



Noble-metal-free Ni₃C cocatalysts decorated CdS nanosheets for high-efficiency visible-light-driven photocatalytic H₂ evolution

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ABSTRACT

In this work, Ni₃C nanoparticles (NPs, 0 D) were for the first time used as H₂-evolution cocatalysts to modify CdS nanosheets (NSs, 2 D) to achieve the high-efficiency photocatalytic H₂ evolution under visible light irradiation. The photocatalytic H₂-evolution activities of the Ni₃C/CdS hybrid NSs were tested under 350 W Xe lamp irradiation ($\lambda \geq 420$ nm) with a sacrificial agent. The results proved that Ni₃C NPs were efficient cocatalysts for photocatalytic H₂ evolution over CdS NSs. The CdS-1% Ni₃C hybrid NSs exhibited the highest photocatalytic H₂-evolution rates of 357 $\mu\text{mol h}^{-1}$ in 0.25 M Na₂S-Na₂SO₃ and 450.5 $\mu\text{mol h}^{-1}$ in lactic acid, which were approximately 7.76 and 4.79 times higher than that of bare CdS NSs, corresponding to the apparent quantum yields of 7.58% and 8.72% at 420 nm, respectively. Clearly, the Ni₃C NPs serve as H₂-evolution electrocatalysts either in acidic or basic media. It is believed that the noble-metal-free Ni₃C cocatalyst NPs on the surface of CdS NSs can effectively increase the visible-light absorbance, promote the charge carriers separation and transfer, improve the surface H₂-evolution kinetics, thus achieving the obviously boosted hydrogen evolution. It is hoped that this study could contribute to the further investigation in exploiting the low-priced, high efficiency and environmentally friendly noble-metal-free cocatalysts for photocatalytic H₂ evolution.

1. Introduction

Hydrogen production by photocatalytic water splitting represents one of the most promising approaches for energy storage and clean fuel generation in a post fossil age [1]. Since the groundbreaking report by Fujishima and Honda about the photoelectrochemical splitting of water on TiO₂ electrodes using UV light in 1972 [2], various inorganic and organic semiconductors have been available for photocatalytic hydrogen evolution from water splitting [1,3,4]. To maximally utilize the visible-light region in the solar spectrum, cadmium sulfide (CdS) with an adequate narrow band gap (2.4 eV) and proper thermodynamic conduction band potential has been considered to be an excellent visible-light-responsive semiconductor for solar H₂ production [5]. Although much progress has been achieved in the field of photocatalytic H₂ evolution over CdS, it is still a huge challenge to rationally design the efficient and robust CdS-based H₂-evolution systems for the practical applications, owing to the poor separating efficiency of photo-excited charges and the undesired deactivation processes driven by photo-generated holes [6]. Accordingly, to tremendously improve the

photocatalytic activity and stability of CdS toward H₂ production, a large number of modification approaches have been widely proposed during the past few decades, including fabricating nanostructured CdS [7–10], constructing semiconductor heterojunctions [11–16], designing Z-scheme systems [17–21], coupling with nano-carbons [5,22–25], loading cocatalysts [26–32], exploiting solid solution and surface doping [33]. Among these pathways, fabricating nanostructured CdS and loading cocatalysts were considered to be two most attractive methods to significantly improve the photocatalytic activity.

On the one hand, various nanostructured CdS photocatalysts, including quantum dots [31,32], nanoparticles [17], nanorod/nanowires [26,27,29,34], nanoflowers [7], etc. have been extensively constructed to achieve the highly boosted photocatalytic H₂ evolution, owing to the unique nanoscale effects for promoting the charge separation and exposing more active sites [35]. However, to the best of our knowledge, there are few works focusing on applications of ultrathin 2D CdS nanosheet-based photocatalysts in the photocatalytic H₂ evolution [19,36–38], which might be due to complicated fabrication procedures. In 2007, Bao et al. synthesized nanoporous CdS nanosheets with sizes

