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The enhancement of CdS photocatalytic activity for water splitting via anti-photocorrosion by coating Ni_2P shell and removing nascent formed oxygen with artificial gill

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ABSTRACT

CdS photocorrosion seriously impeded its application in photocatalysis, especially for water splitting. Here we report new strategies to improve CdS photocorrosion resistance properties significantly by coating Ni_2P shell and assembling an artificial gill to remove newly formed O_2 from water. Ni_2P@CdS catalyst can achieve the over-all water splitting under visible light irradiation without addition of any sacrifice reagent and noble metal loading. Compared with CdS itself, the 10Ni_2P@CdS photocatalyst exhibits excellent photocatalytic activity for hydrogen evolution (251.4 μmol of H_2 in 180 min) with a high AQE (3.89% at 430 nm). This catalyst also presents high photocurrent, low overpotential (-0.32 V *vs* SCE), and long fluorescence lifetime (16.27 ns) of excited charges. Cd^{2+} ions concentration measured by ICP and long term stability results verified the anti-photocorrosion role of Ni_2P shell on CdS during water splitting reaction. The activity and stability of 10Ni_2P@CdS is even superior to typical 1Pt@CdS catalyst. Our results confirm CdS can be an active catalyst for photocatalytic hydrogen generation from water under visible irradiation if its stability is enhanced by protection of anti-photocorrosion overcoating shell and removing the nascent formed oxygen from water.

1. Introduction

Sustainable H_2 production from water via semiconductor photocatalysis driven by solar energy has been regarded as a viable solution to address the increasing environmental and energy issues [1–3]. Exploring efficient, endurable, low-cost, stable and nontoxicity photocatalysts for H_2 evolution reaction (HER) from water still remains a great challenge [4]. Most of these photocatalysts are only active under UV light, which accounts for only approximately 3%–5% of the solar spectrum on the surface of the earth, seriously restricting its solar efficiency [5–10]. To utilize sunlight source more efficiently, it is of significant importance to develop visible light-driven photocatalysts through the modification of wide-bandgap semiconductors or finding new visible light-driven photocatalysts. Recently, many visible light-driven photocatalysts (such as $BiVO_4$ [11], Ta_3N_5 [12], g–C_3N_4 [13,14], and CdS [15,16]) have also been reported. Among them, CdS possesses excellent photoelectrochemical performance due to its relatively narrow band gap (~2.4 eV) and appropriate band position, that meets the thermodynamic requirement for photocatalysis water splitting [17,18]. However, CdS itself has relatively low chemical stability under visible-light irradiation as it can be easily oxidized by O_2 [16].

To date, much works has been carried out to retard the photocorrosion of CdS nanoparticles (NPs). For instance, Su *et al.* reported that the PANI@CdS core-shell nanospheres exhibited enhanced anti-photocorrosion properties and photocatalytic hydrogen production activity [19]. Ikeue *et al.* have synthesized the composite sulfide catalyst ($Mn_{1-x}Cd_xS$) by a hydrothermal method and found that the photocatalytic activity of $Mn_{1-x}Cd_xS$ is higher than that of single CdS [20]. Hu *et al.* indicated that carbon-coating over CdS could prevent CdS from oxidation [21]. Yang *et al.* found that, the GR–CdS–MoS_2 material displayed high photocatalytic activity for HER and anti-photocorrosion ability compared with pure CdS [22]. However, most of these works often invoke harsh synthesis conditions or require continuous feeding of sacrificial agents into the photocatalytic system.

