $CdCl_2{\cdot}2.5H_2O$ and 3.02 g of CH_4N_2S were dissolved in 60 mL of ethylenediamine. The mixture was transferred into a Teflon-lined autoclave, sealed, and maintained at 160 °C for 48 h. After cooling to room temperature, the resulting yellow solid products were collected by filtration, washed with distilled water and ethanol several times each. The product was then dried at 80 °C overnight.

2.2.2. Synthesis of CdS/Cu_2S

Cu_2S shells were coated on the surface of CdS nanorods based on the solvothermal reaction. Typically, 0.4 g CdS nanorods and 0.5 g PVP were added into 40 mL glycerol. The mixture was ultrasonicated for 180 min and then stirred at room temperature for 2 h. Then 10 mL aqueous solution of a certain amount of CH_4N_2S was slowly added into the above reaction solution, followed by stirring overnight. Next, 15 mL CuCl ethylene glycol solution (the molar ratio of CH_4N_2S to CuCl was kept at 3) was slowly added to the above solution and then stirred for 5 h. The mixture was transferred into a Teflon-lined autoclave and then maintained at 100 °C for 24 h. Finally, the product was collected by centrifugation and washed with distilled water and ethanol several times each and vacuum-dried overnight to obtain the final powder. The mass ratios of Cu_2S to CdS nanorods were 0, 5%, 10%, 20%, 30%, 40%and 50%, and the corresponding samples were labeled as CdS/Cu_2S-0, CdS/Cu_2S-5, CdS/Cu_2S-10, CdS/Cu_2S-20, CdS/Cu_2S-30, CdS/Cu_2S-40and CdS/Cu_2S-50, respectively. The pure Cu_2S powder sample was prepared following the same procedure without adding CdS nanorods.

2.3. Characterization

Scanning electron microscopy (SEM) was performed on an S-4800(Hitachi, Japan). Transmission electron microscopy (TEM) images, high-resolution transmission electron microscopy (HR-TEM) images were collected on a JEM-2100F (JEOL, Japan) electron microscope, operated at an acceleration voltage of 200 kV. The crystal structures of the samples were investigated by (XRD) powder X-ray diffraction (D8 Advance, Bruker, Germany) using graphite monochromatized Cu Kα radiation of 1.54178 Å, operating at 40 kV and 40 mA. The scanning rate was $5^\circ\ min^{-1}$ from 10° to 80° (2θ). The UV–vis absorption spectra were obtained using a UV–vis spectrophotometer (Evolution 300, Thermo Scientific, America). X-ray photoelectron spectroscopy (XPS) measurement was performed using a PHI-5000C ESCA X-ray photoelectron spectrometer (Perkin-Elmer, America).

2.4. Photocatalytic hydrogen production

Photocatalytic H_2 production experiments were carried out in a 120 mL round-bottom flask at ambient temperature. The effective irradiation area of the cell is about 33.18 cm^2.A 300 W Xe-lamp(CEL-HXF300, CEAULIGHT, China) equipped with a 420 nm cut-off filter was used to provide the visible light irradiation. In a typical photocatalytic reaction, 20 mg of the powder sample was dispersed in an 80 mL lactic acid and K_2HPO_4 aqueous solution. Before irradiation, the solution was bubbled with high purity nitrogen for 1 h to remove the air inside. The amount of evolved H_2 was detected online by a gas chromatogram (GC-7890A, Agilent Technologies, America) with a thermal conductivity detector(TCD) and Ar working as carrier gas. The apparent quantum yield (AQY) was measured using a 300 W Xe-lamp (CEL-HXF300, CEAULIGHT, China) equipped with a 420 nm (±5 nm) band pass cut filter. The apparent quantum yield (AQY) was calculated by the Eq. (1).

$$AQY(\%) = \frac{\text{the number of reacted electrons}}{\text{the number of incident photons}} \times 100$$

$$= \frac{\text{the number of evolved } H_2 \text{ molecules} \times 2}{\text{the number of incident photons}} \times 100 \qquad (1)$$

3. Results and discussion

The selected samples were investigated by SEM and TEM.

As shown in Fig. 1a, the pure CdS nanorods had a length of 100–200 nm and a diameter of 10–15 nm. Fig. 1b,c demonstrates that after CdS nanorods were coated by Cu_2S, the nanorods remained their original morphology with larger diameter. The shell-core structure and the close integration between these two materials are shown clearly in Fig. 1d. Also, the diameter of CdS nanorod increased by 5–8 nm after deposition of Cu_2S, as shown in Fig. 1c&d and Supplementary data Fig. S1. In the TEM image of coated CdS nanorods(Fig. 1e), a crystal lattice distance of 0.336 nm at the core and 0.281 nm in the shell are demonstrated, which can be indexed to the (002) plane of hexagonal CdS(JCPDS 65-3414) and the (200) plane of Cu_2S(JCPDS 84-1770).

As shown in Fig. 2, the crystalline structure of sample CdS/Cu_2S-10, CdS/Cu_2S-20, CdS/Cu_2S-30, CdS/Cu_2S-40and CdS/Cu_2S-50 were