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up to 60 nm and an average thickness of about 9 nm by a two-step aqueous route, involving the first precipitation of nanoporous Cd(OH)₂ intermediates and a subsequent S²⁻/OH⁻ ion-exchange conversion of the obtained Cd(OH)₂ used as self-template [39]. The as-obtained nanoporous CdS nanostructures loaded with monodisperse 3–5 nm Pt nanocrystals exhibited the highest apparent quantum yield of about 60.34% at 420 nm. In 2013, Zhang and his coworkers reported that the ultrathin CdS nanosheets (NSs) with a thickness of 4 nm could be facilely fabricated through a simple solvothermal and solution-phase ultrasonic exfoliation approach using lamellar CdS-amine inorganic-organic hybrid nanosheets as starting materials [40]. These CdS ultrathin nanosheets show excellent activity and good stability for photocatalytic H₂ evolution under visible light irradiation in sacrificial agent solution. More recently, Zhukovskiy et al. developed a new strategy to fabricate the high-quality, thickness-controlled CdS nanosheets (NSs) with discrete thicknesses of 1.50–2.16 nm and lateral dimensions on the order of 90 nm × 20 nm through the thermal decomposition of cadmium diethyldithiocarbamate in octadecene [38]. The resulting CdS NSs supported Ni NP (a diameter of 6 nm) could achieve the apparent quantum yields of 25% for photocatalytic hydrogen generation in water/ethanol mixtures. In this direction, these reports open new ways to fabricate various 2D CdS nanosheet-based composite photocatalysts, such as 2D-2D coupling CdS-MoS₂ [36] and mediator-free Z-scheme CdS-WO₃ systems [19] for different applications.

On the other hand, it is generally accepted that the noble metals, such as Pt, Au and Ag, have been extensively photo-deposited on the nanostructured CdS photocatalysts to achieve very high quantum efficiency for photocatalytic H₂ generation due to the promoted charge separation and improved H₂-evolution kinetics [41]. However, the high price and scarcity of noble metals significantly restrict their extensive applications. Recently, to construct the highly active H₂-evolution systems without any noble metals, numerous earth-abundant robust cocatalysts have been revealed to boost the photocatalytic H₂-evolution activity over CdS, such as Ni [38,42], nickel complex [43], MoS₂ [44–49], Cu₂S [50], Cu₂MoS₄ [51], NiS [28,52], WS₂ [53,54], Ni₂P [55,56], CoP_x [57,58], Co₃N [59], Ni₃C [60], CoO_x [27,61] and Ni(OH)₂ [62,63]. Especially, tremendous efforts have demonstrated that the transition metal carbides, such as WC [64], Mo₂C [65] and Ti₂C₃ MXene [66], are promising cocatalysts for efficient photocatalytic H₂ generation. More interestingly, a series of nickel carbides, such as high-index faceted dendritic NiCo_{0.2} nanosheets [67], Ni₃C nanocrystals encased in graphene nanoribbons [68] and Ni₃C nanoparticles embedded in a porous carbon network [69] have been found to exhibit superior electrocatalytic activity for H₂ production in acidic or basic media. Notably, to the best of our knowledge, there have been no studies regarding the applications of Ni₃C as cocatalysts for promoting photocatalytic H₂ evolution over CdS. To this end, it is of great interest to exploit the really promising and earth-abundant Ni₃C cocatalyst for improving photocatalytic H₂ evolution over CdS.

Accordingly, it is extremely desirable that the scrupulous integration and design of nanostructured CdS and suitable earth-abundant cocatalysts could fundamentally reduce carrier migration distance from bulk to its surface, increase the specific surface area and effective HER active sites, accelerate H₂-evolution kinetics, and decrease activation energy barrier for H₂ evolution [42], thus achieving the robust and active photocatalytic H₂ evolution. Herein, earth-abundant Ni₃C NPs as cocatalysts were for the first time loaded onto CdS NSs to markedly boost their photocatalytic H₂-evolution activity. The Ni₃C/CdS NSs composite photocatalysts were successfully synthesized by a simple grind method, which exhibited much better photocatalytic H₂-evolution activity than that of pure CdS NSs either in 0.25 M Na₂S-Na₂SO₃ or lactic acid aqueous solution under visible light irradiation. The possible mechanism for improving the photocatalytic activity of Ni₃C/CdS NSs composite photocatalysts was proposed in this study.

