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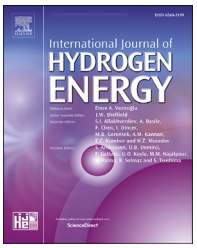

Hydrogenated CdS nanorods arrays/FTO film: A highly stable photocatalyst for photocatalytic H_2 production

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ABSTRACT

To improve the photocorrosion of CdS nanorod arrays (CdS NRAs), we have designed a simple and facile treatment method of in-situ hydrogenation to fabricate CdS@SnS/SnO_2 heterostructure on fluorine-doped tin oxide glass, which is a highly photostable hydrogenated CdS-based film photocatalyst (CdS NRAs-H_2). Over a 25-h long time irradiation, the total photocatalytic hydrogen production of hydrogenated CdS NRAs is almost 2.0 times higher than that of un-hydrogenated CdS NRAs. Moreover, the average hydrogen production rate of CdS NRAs-H_2 can steadily maintain at 23.75 μmol cm^{-2} h^{-1} with 102% of retention rate after 5 reaction cycles, while they are only 6.13 μmol cm^{-2} h^{-1} with 30% of retention rate for un-hydrogenated common CdS NRAs. The photocatalytic mechanism on enhanced activity and stability for hydrogenated CdS NRAs photocatalyst is also investigated and discussed in detail.

Introduction

As a vital and classical II-VI semiconductor and one of the most fascinating photocatalysts, CdS, with a suitable conduction band position and narrow band gap of ca 2.4 eV which corresponding well with the visible spectral range of sunlight, has been extensively investigated in the field of solar energy conversion and environmental treatment [1–4]. However, two major drawbacks, high photo-induced carries recombination rate and serious self photocorrosion, have largely hindered the extensive practical application of CdS [5–7].

In the past few years, there are two main strategies for addressing these two drawbacks. One is to construct various

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novel CdS nanostructures with controllable size, shape and morphology to accelerate the photo-generated electrons transport [8–11]. Especially, one dimensional (1D) ordered CdS nanoarrays (CdS NRAs) have aroused wide concern owing to their unique optical, structural and electronic advantages [12–14]. For example, 1D CdS NRAs can not only provide a direct pathway for electron transport along the vertical axis and decouple the electron-hole pairs, but also remarkably enhance the light absorption and scattering efficiency due to their high length-to-diameter ratios [15–17]. The other more effective strategy is to simultaneously overcome these two drawbacks via constructing binary type II heterojunction photocatalysts [18–20], especially, core-shell heterojunctions [21,22]. These desirably and rationally designed structure catalysts can assist the migration and separation of photo-induced electrons or holes, meanwhile the semiconductor shell can effectively alleviate the photocorrosion of the CdS core. For example, Xu et al. synthesized 1D CdS@TiO_2 core-shell nanocomposites via a two-step solvothermal method and found that the photogenerated holes from CdS can be stuck by the TiO_2 shell [23,24]. Recently, Wang et al. also synthesized CdS core-ZnO shell structure via an atomic layer deposition method, and the synthesized CdS@ZnO exhibited excellent photostability during a long continued photocatalytic test of 20 h [7]. Many of CdS-based semiconductor core-shell photocatalysts have been reported [21], such as CdS@ZnS [25–28], and CdS@MoS_2 [29–32]. It is worth noting that most of these outstanding researches are mainly concentrated on CdS powder samples [33–36]. However, so far, it has been generally accepted that 1D ordered CdS NRAs grown on fluorine-doped tin oxide (FTO) glass is one of the most promising monolithic thin film photocatalysts, which is more practical, convenient and recyclable than CdS powder. Therefore, developing suitable surface engineering methods to improve the energy conversion efficiency and stability of CdS film photocatalyst are of great practical significance.

