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Low-temperature solid-state preparation of ternary CdS/g-C_3N_4/CuS nanocomposites for enhanced visible-light photocatalytic H_2-production activity

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ABSTRACT

Low-temperature solid-state method were gradually demonstrated as a high efficiency, energy saving and environmental protection strategy to fabricate composite semiconductor materials. CdS-based multiple composite photocatalytic materials have attracted increasing concern owning to the heterostructure constituents with tunable band gaps. In this study, the ternary CdS/g-C_3N_4/CuS composite photocatalysts were prepared by a facile and novel low-temperature solid-state strategy. The optimal ternary CdS/g-C_3N_4/CuS composite exhibits a high visible-light photocatalytic H_2-production rate of 57.56 μmol h^{-1} with the corresponding apparent quantum efficiency reaches 16.5% at 420 nm with Na_2S/Na_2SO_3 mixed aqueous solution as sacrificial agent. The ternary CdS/g-C_3N_4/CuS composites show the enhanced visible-light photocatalytic H_2-evolution activity comparing with the binary CdS-based composites or simplex CdS. The enhanced photocatalytic activity is ascribed to the heterojunctions and the synergistic effect of CuS and g-C_3N_4 in promotion of the charge separation and charge mobility. This work shows that the low-temperature solid-state method is efficient and environmentally benign for the preparation of CdS-based multiple composite photocatalytic materials with enhanced visible-light photocatalytic H_2-production activity.

1. Introduction

Photocatalytic H_2 production by semiconductor materials has been considered as a promising method to solve the current energy crisis and environmental issues [1–5]. Therefore, studies on photocatalytic H_2 evolution by semiconductor photocatalysts have captured tremendous attentions, particularly for visible-light-responsive photocatalysts with a high photocatalytic H_2-production efficiency [6–8]. CdS semiconductor material with a suitable bandgap and applicable band position is acknowledged as one of the most appropriate photocatalytic materials for visible-light photocatalytic H_2 production [9]. However, owning to the quick recombination of photoinduced charge carrier and the serious photo-corrosion, the photocatalytic performance of bare CdS is usually far from satisfactory without using noble metal and/or semiconductor materials [10–12]. Hence, a high-efficiency and low-cost strategy for the enhancement of visible-light photocatalytic H_2 production of CdS-based semiconductor materials is in urgent needed.

In general, hydrothermal and solvothermal methods are the most commonly used strategy for the fabrication of CdS-based composite photocatalytic materials [13–15]. However, these described methods is strict for the condition of high pressure, high temperature and the presence of different solvents. Room-temperature solid-state method is considered to be a facile, high-efficiency, energy saving and environmentally friendly method to avoid the aforementioned problems for the synthesis of CdS-based nanocomposites [16,17]. Nevertheless, the researches on low-temperature solid-state synthesis of CdS-based photocatalytic materials haven't received enough attention. To date, the low-temperature solid-state preparation of metal chalcogenides-based binary composite photocatalysts receives only sporadic attention [16–19]. For example, Chen et al. [19] fabricated metal-sulfide/graphene oxide composite photocatalysts with promoted visible-light photocatalytic activity by the low temperature solid-state method. According to our knowledge, no prior work regarding the preparation of CdS-based ternary composite photocatalytic material by a low-temperature solid-state strategy has been reported to date.

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Recent studies indicated that the ternary photocatalytic system has a better photocatalytic H_2-production activity owning to the positive synergistic effect of the co-catalysts and the heterojunction between the interfaces of the different components [20–24]. Cupper sulfides are a series of typical p-type semiconductors, and the bandgap vary from 1.2 to 2.0 eV with alteration the Cu/S atomic ratio [25,26]. Even though pure CuS displays no photocatalytic H_2 production activity, it has already become increasingly popular due to the excellent performances in acting as a co-catalyst to replace rare noble metal [27–29]. Moreover, heterojunctions formed between the interface of CuS and other photocatalysts can effectively reduce the recombination rate of charge carrier. For example, some studies indicated that the CuS-TiO_2, CuS/PbS and CuS/ZnO heterojunction structures can significantly enhanced the photocatalytic H_2 production activity by CuS acting as co-catalysts [30–32]. On the other hand, graphitic carbon nitride (g-C_3N_4) has a great potential for photocatalytic H_2 evolution due to the applicable bandgap structure [33–35]. In addition, g-C_3N_4 nano-sheet has attracted enormous attention for the excellent photoelectric properties and the high specific surface area because of the graphitic structure [36,37]. Especially, the coupled bandgaps of g-C_3N_4 and CdS and the resulting heterojunction can give rise to the enhanced photocatalytic H_2 evolution activity [38–41]. Moreover, either CuS or g-C_3N_4 has been proved to be beneficial for the enhancement of visible-light photocatalytic H_2-production activity of transitional metal chalcogenides [31,32,38–41].

Here we reported a novel low-temperature solid-state synthesis of ternary CdS/g-C_3N_4/CuS nanocomposites for visible-light photocatalytic H_2 production. In order to investigate the function of each component in the ternary composites for photocatalytic H_2 production, the photocatalytic H_2-production activity of the materials including CdS/CuS, CdS/g-C_3N_4, CuS/g-C_3N_4 and simplex CdS synthesized by the same method were also studied. The ternary CdS/g-C_3N_4/CuS composite showed the enhanced photocatalytic H_2-production activity under visible-light illumination. Further research results indicate that the high efficiency of photocatalytic H_2 production of the nanocomposite heterojunctions should be ascribed to the positive synergistic effect of CuS and g-C_3N_4 for the improvement in charge carrier separation and transfer properties. This study demonstrates a novel and simple low-temperature solid-state method for the preparation of CdS-based nanocomposite photocatalytic materials.