The photocorrosion processes of CdS in the absence and presence of H_2O and O_2 can be described by Eqs. (1) and (2), respectively:

$$CdS+2h^{+} \rightarrow Cd^{2+}+S \tag{1}$$

$$CdS+4h^{+} + 2H_2O + O_2 \rightarrow Cd^{2+}+SO_4^{2-} + 4H^{+} \tag{2}$$

In fact, the photocorrosion is not only related to the photogenerated hole (h^+) in semiconductor itself, but also related to the newly formed

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oxygen in the water [23]. In addition, since the dissolved oxygen is about 5 times higher than that of hydrogen in water, the reaction of hydrogen and oxygen recombination occurred very fast over the photocatalysts surface [24], which further inhibited the performance of catalyst for water splitting consequently. Domen and co-workers have previously achieved overall water splitting under visible light using $LaMg_{1/3}Ta_{2/3}O_2N$ modified with a metal oxyhydroxide layer [25], which could inhibit hydrogen and oxygen recombination reaction. Li *et al*. also indicated that the recombination of hydrogen and oxygen could be inhibited by addition of oxygen transfer reagent hemin chloride [26]. Inspired by the respiratory system of fish, the application of artificial gill in photocatalytic overall water splitting might remove neonatal formed O_2 from water and prevent the oxygen leading photocorrosion, as a result, the reverse reaction of hydrogen and oxygen recombination back to water could be retarded.

Another important challenge is replacement noble metal co-catalyst in photocatalysis by earth abundant elements because Pt-group metals are scarceness and high-cost [27], for example by transition-metal phosphides, which exhibited noble-metal-like properties for HER [28–35]. Herein, we develop core-shell structured Ni_2P@CdS photocatalyst by solvothermal method for high efficient HER under visible light irradiation without sacrifice reagent and noble metal loading. With help of artificial gill removing newly formed O_2 from water, the oxygen leading photocorrosion was prevented and the hydrogen and oxygen recombination to water was inhibited. Compared with CdS itself, Ni_2P@CdS core-shell photocatalyst exhibits excellent photocatalytic activity for water splitting. Characterization results further indicate the Ni_2P shell over CdS surface can inhibit CdS from photocorrosion. More importantly, Ni_2P co-catalyst is a promising substitute for replacement of noble-metals in photocatalytic HER.

2. Experimental methods

2.1. Materials

All chemicals were commercial purchased and used without further purification. Cadmium nitrate ($Cd(NO_3)_2·4H_2O$, Tianjin Kemiou Chemical Reagent Co., Ltd, AR, ≥99.0%), sodium sulfide ($Na_2S·9H_2O$, Chengdu Kelong Chemical Reagent Co., Ltd, AR, ≥98.0%), chloroplatinic acid ($H_2PtCl_6·6H_2O$, Tianjin Kemiou Chemical Reagent Co., Ltd, AR, ≥99.0%), ethylenediamine ($NH_2CH_2CH_2NH_2$, Shanghai Aladdin Bio-Chem Technology Co., Ltd, > 99.0%), thioacetamide (CH_3CSNH_2, Sinopham Chemical Reagent Co., Ltd, AR, ≥99.0%), hydrazine hydrate ($H_4N_2·H_2O$, Xilong Chemical Co., Ltd., AR, > 80%), nickelnitrate ($Ni(NO_3)_2·6H_2O$, AR, J & K Scientific Ltd., ≥96.0%), phosphorus white (P_4, Sinopham Chemical Reagent Co., Ltd, AR, ≥99.8%), benzene (C_6H_6, Tianjin Kemiou Chemical Reagent Co., Ltd, AR, ≥99.0%), deuteroxide (D_2O, J & K Scientific Ltd., AR, > 99%), water-^{18}O ($H_2{}^{18}O$, J & K Scientific Ltd., AR, > 97%), ethanol (C_2H_5OH, Xilong Chemical Co., Ltd., > 99.8%), sodium sulfate anhydrous (Na_2SO_4, Xilong Chemical Co., Ltd, AR, ≥99%), potassium hydroxide (KOH, Xilong Chemical Co., Ltd, AR, ≥99%), potassium bromate ($KBrO_3$, Xilong Chemical Co., Ltd, AR, ≥99%). 5,5-dimethyl-1-pyrrolineN-oxide (DMPO, J & K Scientific Ltd., ≥98.0%). De-ionized water with a specific resistance of 18.2 MΩ cm was obtained by reverse osmosis followed by ion–exchange and filtration (Milli-Q™ Advantage A10™, France). All of the reagents were used in the experiments.

