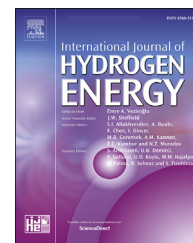




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In-situ synthesis of well dispersed CoP nanoparticles modified CdS nanorods composite with boosted performance for photocatalytic hydrogen evolution

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ABSTRACT

Development of photocatalysts with characters of low-cost, environment friendliness, visible light response and good performance is vital for the transformation of solar energy into hydrogen fuel. Here, we constructed CoP–CdS nanorods hybrid composites via a novel two-step in-situ growth method for the first time. The obtained CoP–CdS composites exhibited remarkably enhanced photocatalytic performance and excellent stability in comparison with bare CdS nanorods. Notably, the optimum H₂ evolution rate of 1 wt%–CoP–CdS was 9.11 times higher than that of pristine CdS. The apparent quantum efficiency of the photocatalyst was calculated to be 11.6%. The superior activity of this material could be attributed to the role of well dispersed CoP nanoparticles and the intimate interface between CoP cocatalysts and CdS nanorods, which efficiently accelerated the separation and transfer of photogenerated electrons. This work provided a new in-situ growth method for the preparation of transition metal phosphides coated photocatalysts with boosted photocatalytic activity of hydrogen evolution.

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Introduction

In this century, human society are facing two major problems: energy crisis and environmental pollution which stem from the heavily dependency on the non-renewable energy resources such as oil, coal and natural gas [1–8]. Efficient solar energy conversion for clean and renewable fuels is one of the most promising strategies [9–16]. Among the technologies of utilizations of solar energy, the solar-induced water splitting is a

promising one. It can produce hydrogen, which acts as a green, safe energy resource and holds great potential to replace fossil fuels in the future [15,17–23]. Photocatalysis using earth-abundant elements is an advanced process applied in the hydrogen evolution reaction since the discovery of water splitting over TiO₂ photoanode by Fujishima [24]. Unfortunately, TiO₂ responds only to the ultraviolet light due to its wide band gap. After that, a series of photocatalysts which can harvest both UV and visible light have been investigated, such as simple oxides (Bi₂O₃) [25], sulfide (CdS) [26,27], complex oxides (Bi₂WO₆)

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[28] and nitrides (C_3N_4) [29–32]. Among them, cadmium sulfide has been proved to be one of the excellent photocatalysts for hydrogen evolution due to its suitable band gap of 2.4 eV [33–37]. However, the practical application of CdS was severely limited because of fast recombination of photogenerated electron-hole pairs and poor photostability [36,38].

To boost the photocatalytic hydrogen evolution activity, various strategies have been employed, including suitable textural design, doping, modification with cocatalysts and forming heterojunction [39]. Among those, modification of photocatalysts with cocatalysts has gained intensive interest for the obtaining of excellent photocatalytic performance. The enhanced performance mainly arises from the fact that the loaded cocatalysts suppress the recombination of hole-electron pairs and lower the overpotential of hydrogen evolution [40]. Many noble-metal-free materials have been used as cocatalysts, such as transition metal oxides [41–45], carbon-based materials [46,47], hydroxides and sulfides [48–50]. Recently, it has been reported that transition metal phosphides with metalloid characteristics and good electrical conductivity (e.g., Ni_2P [51–55], $Ni_{12}P_5$ [56], Cu_3P [57], FeP [58,59], CoP [60–65], etc.) showed excellent activity as cocatalysts in the photocatalytic hydrogen generation process. Among them, CoP has been developed as an efficient cocatalyst with good stability. For instance, Zhao et al. reported that the CoP cocatalysts largely accelerated the H_2 generation rate of CdS semiconductor, deriving from the low H^+ reduction overpotential and efficient electron transfer [66]. Cao et al. also prepared CoP/CdS composites which exhibited excellent photocatalytic activity [63]. Nevertheless, in the traditional method, the CdS nanorods were obtained firstly, then the prepared CoP nanoparticles were supported on the surface of CdS . The resultant composites probably suffer from the sintering and agglomeration of CoP nanoparticles, which impede the transfer of electrons and further influence the hydrogen evolution performance.

