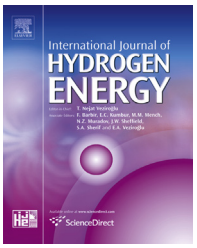
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2017) 1–7

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



One-pot hydrothermal synthesis of CdS/NiS photocatalysts for high H_2 evolution from water under visible light

Xiaozhou Zhou, He Sun, Huaizhang Zhang, Weixia Tu *

State Key Laboratory of Organic-Inorganic Composites, Beijing University of Chemical Technology, Beijing 100029, China

ARTICLE INFO

Article history:
Received 19 December 2016
Received in revised form
24 March 2017
Accepted 25 March 2017
Available online xxx

Keywords:
Hydrogen evolution
Photocatalyst
Non-noble metal
Metal sulfide
Visible light

ABSTRACT

The development of efficient and stable noble-metal-free photocatalysts is crucial for hydrogen evolution from water splitting as clean energy. This study reports uniform CdS/NiS spherical nanoparticles through a simple one-pot hydrothermal method with the aid of KOH. The prepared CdS/NiS composites show superior photocatalytic activities toward the water splitting under visible light. A suitable amount of KOH in the synthesis benefits to form CdS/NiS photocatalysts with the improved activity. The CdS/NiS composite including 10 mol % metal percentage of Ni exhibits the highest photocatalytic activity. The high hydrogen evolution rate of 24.37 mmol h^{-1} g^{-1} is achieved over the CdS/NiS composite photocatalyst. The CdS/NiS photocatalyst has good photocatalytic stability in the recycling uses. The present CdS/NiS as a noble-metal-free photocatalyst provides the superior visible-light driven catalytic activity for hydrogen evolution.

Introduction

Hydrogen (H_2) from water splitting over photocatalysts using solar energy has received much attention due to its sustainability and environmental friendliness [1–3]. In order to improve the utilization of solar energy, high visible-light-responsive photocatalysts should be developed. Up to now, kinds of visible-light-driven photocatalysts have been obtained, such as CdS [4], In_2S_3 [5], Ta_3N_5 [6] and g-C_3N_4 [7]. Thereinto, CdS has elicited more and more attention because of its appropriate band gap (2.4 eV). However, pure CdS is usually not active in hydrogen production because of the rapid recombination of photo-generated charge carriers [8–10]. Although this problem can be solved by doping some noble metal co-catalysts [11–13], the high cost limits their further application in photocatalyst. Therefore, it is eager to develop highly efficient and inexpensive cocatalysts for the replacement of noble metals.

Earth abundant element-based compounds as co-catalysts have been attempted to improve the photocatalytic activity of CdS. Zhou et al. synthesized $Co(OH)_2$/CdS nanowires through precipitation method and the H_2 evolution rate is 14.43 mmol h^{-1} g^{-1} [14]. Ran et al. modified CdS nanorods with $Ni(OH)_2$ resulting in a 5.08 mmol h^{-1} g^{-1} of H_2-production rate [15]. Recently, extensive studies have indicated that transition metal sulfides can be ideal choices of the alternative to noble

* *Corresponding author*. P. O. Box 100, College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, China.
E-mail address: tuwx@mail.buct.edu.cn (W. Tu).

http://dx.doi.org/10.1016/j.ijhydene.2017.03.179
0360-3199/

metals, such as MoS_2 [16,17], NiS [18], CuS [19,20], WS_2 [21]. Among them, nickel sulfide (NiS) has received increasing attention owing to its low-cost, good electrical properties, and other unique properties. Zhang et al. prepared NiS modified TiO_2 using solvothermal method for the photocatalytic H_2 production and the H_2 evolution rate is 0.7 mmol h^{-1} g^{-1} [22]. Chen et al. synthesized g-C_3N_4/NiS hybrid photocatalysts through in situ template-free ion-exchange process and the H_2 production rate is 0.45 mmol h^{-1} g^{-1} [23]. Furthermore, Xu et al. reported that NiS can be used as cocatalyst of CdS for photocatalytic water splitting via hydrothermal loading method, and the H_2 evolution rate can reach 7.3 mmol h^{-1} g^{-1} [24]. Yu et al. also developed NiS modified CdS nanorod photocatalysts with a two-step hydrothermal method, exhibiting an H_2 evolution rate of 1.13 mmol h^{-1} g^{-1} [25]. Guo et al. reported an efficient $Cd_{0.5}Zn_{0.5}S$ photocatalyst with unanchored NiS_x co-catalyst for photogeneration of hydrogen [26]. Meng et al. used PdS to modify the CdS/NiS composite as a photocatalyst for H_2 evolution under visible light [27]. For CdS/NiS photocatalyst, different synthesis methods are still necessary to be explored for improving its catalytic activity.

In this study, we present a simple one-pot hydrothermal method to synthesize CdS/NiS composites. The uniform CdS/NiS nanoparticles are obtained with the aid of KOH and structure promoter (CTAB). Their photocatalytic performances are evaluated for H_2 evolution from water splitting under visible light irradiation. The synthesis conditions for CdS/NiS nanocomposites are optimized for the superior photocatalytic H_2-production activity. A possible mechanism for the enhanced photocatalytic activity is also discussed.

