Chemical Engineering Journal 353 (2018) 15–24

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Fabrication of two-dimensional $Ni_2P/ZnIn_2S_4$ heterostructures for enhanced photocatalytic hydrogen evolution

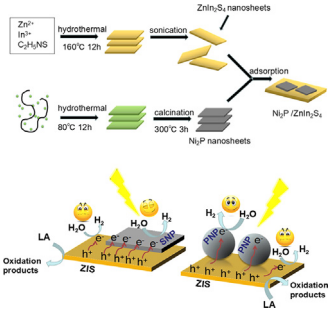
Xu-li Li[a], Xiao-jing Wang[a,b,*], Jia-yu Zhu[a], Yu-pei Li[a], Jun Zhao[a], Fa-tang Li[a,*]

[a] College of Science, Hebei University of Science and Technology, Shijiazhuang 050018, China
[b] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, China

HIGHLIGHTS

- Lower overpotential of 2D Ni_2P nanosheets in photocatalytic H_2 evolution are reported.
- 2D/2D $Ni_2P/ZnIn_2S_4$ photocatalyst is fabricated for enhanced HER performance.
- Apparent quantum efficiency of 7.7% at 420 ± 20 nm is achieved.
- 2D structure exhibits lower surface energy barrier and shorter carriers distance.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Photocatalytic hydrogen evolution
2D-2D
Overpotential
Interfacial charge transfer
Ni_2P
$ZnIn_2S_4$

ABSTRACT

Promoting electron-hole separation and migration and lowering the overpotential of hydrogen evolution reactions are two effective solutions for improving photocatalytic hydrogen performance. Suitable co-catalyst and appropriate interfacial contacts can effectively lower overpotential and can also construct an electric field at the interface to increase the separation efficiency of the carriers. In this work, we design and fabricate a 2D-2D type of Ni_2P co-catalyst modified with $ZnIn_2S_4$ for boosting the performance of photocatalytic hydrogen evolution. As a co-catalyst, the 2D Ni_2P nanosheets exhibit a lower overpotential and smaller charge transfer resistance in hydrogen evolution reactions, and is much improved in both respects compared to Ni_2P nanoparticles. Based on this, 2D/2D $Ni_2P/ZnIn_2S_4$ nanohybrids with large contact regions and shorter transmission distances of the charges were fabricated, which effectively improve the separation of photo induced carriers and the interfacial charge transfer. By taking advantage of the above features, the fabricated 2D-2D $Ni_2P/ZnIn_2S_4$hybrid exhibits a superior hydrogen evolution rate of 2066 $\mu mol \cdot h^{-1} \cdot g^{-1}$ under visible light irradiation, and the apparent quantum yield was 7.7% at 420 ± 20 nm. This activity far exceeds performance of the 0D/2D $Ni_2P/ZnIn_2S_4$ hybrid, and is ascribed to better charge separation and accelerated surface reactions of the Ni_2P nanosheets.

1. Introduction

The overuse of fossil fuels and related environment issues have stimulated more researchers to exploit renewable and carbon-free energy alternatives. Hydrogen fuel is the cleanest proposed energy source and has zero emissions, and photocatalysis technology is considered to be a sustainable and environmentally friendly strategy for solving the increasing environmental and energy crisis. Hitherto, unremitting efforts have been devoted to developing technologies for the photocatalytic evolution of hydrogen using various semiconductors [1,2].