Herein, we first adopted the in-situ synthesis method to prepare $CoP-CdS$ composites and explored their hydrogen evolution activity. The obtained 1 wt%– $CoP-CdS$ hybrid showed relatively high H_2 evolution rate of $13785 \mu\text{mol h}^{-1} \text{g}^{-1}$, which was 9.11 times higher than that of pure CdS . The excellent photocatalytic activity of $CoP-CdS$ is resulted from the CoP cocatalysts on the surface of CdS , intimate interface between them and faster transfer of electrons from CdS to CoP cocatalysts.

Experimental section

Chemicals

Cadmium chloride ($CdCl_2 \cdot 2.5H_2O$), thiourea (NH_2CSNH_2), ethylenediamine, cobalt chloride hexahydrate, sodium hypophosphite ($NaH_2PO_2 \cdot H_2O$), sodium sulfide (Na_2S), sodium sulfite (Na_2SO_3) and ethanol were purchased from Sinopharm Chemical Reagent Co., Ltd and used without additional treatment.

Preparation of photocatalysts

Preparation of $Co-CdS$ nanorods

The $Co-CdS$ nanorods sample was synthesized by a simple solvothermal method. Specifically, 4.62 g of $CdCl_2 \cdot 2.5H_2O$ and

4.62 g of NH_2CSNH_2 were dissolved in 60 mL ethylenediamine solution via vigorous stirring. After that, a certain amount of cobalt chloride hexahydrate was added into the solution according to the designed mass ratio of Co to CdS (0.5%, 1%, 2%, 5%) under continuous stirring. After complete dissolution, the solution was transferred to a 100 mL Teflon-lined stainless steel autoclave and heated at 160°C for 48 h. After that, the obtained products were separated and washed three times with distilled water and ethanol. Finally, the samples were dried at 60°C .

Preparation of $CoP-CdS$ photocatalysts

200 mg of above obtained $Co-CdS$ products and 50 mg of $NaH_2PO_2 \cdot H_2O$ were ground together in an agate. Then the mixture were annealed at 300°C for 2 h under the protection of argon atmosphere. The heating rate was $2^\circ\text{C}/\text{min}$. Finally, the solid was collected and washed with distilled water and ethanol for several times. The obtained samples were defined as 0.5 wt%– $CoP-CdS$, 1 wt%– $CoP-CdS$, 2 wt%– $CoP-CdS$ and 5 wt%– $CoP-CdS$, respectively.

Characterizations

X-ray diffraction (XRD) was performed on a Rigaku/Smartlab diffractometer equipped with $Cu K\alpha$ radiation at 40 kV and 40 mA with the 2θ range of $5^\circ-70^\circ$. Transmission electron microscope (TEM) images and corresponding high-resolution TEM images were acquired on a JEM-2100. Ultraviolet-visible diffuse reflection spectra (DRS) were recorded by Shimadzu, UV-3600. Surface area of Brunauer-Emmett-Teller were conducted on a Micromeritics ASAP 2020 HD88 apparatus. Raman spectra were taken by a Jobin Yvon LabRAM HR800 spectrometer with a 532 nm Ar^+ laser for excitation. The X-ray photoelectron spectroscopy (XPS) were obtained by a Thermo Scientific ESCALAB 250 instrument using a monochromatized $Al K\alpha$ excitation. Room temperature Photoluminescence (PL) pattern was conducted by Hitachi F-700 fluorescence spectrophotometer with an excitation wavelength of 350 nm. Time-resolved PL spectra were carried out on a FLS980 spectrofluorometer (Edinburgh Instruments) with excitation wavelength of 350 nm.

Photocatalytic H_2 evolution

The H_2 evolution reactions were taken place in a 100 mL pyrex vessel filled with 5 mg as-prepared photocatalysts, 0.35 M sodium sulfide, 0.25 M sodium sulfite and 50 mL pure water. A 300 W Xe lamp combined with a 420 nm UV-cut-off filter was served as the simulated visible light source to trigger the H_2 evolution reaction. Importantly, the system must be thoroughly degassed with the help of a vacuum pump. The generated hydrogen was in situ analyzed periodically by an online chromatograph-GC-7900 (nitrogen as the carrier gas) equipped with the thermal conductivity detector. The photostability of the photocatalysts was further measured for 5 cycles, while each cycle lasted for 4 h. The apparent quantum efficiency (AQE) was calculated through the equation below:

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

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