Journal of Power Sources 379 (2018) 249–260

Contents lists available at ScienceDirect

Journal of Power Sources

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

Rational construction of multiple interfaces in ternary heterostructure for efficient spatial separation and transfer of photogenerated carriers in the application of photocatalytic hydrogen evolution

Jian-Wen Shi[a,*], Dandan Ma[a], Yajun Zou[a], Zhaoyang Fan[a], Jinwen Shi[b], Linhao Cheng[a], Xin Ji[a], Chunming Niu[a,**]

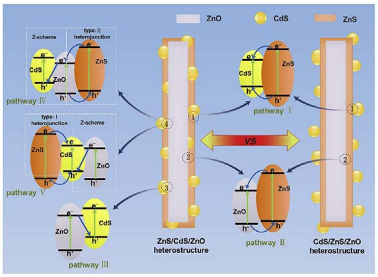
[a] *Center of Nanomaterials for Renewable Energy, State Key Laboratory of Electrical Insulation and Power Equipment, School of Electrical Engineering, Xi'an Jiaotong University, Xi'an 710049, China*

[b] *International Research Center for Renewable Energy (IRCRE), State Key Laboratory of Multiphase Flow in Power Engineering (MFPE), Xi'an Jiaotong University, Xi'an 710049, China*

HIGHLIGHTS

- A novel ZnS/CdS/ZnO ternary heterostructure (ZCZ) was developed by in-situ sulfuration.
- The ZCZ includes four contact interfaces forming three charge carrier-transfer modes.
- Type-I, type-II and direct Z-Scheme were constructed through five carrier-transfer pathways.
- The separation and transfer of photo-excited electron-hole pairs are promoted significantly.
- A high hydrogen evolution rate of 44.70 mmol/g/h was achived.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Photocatalysis
H_2 evolution
Water splitting
Heterostructure
Multiple interfaces
Carrier-transfer pathways

ABSTRACT

The design of efficient and stable photocatalyst plays a critical role in the photocatalytic hydrogen evolution from water splitting. Herein, we develop a novel ZnS/CdS/ZnO ternary heterostructure by the in-situ sulfuration of CdS/ZnO, which includes four contact interfaces: CdS-ZnS interface, ZnS-ZnO interface, CdS-ZnO interface and ZnS-CdS-ZnO ternary interface, forming three charge carrier-transfer modes (type-I, type-II and direct Z-scheme) through five carrier-transfer pathways. As a result, the separation and transfer of photoexcited electron-hole pairs are promoted significantly, resulting in a high hydrogen evolution rate of 44.70 mmol h^{-1} g^{-1}, which is 2, 3.7 and 8 times higher than those of binary heterostructures, CdS/ZnO, CdS/ZnS and ZnS/ZnO, respectively, and 26.5, 280 and 298 times higher than those of single CdS, ZnO and ZnS, respectively. As a counterpart ternary heterostructure, CdS/ZnS/ZnO contains only two interfaces: CdS-ZnS interface and ZnS-ZnO interface, which form two charge carrier-transfer modes (type-I and type-II) through two carrier-transfer pathways, leading to its much lower hydrogen evolution rate (27.25 mmol h^{-1} g^{-1}) than ZnS/CdS/ZnO ternary heterostructure. This work is relevant for understanding the charge-transfer pathways between multi-interfaces in multicomponent heterojunctions.

---

[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: jianwen.shi@mail.xjtu.edu.cn (J.-W. Shi), cniu@mail.xjtu.edu.cn (C. Niu).

https://doi.org/10.1016/j.jpowsour.2018.01.031
Received 27 September 2017; Received in revised form 11 December 2017; Accepted 9 January 2018
0378-7753/

1. Introduction

Due to the sustainable conversion of endless solar energy into clean hydrogen energy, photocatalytic hydrogen evolution from water splitting presents an attractive prospect to solve the issues of fossil fuel shortage and environmental deterioration [1–7]. To date, many semiconductors, such as TiO_2 [8–10], g-C_3N_4 [11–13], ZnO [14,15], and CdS [16,17], have been explored as photocatalysts to generate hydrogen from water splitting, but the fatal drawbacks including low efficiency and instability are still in the top urgent to overcome [18,19]. Among the numerous photocatalysts, heterostructures (HSs) consisting of two or more semiconductors are found more effective in photocatalytic hydrogen evolution, mainly due to two prominent advantages over single semiconductors [20–23]. Firstly, the bandgap of HSs can be facilely adjusted by introducing guest semiconductors with suitable bandgap positions, which is useful in expanding the light absorption region of photocatalysts and improving the utilization efficiency of solar energy [24,25]. Moreover, HSs not only can provide abundant active interfaces for the photocatalytic process, but also the formed heterojunction in HSs can promote the separation and transfer of charge carriers, resulting in high photocatalytic efficiency [26,27].

Among the numerous heterostructured photocatalysts, the traditional HSs with a staggered band alignment (type-II, one semiconductor has a higher conduction band, and the other has a deeper valence band) have been widely investigated due to their efficient charge separation, such as TiO_2/CdS [28], ZnO/$ZnGa_2O_4$ [29], CdS/g-C_3N_4 [30], etc. Since Bard introduced the concept of Z-scheme water splitting in 1979 [31], many efforts have been made to develop such Z-scheme systems to further enhance the photocatalytic hydrogen evolution rate [32–34]. For example, Wang et al. synthesized α-Fe_2O_3/Cu_2O nanocomposites, which exhibited good photocatalytic activity due to the efficient separation of photogenerated electron-hole pairs via a direct Z-scheme process [33]. Zhang et al. constructed CdS/WO_3 HSs, which exhibited 5 times higher photocatalytic efficiency than CdS due to the direct Z-scheme mechanism [34]. Additionally, the type-I HSs (one semiconductor has both a higher conduction band and a deeper valence band) are emerging in recent years due to the promotion in the separation of photo-generated electrons and holes, $CdIn_2S_4$/g-C_3N_4 [35], CdSe/CdS [36], and CdS/ZnS [37], for instance. Based on these successful examples, we have an idea that if a heterostructure including the three charge carrier-transfer modes (type-I, type-II and direct Z-Scheme) is rationally constructed, will its photocatalytic efficiency be further improved? However, to the best of our knowledge, there is still no report on this point.