2. Experiment section

2.1. Sample preparation

All reagents including $Cd(Ac)_2{\cdot}2H_2O$, $Cu(Ac)_2{\cdot}H_2O$, melamine and thioacetamide (TAA) used in the sample preparation process were analytical grade (purchased from Shanghai Chemical Industrial Company) and without further purification.

Graphitic carbon nitride (g-C_3N_4) was synthesized by a calcination method [37] as follow: melamine powder was used as precursor, 10 g of precursor was heated to 550 °C at a heating rate of 5 °C min^{-1} and kept at this temperature for 4 h, then cooled the resultant to room temperature. The aforementioned process was conducted under the protection of flowing N_2. The cooled g-C_3N_4 is ground to the powder for following experiments.

CdS/g-C_3N_4/CuS (CGC) ternary nanocomposites were synthesized through a facile room-temperature solid-state method [16–19]. In a typical synthesis of CGC0.10, 0.9248 g of $Cd(Ac)_2{\cdot}2H_2O$ and 0.0693 g of $Cu(Ac)_2{\cdot}H_2O$ were mixed and ground for 10 min in an agate mortar into homogenize the mixture. On the other hand, 0.016 g of g-C_3N_4 and 0.4302 g of thioacetamide (TAA) were mixed and ground for 10 min. Then gather and mix the obtained mixtures and ground for another 20 min into a slurry. Next, the as-ground slurry was transferred into a beaker and kept in an oven at 100 °C for 60 min, ground the cooled samples into power, and rinsed with distilled water and ethanol for three times, respectively. Finally, the samples were collected by centrifugation and dried at 60 °C for 10 h. The theoretically weight ratio of g-C_3N_4 to metal sulfide in all the ternary CGC samples or the following metal-sulfide/g-C_3N_4 composites is 3 wt%, and the nominal atomic ratio of CuS to CdS are 1%, 5%, 10% and 20% (the resulting samples were labeled as CGCx, where x = 0.01, 0.05, 0.10 and 0.20, respectively). In addition, other simplex and binary photocatalytic materials including CdS/CuS0.10 (CC0.10), CdS/g-C_3N_4 (CdS/G), CuS/g-C_3N_4 (CuS/G) and simplex CdS were fabricated by the same method as CGCx, but the ratio of g-C_3N_4 or CuS is controlled. The detailed substrate of the synthesis process for the aforementioned samples was listed in Table 1.

2.2. Characterization

Powder X-ray diffraction (XRD) of the materials were detected on a Bruker D8 Advance diffractometer with Ni-filtered Cu Kα radiation at a scan rate (2θ) of 10° min^{-1}. The applied accelerating voltage and current were set as 40 KV and 40 mA, respectively. The UV–vis diffuse reflectance spectrum (UV-vis DRS) of the solid dry-pressed disk samples were performed on a UV–vis spectrophotometer (Lambda 650s) with Teflon as the reflectance standard. X-ray photoelectron spectroscopy (XPS) was obtained from a Leybold Heraeus-Shenyang SKL-12 X-ray photoelectron spectrometer, and the spectra were excited by the Mg Kα radiation at 10 kV and 15 mA. The transmission electron microscopy (TEM) images were acquired by a Hitachi H-7650 (HITACHI, Japan) transmission electron microscope at an acceleration voltage of 200 kV. The high-resolution TEM (HRTEM) images were performed on a JEM2100 F transmission electron microscope at an acceleration voltage of 200 kV.

2.3. Photocatalytic H_2-production activity

The photocatalytic H_2-production activity of the samples were performed in a 100 mL Pyrex flask with three openings sealed with silicone rubber septum. All the experiments were tested at room temperature and atmospheric pressure. The visible-light was pro-

Table 1
The detailed information and substrate of the synthesized samples.

Lable	Sample	$Cd(Ac)_2{\cdot}2H_2O$		$Cu(Ac)_2{\cdot}H_2O$		TAA		g-C_3N_4
		μmol	g	μmol	g	mol	g	g
CGC0.01	CdS/g-C_3N_4/CuS0.01	3.47	0.9248	0.0347	0.0069	5.257	0.3950	0.151
CGC0.05	CdS/g-C_3N_4/CuS0.05	3.47	0.9248	0.1735	0.0346	5.465	0.4106	0.155
CGC0.10	CdS/g-C_3N_4/CuS0.10	3.47	0.9248	0.3470	0.0693	5.726	0.4302	0.161
CGC0.20	CdS/g-C_3N_4/CuS0.20	3.47	0.9248	0.6940	0.1386	6.246	0.4693	0.170
CC0.10	CdS/CuS0.10	3.47	0.9248	0.3470	0.0693	5.726	0.4302	0.161
CdS/G	CdS/g-C_3N_4	3.47	0.9248	0	0	5.205	0.3911	0.150
CuS/G	CuS/g-C_3N_4	0	0	5.23	1.0442	5.205	0.3911	0.150
CdS	CdS	3.47	0.9248	0	0	5.205	0.3911	0.150

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