Experimental

Synthesis of CdS/NiS composites

CdS/NiS samples were prepared by a one-pot hydrothermal method. Typically, X mmol nickel acetate tetrahydrate ($Ni(Ac)_2{\cdot}4H_2O$), Y mmol cadmium acetate ($Cd(Ac)_2{\cdot}2H_2O$) together with 2 mmol thiourea (NH_2CSNH_2) were dissolved into 80 mL aqueous solution of cetyltrimethyl ammonium bromide (CTAB) under the strong magnetic stirring ($X + Y = 1$, $0 < X < 1$). Ten minutes later, 10 mmol potassium hydroxide (KOH) was added, and kept stirring for 24 h. Then, the mixtures were transferred into a 100 mL Teflon autoclave and heated at 200 °C for 24 h in a vacuum oven. The resulting mixtures were filtered and washed three times with absolute ethanol. Finally, the precipitate was dried overnight at 60 °C. The obtained powder was the CdS/NiS composite. The nominal molar percentages of Ni/(Cd + Ni), designated as R, were 5, 7.5, 10, 15, 20, 50, and 80 mol%, and the resulting samples were named as CdS/NiS-5, CdS/NiS-7.5, CdS/NiS-10, CdS/NiS-15, CdS/NiS-20, CdS/NiS-50, CdS/NiS-80, respectively. Pure CdS and NiS samples were also prepared using the same method for comparison.

Characterization

X-ray diffraction (XRD) patterns were obtained through the measurement on a Bruker D8 Advance diffractometer (Germany Bruker AXS Ltd.) using Cu-Ka radiation at a scan rate of 0.02°/s. S-4700F electron microscope (SEM, Japan JEOL Ltd.) was used to know about the morphology of the samples. The HRTEM analysis was taken on a J-3010 electron microscope (Japan JEOL Ltd.). The UV–Vis diffuse-reflectance spectra were recorded by a UV–Vis spectrophotometer (Tu-1901, Beijing Persee General Instrument Co. Ltd.), using $BaSO_4$ as a reflectance standard. The photoluminescence (PL) spectra were conducted using FL spectrophotometer (Hitachi F-7000). The XPS measurements were taken on a VG ESCALAB 250 electron spectrometer using a multichannel detector. ICP-AES results were determined on an inductively coupled plasma spectrometry-atomic emission spectrometer (ULTIMA, JY Inc.). The Brunauer–Emmett–Teller (BET) surface areas of the powders were measured using a Micrometrics ASAP 2020HD88 nitrogen adsorption apparatus.

Photocatalytic H_2-production activity

A 500 mL Reactor equipped with a 500 W Xe lamp was used to conduct the photocatalytic reactions. 60 mg of CdS/NiS photocatalyst was dispersed in a 400 mL mixed solution of lactic acid (40 mL) and water (360 mL) by ultrasonic treatment for 10 min. Then, the solution was decanted into a 500 mL Pyrex reactor under a constant stirring. The reaction system was maintained at room temperature and atmospheric pressure during the reaction under Xe lamp irradiation. 1 mL of gas was intermittently sampled every 1 h, and was analyzed by gas chromatography (TCD with TDX-01 molecular sieve column, N_2 carrier). The quantum efficiency (QE) of photocatalyst was measured through the photocatalytic reaction in a 65 mL Pyrex flask. The opening of the flask was sealed with a silicone rubber septum. 3 mg of the catalyst was sonically dispersed in an aqueous solution (20 mL) containing 10 vol% lactic acid. A 300 W Xe lamp coupled with a mono-tone filter ($\lambda = 420$ nm) served as the light source, and was placed at 15 cm away from the reactor. Before irradiation, the system was bubbled with N_2 for 20 min to ensure anaerobic conditions. The focused intensity was determined to be 28.92 mW cm^2 and the irradiation area was 12.5 cm^2. The QE is equal to the ratio of the reacted electrons number to the incident photons number, while the reacted electrons number is twice of the evolved H_2 molecules number.

Results and discussion

Photocatalytic H_2-evolution activity of the CdS/NiS composites

Through adjusting the ratio of metal precursors (R), a series of the CdS/NiS composites were synthesized by the one-pot hydrothermal method detailed above. Photocatalytic reactions over the CdS/NiS composites were carried out under a 500 W Xe lamp irradiation with lactic acid as sacrificial agent. Fig. 1 shows the H_2 evolution rate in 4-h water splitting reaction over the photocatalysts with different R. As can be seen, the pure NiS ($R = 100$) sample shows no appreciable photocatalytic activity for H_2 production. The pure CdS ($R = 0$) has photocatalytic activity with the H_2 evolution rate of 2.30 mmol h^{-1} g^{-1}. Pure CdS

Please cite this article in press as: Zhou X, et al., One-pot hydrothermal synthesis of CdS/NiS photocatalysts for high H_2 evolution from water under visible light, International Journal of Hydrogen Energy (2017), http://dx.doi.org/10.1016/j.ijhydene.2017.03.179