In our previous work, we successfully developed CdS/ZnO 0D/2D HSs with a high hydrogen evolution rate of 22.12 $mmol\,h^{-1}\,g^{-1}$, and the tiny size effect, intimate contact interface and formed direct Z-scheme mechanism between CdS and ZnO were found to be the primary contribution to the high hydrogen evolution rate [38]. In current work, we rationally constructed a series of ZnS/CdS/ZnO ternary HSs by the in-situ sulfuration of CdS/ZnO 0D/2D HSs developed in our previous work (the preparation route of the ZnS/CdS/ZnO ternary HSs is shown in Scheme 1). We found four contact interfaces are constructed in the as-prepared ZnS/CdS/ZnO ternary HSs: (1) CdS-ZnS interface, (2) ZnS-ZnO interface, (3) CdS-ZnO interface and (4) ZnS-CdS-ZnO ternary interface, which form three charge carrier-transfer modes (type-I, type-II and direct Z-scheme) through five carrier-transfer pathways. Benefited from this, the separation and transfer of photogenerated electrons and holes are significantly promoted, resulting in a higher hydrogen evolution rate of 44.70 $mmol\,h^{-1}\,g^{-1}$, which is second among all CdS-based ternary HSs reported in literature.

2. Experimental section

2.1. Materials

Thiourea (CH_4N_2S), sodium sulfite anhydrous (Na_2SO_3) and sodium sulfate (Na_2SO_4) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. Sodium sulfide ($Na_2S{\cdot}9H_2O$) was received from Tianjin Tianli Chemical Reagent Co., Ltd, China. Chloroplatinic acid solution (H_2PtCl_6 8 wt % in H_2O) was ordered from Shanghai Aladdin Bio-Chem Technology Co., Ltd, China. All reagents were analytical grade and used as received without further purification. Deionized water with resistivity of 18.2 MΩ cm was used throughout the experiments.

2.2. Synthesis of catalysts

The ZnS/CdS/ZnO ternary HSs were prepared by an in-situ sulfidation procedure. In typical, 100 mg of flowerlike CdS/ZnO-12, the best sample for hydrogen production in our previous work [38], was ultrasonically dispersed into the aqueous solution of thiourea (100 mg of thiourea dissolved in 20 mL of water). The resultant suspension was then transferred to a Teflon autoclave (80 mL) and maintained at 150 °C for 30, 45 and 60 min, resulting in three ZnS/CdS/ZnO ternary HSs with different sulfidation degree. For convenience, the obtained ZnS/CdS/ZnO ternary HSs were labeled as ZCZ-x where x stood for the sulfidation time.

For comparison, three single semiconductors (CdS, ZnO and ZnS) and three binary HSs (ZnS/ZnO, CdS/ZnO and CdS/ZnS) were also prepared. CdS and ZnO were synthesized according to the same procedure described in our previous work [38]. ZnS was prepared by the complete sulfidation of ZnO according to the aforementioned in-situ sulfidation procedure where the sulfidation time was extended to 120 min (the complete sulfidation of ZnO can be confirmed by the results shown in Fig. S1). When the sulfidation time was shortened to 45 min, partial ZnO was sulfated into ZnS, resulting in ZnS/ZnO. CdS/ZnO in this work was the sample labeled as CdS/ZnO-12 in our previous work [38]. CdS/ZnS was prepared by the same in-situ deposition of CdS QDs on ZnS using the successive ionic-layer absorption and reaction (SILAR) method [38], and the number of deposition cycles was 12.

2.3. Photocatalytic hydrogen evolution

The photocatalytic hydrogen evolution from water splitting was carried out in a top-irradiation quartz cell connected to a closed glass gas circulation system (CEL-SPH2N, Beijing). 10 mg of the photocatalyst was dispersed in 25 mL of aqueous solution with 0.35 M of sodium sulfite anhydrous and 0.25 M of sodium sulfide as sacrificial agent, and then 0.1 mL of H_2PtCl_6 solution (1 mg/mL) was added as co-catalyst. The reaction temperature was maintained around 6 °C. A 225 W xenon arc lamp was used as simulated solar light source (320-780 nm). The amount of H_2 evolved under irradiation was determined via a TCD gas chromatograph (GC-9720).

2.4. The measurements of hydroxyl radicals (·OH)

The hydroxyl radicals (·OH) formed in the presence of ZnS, CdS/ZnS and CdS/ZnO photocatalysts under simulated sunlight irradiation were determined by a fluorescence technique using terephthalic acid (TA) as a probe molecule [39]. In detail, 10 mg of photocatalyst was dispersed in 25 mL of TA solution (5×10^{-4} M) containing 2×10^{-3} M NaOH. Then, the reaction mixture was irradiated under simulated sunlight. After every 10 min irradiation, 0.2 mL of suspension was taken out, and centrifuged to remove the photocatalyst, and then diluted to 2 mL for fluorescence spectral measurements. The photoluminescence (PL) intensity of TAOH was detected with a fluorescence spectrophotometer (Edinburgh Instruments FLS 980). The excitation light employed in recording fluorescence spectra was 315 nm.