2. Experimental

2.1. Preparation of photocatalysts

2.1.1. Materials

All materials used in this research were of analytical grade and used as received, including cadmium chloride (CdCl₂·2.5H₂O), sulfur powder, diethylenetriamine (DETA), nickel acetate anhydrous (Ni(Ac)₂), and oleylamine.

2.1.2. Synthesis of CdS NSs

The CdS NSs were synthesized by a facile solvothermal method [40]. 10 mmol of sulfur powder was added into 60 mL of DETA with vigorous stirring until it dissolved completely. Then, 1.6 mmol of CdCl₂·2.5H₂O was dispersed in the mixture with stirring and sonication. After that, the suspension was transferred into a 100 mL Teflon-lined autoclave, heated at 80 °C for 48 h, and then naturally cooled to room temperature. The pale yellow precipitate was collected by centrifugation (8000 rpm, 5 min) and washed three times with deionized water and ethanol, respectively. Finally, it was dried at 80 °C for 10 h in a vacuum drying oven.

2.1.3. Synthesis of Ni₃C NPs

The Ni₃C NPs were synthesized by a reported method [70]. 2 mmol of Ni(Ac)₂ and 14.1 mL of oleylamine were mixed into a 100 mL three-neck round-bottom flask. The mixture was stirred magnetically under a nitrogen atmosphere. Then, it was heated to 250 °C and kept this temperature for 2 h. 30 mL of acetone was added into the mixture after cooling to room temperature. The Ni₃C NPs were collected by centrifugation (5000 rpm, 15 min) and dried at 60 °C for 10 h in an oven.

2.1.4. Synthesis of Ni₃C/CdS NSs composites

In a typical synthesis method, 400 mg CdS NSs and 4 mg Ni₃C NPs powders were grounded together in an agate mortar for 1 h and stored for further characterization. The whole synthesis process was shown in Scheme 1.

The obtained composite powder with 1 wt% Ni₃C NPs was denoted as CdS-1.0%Ni₃C. The other composites with different contents of Ni₃C were prepared according to the same method. The other Ni₃C/CdS NSs composites with 0.5 wt%, 1.5 wt% and 2 wt% Ni₃C NPs, were denoted as CdS-0.5%Ni₃C, CdS-1.5%Ni₃C and CdS-2.0%Ni₃C, respectively.

2.2. Characterization

Power X-ray (XRD) patterns were collected on a MSAL-XD2 diffractometer using a Cu K α radiation source (operated at 36 kV and 30 mA, $\lambda = 1.54056 \text{ \AA}$) to determine the crystal phase of CdS NSs, Ni₃C NPs, and their composites. The morphology images of the samples were obtained by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) using a JEM-2100HR (200 kV, Japan) operated at 200 kV. The UV-vis diffuse reflection spectra (UV-vis DRS) were recorded with a Daojin UV-2550PC diffuse reflectance spectroscopy, 100% BaSO₄ was used as the reference. X-ray photoelectron spectroscopy (XPS) data was performed with a VG ESCALAB250 surface analysis system using a 300 W Al K α X-ray radiation source (5 mA and 15 kV). All the binding energies were calibrated using the C 1s level at 284.8 eV as the reference. The pure CdS NSs and CdS-1.0%Ni₃C samples were degassed at 120 °C before nitrogen absorption measurements. A Brunauer-Emmett-Teller (BET) method was used to determine the specific surface area in the relative pressure (P/P₀) range of 0.05–0.99. The pore-size distributions were researched from the desorption branches of the isotherms using the Barrett-Joyner-Halenda (BJH) method. The nitrogen adsorption volume at the relative pressure (P/P₀) of 0.99 was used to investigate the pore volume and the mean pore diameter. The photoluminescence (PL) spectra of the photocatalysts were

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