* Corresponding authors at: College of Science, Hebei University of Science and Technology, Shijiazhuang 050018, China (X.J. Wang).
E-mail addresses: propyl@163.com (X.-j. Wang), lifatang@126.com (F.-t. Li).

https://doi.org/10.1016/j.cej.2018.07.107
Received 1 May 2018; Received in revised form 21 June 2018; Accepted 14 July 2018
Available online 17 July 2018
1385-8947/

TiO_2 is the most widely studied photocatalyst owing to its high photocatalytic activity, stability, nontoxicity and low cost. However, TiO_2 has a wide band gap, which affects its ability to harvest of solar energy [3]. Compared with metal oxides, metal sulfides possess relatively lower conduction band (CB) positions and narrower band gaps, which are beneficial for expanding the response to light in the visible light range [4,5]. $ZnIn_2S_4$, as one of the important ternary chalcogenide semiconductors (AB_2S_4), is a good photocatalyst candidate due to its low toxicity, suitable band-gap (~2.4 eV), and relatively high chemical stability [6–8]. Nonetheless, as with most of the semiconductor-based photocatalysts, bare $ZnIn_2S_4$ usually has low activity during the process of photocatalytic hydrogen production because it has a large hydrogen evolution overpotential, and the photocatalytic efficiency is strictly restricted by fast electron-hole recombination [9]. Generally, the photocatalytic hydrogen evolution performance of semiconductor photocatalysts can be improved in several: (i) enhancing the utilization of solar energy, (ii) improving charge separation and migration to the surface, (iii) lowering the surface overpotential of redox reactions and (iv) increasing the number of reactive sites [10].

It is well known that suitable co-catalysts are indispensable in artificial photocatalytic hydrogen evolution systems, which can decrease the overpotential for hydrogen production, improve host reaction active sites, create an electric field at the interface, and thereby increase the separation efficiency of electrons and electron holes. Noble metals have usually been employed as co-catalyst candidates in the majority of previous studies [11]. However, noble metals suffer from high costs and low reserves. In consideration of large-scale applications, it is essential to find low cost and efficient noble metal-free co-catalysts. Up until now, various noble-metal-free co-catalysts have been available, such as nickel-based alloys [12], sulfide-based materials [13,14], carbides [15], nitrides [16] and multicomponent co-catalysts [17,18]. Recently, transition metal phosphides (TMPs), typical representatives of burgeoning non-noble metal co-catalysts (including CoP, Ni_2P, and MoP), have been intensively studied for both electrocatalytic [19] and photocatalytic [20–25] hydrogen evolution due to their high stability and low overpotential during hydrogen evolution. Meanwhile, metal phosphides can promote the release of hydrogen from active sites owing to structural arrangements [26]. As a low-cost TMP, it has been reported that Ni_2P is destined to act as an excellent hydrogen evolution catalyst because of weak binding of hydrogen on the Ni_2P surface [27]. Research has achieved superior photocatalytic hydrogen activity employing Ni_2P as co-catalyst for CdS [28,29]. Chen et al. [30] reported on the general applicability of nanocrystalline Ni_2P as a noble-metal-free co-catalyst to boost photocatalytic hydrogen generation. Other researches anchored zero-dimensional nanocrystalline Ni_2P onto g-C_3N_4, which exhibited a conspicuous enhancement in hydrogen evolution activity under visible light radiation [31,32]. In our previous work, we also identified that the analogous metallic character of Ni_2P nanoparticles can accelerate the transfer and consumption of photo-generated electrons [33]. However, how to maximize the function of suitable transition metal phosphides as co-catalysts still remains a formidable challenge.

Two-dimensional (2D) ultrathin materials have been extensively studied as ideal materials because of their large specific surface area, short electron/carrier transfer distance and richness in active sites. For instance, graphene is employed as an effective electrocatalyst [34] or co-catalyst for photocatalysis [35] in hydrogen evolution processes due to its superior electrical transport properties. Xia et al. [36]constructed different carbon materials by modifying ZIS nanosheets to enhance the photoactivity on hydrogen evolution and found that the 2D RGO exhibited unique advantages among the studied carbon materials. Li et al. [37] assembled $ZnIn_2S_4$ nanosheets on several layers of MoS_2 nanosheets to produce ultra-thin and intimate-contacting 2D hybrid photocatalysts, and Yuan et al. [10] reported a 2D Cu^{2+}-doped $ZnIn_2S_4$ nanosheets modified with 2D MoS_2 presents highly photocatalytic hydrogen evolution performance. The enhancement of photocatalytic performance above was attributed to better charge separation and more active sites provided by MoS_2 nanosheets. However, little research has focused on the fabrication of two dimensional TMP nanosheet co-catalysts and the substantial effect of those TMP materials with different dimensionality on physicochemical properties during the photocatalytic hydrogen production process.

