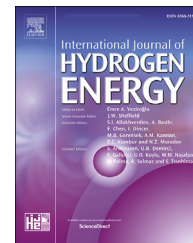




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Fabrication of CdS/Ni–Fe LDH heterostructure for improved photocatalytic hydrogen evolution from aqueous methanol solution

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ABSTRACT

2D CdS/Ni–Fe LDH (short for layered double hydroxide) heterostructures were designed and fabricated by following a facile in-situ growth method. The CdS nanoparticles are well dispersed on the surface of Ni–Fe LDH to form nanoscale heterojunctions, as suggested from the TEM and elemental mapping images. The composites with optimum CdS amount (15 wt%) take on notably higher hydrogen evolution activity ($469 \mu\text{mol h}^{-1} \text{g}^{-1}$) than the independent CdS and Ni–Fe LDH from aqueous methanol solution under xenon lamp irradiation. The nano-heterojunction notably promotes the H_2 evolution kinetics and greatly suppresses the recombination of photo-induced electrons and holes, which is responsible for the enhanced photocatalytic activity of the composites, as demonstrated by the reducing onset potential and increasing photocurrent of the composites in the photoelectrochemical experiments. The possible photocatalytic mechanism is proposed on the basis of the defined position of energy band edges.

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Introduction

Conversion of solar energy into hydrogen fuels by following photocatalytic water splitting has aroused the concern from researchers by virtue of its environmental friendliness and sustainability [1]. Developing cost-effective and stable photocatalysts is a key objective to perform such process. Although numerous semiconductor materials have been developed in recent years, such as metal oxides, metal sulfides and metal-free polymeric graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) [2], their performance remains unable to realize their practical

application. It is now a critical issue to improve the photocatalytic performance of the materials by following various modification methods, e.g. ion doping [3,4] and constructing heterojunction composites [5].

LDHs (short for Layered double-metal hydroxides) are a class of inorganic layered matrices, generally expressed as the equation $[\text{M}^{\text{II}}_{1-x}\text{M}^{\text{III}}_x(\text{OH})_2]^{z+}(\text{A}^{n-})_{z/n} \cdot y\text{H}_2\text{O}$ (M^{II} and M^{III} : divalent and trivalent metals, respectively; A^{n-} : the interlayer anion compensating for the positive charge of the brucite-like layers) [6], and have aroused huge attention as low-cost electrocatalytic [7–10] or photocatalytic [11–15] materials in

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catalytic activity to H₂ or O₂ evolution from water splitting. 2D Ni–Fe LDH nanosheets have a potent performance for H₂ evolution from water splitting as electrocatalysts by virtue of the large surface area, much active sites and improved conductivity, as suggested by many reports [16–19]. Yet they rarely serve as photocatalysts alone, which is primarily attributed to their weak visible-light absorption and poor separation efficiency of carriers. Ni–Fe LDH was coupled with other photo-active semiconductors such as Cu₂O [20], g-C₃N₄ [21,22], and BiOCl [23,24] in recent reports to form heterostructures, thus increasing the visible-light absorption intensity and accelerating the separation of photogenerated electron-hole pairs. As a result, the high photocatalytic activity of the composites was acquired for H₂ evolution or dye degradation.

Given their strong solar light absorption and high water reduction capacity, CdS nanocrystals have an appropriate band gap (~2.4eV) and higher conduction band edge [25]. And yet when used alone, they are normally subject to the easy aggregation, poor electron-hole separation and H₂ evolution kinetics, as well as the instability. Incorporating CdS into the composites with other components was often studied to overcome these above noted issues [26–36]. For instance, the incorporation with MoS₂ high in H₂ evolution activity brought the good H₂ evolution kinetics and efficient charge separation to the composites [29–32], and the incorporation with 2D g-C₃N₄ or graphene made CdS nanoparticles well dispersed to form multiple nanoscale heterojunction, which increased the photocatalytic activity [33–36]. Furthermore, the photo-corrosion resistance of CdS increased notably after its coupling into the composites with other stable materials. Given this, 2D Ni–Fe LDH shows multi-advantages as one component constructing heterostructure composites with CdS due to its large surface area and good H₂ evolution kinetics as well as good stability. To our knowledge, the composites of Ni–Fe LDH and CdS have not been reported as yet, even other sulfide semiconductors.