2.2. Catalyst preparation

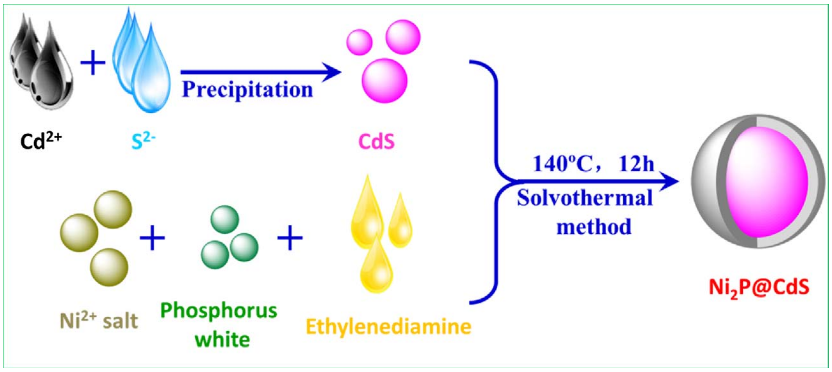
2.2.1. Synthesis of CdS and CdS-H samples

CdS sample was prepared by a typical precipitation method. Briefly, 3.5 mmol (1.0797 g) $Cd(NO_3)_2·4H_2O$ was dissolved in 20 mL of deionized water and stirred vigorously for 60 min, 7.0 mmol (1.6813 g) $Na_2S·9H_2O$ was dissolved into another 10 mL of deionized water by ultrasonication to obtain the Na_2S solution. Then the Na_2S solution was slowly added into the above-mentioned $Cd(NO_3)_2$ solution in a drop-by-drop process under vigorous stirring. After stirring for 3 h, the obtained yellow precipitate was filtrated, washed with deionized water several times, and dried at 80 °C for 12 h. Finally, the products were collected and ground into powder by an agate mortar for further use.

For comparison, the small-sized CdS catalyst was also synthesized by hydrothermal method [36]. CdS nanocrystal was prepared by sequentially adding 5 mL of ethylenediamine and 12.5 mmol (0.9391 g) of thioacetamide to a 20 mL aqueous solution containing 5 mmol (1.5424 g) of cadmium nitrate. The volume of the reaction solution was adjusted to be 30 mL by introducing additional water. The entire process was carried out under magnetic stirring. The reaction mixture was further stirred for 20 min, sealed in a 50 mL capacity Teflon-lined autoclave, and heated to 230 °C at a ramping speed of 30 $°Cmin^{-1}$ in the presence of microwave irradiation. The reaction was allowed to proceed for 30 min. After cooling, the product was separated by centrifugation, washed several times with deionized water and ethanol, and dried at 80 °C for 5 h in a vacuum oven. Finally, the products were collected and ground into powder by an agate mortar for further use. The synthesized CdS catalysts by precipitation and hydrothermal methods were denoted as CdS and CdS-H, respectively.

2.2.2. Synthesis of Ni_2P

The Ni_2P was successfully prepared through a simple solvothermal process according to the previous literatures [37]. Typically, 0.7270 g (2.5 mmol) $Ni(NO_3)_2·6H_2O$ and 1.5487 g (12.5 mmol) phosphorus white were put into an 100 mL autoclave with Teflon liner, which was then filled with ethylenediamine up to 80% of its capacity. The mixture was sonicated for about 20 min until it became homogeneous. The autoclave was maintained at 140 °C for 12 h and then cooled to room temperature naturally. The black precipitates were collected and washed with benzene, ethanol, and distilled water in sequence to remove the byproducts and possible impurities. The final products were dried in vacuum at 60 °C for 12 h.



Scheme 1. Schematic illustration on the synthesis of Ni_2P@CdS core-shell structure sample.