Zhang et al. [38] demonstrated a kind of CoP nanosheets with outstanding electrochemical hydrogen evolution performance: a lower overpotential and smaller Tafel slope which is far better than that of CoP nanoparticles. Smaller Tafel slope of the electrocatalyst often means faster reaction kinetics, which is beneficial to accelerate the surface reaction of hydrogen evolution. Inspired by this report and to fully maximize the merits of 2D TMP materials, we prepare 2D–2D $Ni_2P/ZnIn_2S_4$ photocatalyst for the first time using a post-synthesis method. This work presents an efficient route for maximizing the function of transition metal phosphides as co-catalysts.

2. Experimental

2.1. Chemicals

All raw materials were used without further purification. Red phosphorus, lactic acid, ammonia, sodium carboxymethyl cellulose (CMC_{300}), thioacetamide, $NaH_2PO_4{\cdot}2H_2O$, $H_2PtCl_6{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $Ni(AC)_2{\cdot}4H_2O$ and $In(NO_3)_3{\cdot}4.5H_2O$ were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Nafion (Sigma-Aldrich) was used for electrode preparation.

2.2. Preparation of $ZnIn_2S_4$ (ZIS) nanosheets

In a typical experiment, 1.439 mmol $Zn(NO_3)_2$, 2.439 mmol $In(NO_3)_3{\cdot}xH_2O$ and 10 mmol thioacetamide were dissolved in 35 mL water with vigorous stirring for 20 min at room temperature. Next, the mixture was transferred into a 50 mL Teflon-lined autoclave and maintained at 160 °C for 12 h. After cooling to room temperature naturally, the precipitate was washed with distilled water and combined with ultrasound irradiation several times and was finally placed in 10 mL ethanol for the subsequent synthesis.

2.3. Preparation of Ni_2P nanosheets (SNPs)

To prepare $Ni(OH)_2$ nanosheets, 0.5 g $Ni(AC)_2{\cdot}4H_2O$ was dissolved in a mixture of 10 mL deionized water and 20 mL 1 g/L CMC_{300} solution while stirring, followed by the addition of 2 mL of ammonia aqueous solution (25 wt%). After stirring for another 3 h at room temperature, the suspension was transferred into a 50 mL Teflon-lined autoclave and heated at 160 °C for 12 h. The precipitate was collected by centrifugation and sonication, washed with hot deionized water several times, and then dried via vacuum freeze-drying [39].

To prepare SNPs. Ni_2P nanosheets were obtained by putting $Ni(OH)_2$ (100 mg) and $NaH_2PO_2{\cdot}2H_2O$ (700 mg) into a steamer like porcelain boat, which was separated by a ceramic filter. $NaH_2PO_2{\cdot}2H_2O$ was put on bottom and $Ni(OH)_2$ was placed on the ceramic filter. Subsequently, the samples were heated at 300 °C for 180 min in a fluent Ar_2 atmosphere at a warming rate of 5 °C min^{-1}. During the calcining process, the $Ni(OH)_2$ nanosheets captured PH_3, which was generated from the thermal decomposition of NaH_2PO_4. After cooling to room temperature under the Ar_2 environment, the products were collected for further measurements.

In comparison, Ni_2P nanoparticles (PNPs) were prepared using a hydrothermal method, which was performed according to preciously described methods [40].

2.4. Preparation of 2D-2D $Ni_2P/ZnIn_2S_4$(SNP/ZIS) composites

The process for preparing SNP/ZIS composites is illustrated in