Herein, for the first time, we designed a simple and facile method to in-situ hydrogenate CdS NRAs film photocatalyst and synthesize a new class of ternary photocatalyst with both SnS and SnO_2 nanoparticles (SnS/SnO_2) simultaneously covered on the surface of CdS NRAs, where the in-situ grown SnS/SnO_2 came from the interaction between CdS and FTO (SnO_2) during the hydrogenating process. The hydrogenated CdS NRAs/FTO film (CdS NRAs-H_2) exhibits a remarkably photoactivity and photostability. The total photocatalytic hydrogen production of CdS NRAs-H_2 under visible light reaches 600 μmol cm^{-2} over a 25-h long time irradiation, which is almost 2.0 times higher than that of un-hydrogenated CdS NRAs/FTO (CdS NRAs-N_2). Especially, the photocatalytic recycling result reveals that the average hydrogen production rate of CdS NRAs-H_2 can steadily maintain at 23.75 μmol cm^{-2} h^{-1} (102% of retention rate) after 5 reaction cycles, while it is only 6.13 μmol cm^{-2} h^{-1} for CdS NRAs-N_2 (30% of retention rate). In-depth investigation on photocatalytic mechanism was carried out, three conclusions are as follows. (i) The Sn species in SnS and SnO_2 originated from the FTO conductive layer during the hydrogenation thermal treatment process. (ii) Thanks to the suitable stair-like band structure and the intimate heterojunction interface between CdS and SnS/SnO_2, under visible light irradiation, the photoinduced electrons from SnS NPs and CdS NRAs can effectively transfer to the SnO_2 NPs and enhance the photocatalytic property. Simultaneously, the photogenerated holes from CdS NRAs cores transfer to the SnS NPs and therefore the photooxidation of sulfur species (S^{2-}) in CdS is inhibited. (iii) The hydrogenated CdS NRAs/FTO film exhibits an exceptionally stable and efficient photocatalytic activity for hydrogen production compared with ordinary un-hydrogenated CdS NRAs/FTO film.

Experimental section

Materials preparation

Preparation of CdS NRAs/FTO film and the hydrogenated CdS NRAs (CdS NRAs-H_2)

CdS NRAs film was prepared by hydrothermal method [37,38]. Firstly, cadmium nitrate (5 mM), thiourea (5 mM), and glutathione (1 mM) were added to a 100 mL autoclave containing 40 mL of deionized water. After stirring for 5 min, a piece of clean FTO glass was placed vertically to the bottom of the Teflon-lined stainless-autoclave, which was sealed and maintained at 210 °C for 12 h. After the reaction, the CdS NRAs/FTO film was rinsed with distilled water and alcohol for several times and dried naturally. Finally, the as-prepared sample was then annealed at 450 °C for 2 h under pure N_2 gas (99.99%) atmosphere, denoted as CdS NRAs-N_2.

The synthesized CdS NRAs/FTO was undergone a simple hydrogenation process under 20% of H_2 gas and N_2 gas mixture flow at 450 °C for different times to synthesize hydrogenated CdS NRAs film. The prepared sample was denoted as CdS NRAs-xH_2, where x indicated the hydrogenation time (hours). The preparation process is illustrated in Scheme 1.

Contrast experiments

In order to clearly confirm the heterojunction formation process of CdS NRAs-xH_2, pure CdS nanorods powders without FTO substrata were also synthesized as previous report [39]. The CdS powders were also annealed at 450 °C for 2 h under pure N_2 and H_2–N_2 mixture gas atmosphere, respectively, which were denoted as CdS–N_2 and CdS–H_2. Moreover, two pieces of barely fluorine-doped tin oxide glass were also treated as the same way and denoted as FTO-N_2 and FTO-H_2, respectively.

Material characterizations

Morphology and microstructure of the samples were identified by field emission scanning electron microscope (SEM, ZEISS Merlin, In-lens, Germany) and high-resolution transmission electron microscope (HRTEM, JEOL 2100F, 200 KV) equipped with an energy dispersive spectrometer (EDS, X-MaxN20, Oxford). X-ray photoelectron spectroscope (XPS, Kratos Axis Ultra DLD) was used to measure the surface composition and elemental chemical state of the samples. X-ray diffraction (XRD, X'pert 3 Powder, DS = 1/4°; SS = 1/2°; RS = 7.5 mm) was employed to analyze the crystal structures and phase composition of the samples. The UV-visible absorption spectra (UV-3010, Shimadzu, Japan) of the samples

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