It is challenging to form efficient heterojunction with the intimate contact between CdS and Ni–Fe LDH phase as the Ni–Fe LDH provides limiting bonding sites to CdS particles [37]. Additionally, given that metal ions (Ni(II) and Fe(III)) in the host layer of LDH could easily react with S²⁻ to destroy the structure of LDH, the heterostructure was hard to form by depositing CdS on the surface of Ni–Fe LDH from the precursor solution containing Cd²⁺ and S²⁻. Thus, the 2D CdS/Ni–Fe LDH heterostructure was fabricated by *in-situ* growing CdS nanoparticles on the surface of 2D Ni–Fe LDH in this study. First, an excessive amount of Cd cations were grafted on the surface of Ni–Fe LDH by spraying and drying treatment. Next, an adequate amount of S anions could bond with the Cd cations on the surface of the Ni–Fe LDH to form *in-situ* CdS nanoparticles using the similar spraying and drying treatment. The catalytic hydrogen evolution activity of as-prepared CdS/Ni–Fe LDH nano-heterojunctions at optimum CdS loading increased notably. The photocatalytic mechanism of the composites was further discussed. This study may provide a new sight to fabricate highly efficient photocatalysts with low cost in energy and environmental applications.

Experimental method

Materials

All reagents are analytical pure, commercially available, and were used without any treatment.

Synthesis of photocatalytic materials

Synthesis of 2D Ni–Fe LDH

Ni–Fe LDH nanosheets were fabricated in reverse microemulsion systems [12,38]. Specifically, this study mixed 7.20 g SDS (short for sodium dodecyl sulfate), 250 ml of isooctane, and 5.5 ml of deionized water in a flask under magnetic stirring. 7.5 mL of 1-butanol constantly stirred was added dropwise to acquire the stable and transparent reverse microemulsion. Then, 0.81 g Fe(NO₃)₃·9H₂O and 1.75 g Ni(NO₃)₂·6H₂O were added into the microemulsion and stirred till dissolved. Eventually, 1.39 g urea was added into the mixture, and the reaction solution was refluxed at 110 °C for 48 h with magnetic stirring. The precipitate was collected by centrifuging, washing with the mixture solvent of ethanol and water (1:1), and then drying at 80 °C.

Synthesis of CdS/Ni–Fe LDH composites

This study placed 0.15 g of the as-prepared Ni–Fe LDH into a beaker. 0.34 g Cd(NO₃)₂·4H₂O and 0.044 g Na₂S·9H₂O were dissolved into 2 mL of deionized water in a typical process, respectively. The Cd(NO₃)₂ solution was sprayed on the Ni–Fe LDH nanosheets in the beaker till uniformly moist under stirring with a glass rod. Then, the humid powder was dried in the oven at 60 °C. The process was repeated till the solution was used up. Afterwards, by performing a similar process as above, the Na₂S solution was uniformly sprayed on the as-obtained powders. Eventually, the CdS/Ni–Fe LDH composites with 15 wt% CdS loading were collected by washing with deionized water and drying at 60 °C, and named as 15%CdS/Ni–Fe LDH. Similarly, 5%, 10%, and 30%CdS/Ni–Fe LDH composites were fabricated by changing the quantity of Cd(NO₃)₂·4H₂O and Na₂S·9H₂O, respectively.

As a controlled experiment, the single CdS was prepared by traditional precipitation method from the Cd(NO₃)₂ and Na₂S aqueous solutions.

Characterization method

The crystal structures of the prepared samples were recorded by D/MAX-RB X-ray powder diffraction (XRD, Rigaku) with Cu K α radiation ($\lambda = 0.15405$) at 40 KV and 30 mA. The morphologies were observed using a scanning electron microscopy (SEM, SUPRA 55, Sapphire) at 3.00 KV. HRTEM (short for High resolution transmission electron microscopy) images were observed using a transmission electron microscope (TEM, F-20, FEI) at an accelerating voltage of 200 kV. The chemical status of elements in samples was determined using X-ray photoelectron spectroscopy (ESCALAB 250Xi) with an Al K α line. UV–Vis DRS (short for diffuse reflectance spectra) were carried out on a TU-1901 UV–Vis spectrophotometer equipped with an integrating sphere attachment in the 400–800 nm range.

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