



Full Length Article

Highly dispersed and noble metal-free MP_x ($M = \text{Ni}, \text{Co}, \text{Fe}$) coupled with $\text{g-C}_3\text{N}_4$ nanosheets as 0D/2D photocatalysts for hydrogen evolution

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ABSTRACT

Developing high-efficiency and low-cost photocatalysts by avoiding expensive noble metals is a great challenge. Here, highly dispersed metal ($M = \text{Ni}, \text{Co}, \text{Fe}$) phosphides modified $\text{g-C}_3\text{N}_4$ nanosheets (CNNS) were prepared through in situ precipitation and solid/gas-phase phosphorization. The results confirmed that metal phosphides (MP_x) nanoparticles with high dispersion were well loaded on CNNS surface. The property well reveals the transfer path of photogenerated charges and the origin of high charge separation efficiency in photocatalytic reaction, thus yielding a remarkable catalytic activity. The apparent quantum efficiency (AQY) based on the $\text{NiP}_x/\text{CNNS-900}$ is up to 6.61% at 400 nm while the H_2 evolution rate boosts to $4068.84 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, which is 50 times higher than that of pristine CNNS. The mechanism could be attributed to the highly dispersed MP_x nanoparticles on the surface of CNNS, which acted as effective active sites to promote the separation and migration of photogenerated charges, leading to greatly increase in H_2 production. This study is beneficial to further develop the high-efficient, low cost and environmentally-friendly CNNS-based photocatalytic materials for H_2 production.

1. Introduction

The depletion of fossil resources and the deterioration of the global environmental are the two major factors that restrict the sustainable development of human beings, which have led to an evergrowing demand in green renewable energy [1]. Among the multitudinous energy carriers, H_2 was regarded as a potential energy source for solving the global energy crisis and severe environmental concerns [2,3,4]. The most promising and simplest method for H_2 was to obtain hydrogen from water due to its abundance on the earth [5,6]. Therefore, photocatalytic H_2 production became a valuable way for generating H_2 , which has been widely concerned by the researchers [7,8]. As we all known, $\sim 43\%$ of the solar radiation is visible light, and the ultraviolet light is only $\sim 4\%$ of it, so the study of photocatalytic materials with visible-light responsive, high efficiency and excellent stability has received extensive attention in the realm of photocatalysis [9].

Today, $\text{g-C}_3\text{N}_4$, as an important photocatalytic material, was of tremendous interest owing to its extraordinary features, such as non-toxicity, suitable band gap positions, simple preparation and excellent chemical- and photo-stability [10]. However, the single-component $\text{g-C}_3\text{N}_4$ suffered from the fast recombination rates of photogenerated carriers (i.e. e^- and h^+), which inevitably led to the low photocatalytic activity, greatly hindering the photocatalytic performance of H_2

production [11–13]. Up to now, many researchers have been committing to the study of co-catalysts-modified $\text{g-C}_3\text{N}_4$ to increase its photocatalytic performance for H_2 production. Generally speaking, noble metals, such as Ag, Ru, Au, and Pt, are the best co-catalysts to increase the H_2 -evolution performance of $\text{g-C}_3\text{N}_4$ in most previous studies [10]. Of course, the rarity and high price of these noble metals have seriously inhibited their large-scale applications in large-scale H_2 production [14]. Therefore, it is significantly important to develop non-precious metals decorated $\text{g-C}_3\text{N}_4$ -based photocatalysts to form genuine earth-abundant photocatalytic systems for H_2 production [15,16].

In the last several years, many researchers have been working on the study of the high efficient, low-cost and stable non-noble-metal co-catalysts to load on $\text{g-C}_3\text{N}_4$ toward photocatalytic H_2 production for replacing noble-metal co-catalysts. Xu et al. reported the high efficiency photocatalytic water splitting using 2D $\alpha\text{-Fe}_2\text{O}_3/\text{g-C}_3\text{N}_4$ Z-scheme catalysts [17]. Lu et al. demonstrated the highly efficient hydrogen evolution over Co(OH)_2 nanoparticles modified $\text{g-C}_3\text{N}_4$ co-sensitized by Eosin Y and Rose Bengal under visible-light irradiation [18]. Gu et al. presented amorphous NiO acted as co-catalyst to enhance visible-light-driven H_2 production over $\text{g-C}_3\text{N}_4$ photocatalyst [19]. More interestingly, transition metal phosphides as excellent co-catalysts have been used for significantly improving photocatalytic H_2 production over various metal compounds. For example, Ni_2P , CoP , and MoP as efficient

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co-catalysts could be used to modify CdS, thus significantly enhanced the activity of H_2 production by photolysis of water [20–23]. Very recently, a few reports have shown that transition metal phosphides modify g- C_3N_4 for photocatalytic H_2 production. For example, Wang et al. illustrated that decorating CoP and Pt nanoparticles on graphitic carbon nitride nanosheets to promote overall water splitting by conjugated polymers [9]. Peng et al. demonstrated that toward noble-metal-free visible-light-driven photocatalytic hydrogen evolution by monodisperse sub-15 nm Ni_2P nanoparticles anchored on porous g- C_3N_4 nanosheets to engineer heterojunction interfaces [2]. Han et al. reported that $Ni_{12}P_5$ nanoparticles embedded into porous g- C_3N_4 nanosheets as a noble-metal-free hetero-structural photocatalyst for efficient H_2 production under visible light [13]. However, there are some disadvantages in these reports, such as poor dispersivity, narrow light response range and low photocatalytic activity. Therefore, the preparation and hybridization of MP_x nanoparticles with excellent dispersivity was an onerous task in the g- C_3N_4 -based nanocomposites systems. It is worth noting that it has become a great challenge to study a convenient method to modify g- C_3N_4 with transition metal phosphides for improving photocatalytic H_2 production performance, and the nanocomposites have intimate connection and tight heterojunction [19,24,25].

Herein, we presented the excellent photocatalytic H_2 production of g- C_3N_4 by transition metal phosphides ($M = Ni, Co, Fe$) as effective co-catalyst, and transition metal phosphides is abundant and easy to obtain in the world. Metal phosphides/g- C_3N_4 nanocomposites were prepared by two steps including the facile in situ precipitation and solid/gas-phase phosphorization. From the photocatalytic results, the as-obtained $NiP_x/CNNS$ and $MP_x/CNNS$ nanocomposites has better photocatalytic H_2 production performance comparing with CNNS. In addition, the maximum rate of photocatalytic H_2 production is $4068.84 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ (full spectrum) and $2077.89 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ (400 nm cutoff filter), which can be achieved from $NiP_x/CNNS-900$. Photocatalytic H_2 production rate of $NiP_x/CNNS-900$ is about 50 times higher than pure CNNS under full spectrum. To this end, we hope that our research would be conducive to develop new research ideas with the rational exploitation of high-efficient, cost-effective, and sustainable solar energy production with environmentally friendly hybrid heterojunction materials.

2. Experimental sections

2.1. Materials

All of the reagents were of analytical grade and used as received without further purification. Iron chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), nickel chloride hexahydrate ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), urea, and ethanol came from Sinopharm Chemical Reagent Co., Ltd. Triethanolamine (TEOA) was purchased from Shanghai Macklin Biochemical Co., Ltd. Ammonium bicarbonate (NH_4HCO_3) was obtained from Tianjin Kermel chemical industry Co., Ltd.

2.2. Preparation of g- C_3N_4 nanosheets (CNNS)

CNNS was synthesized by urea. Firstly, urea was loaded into a covered ceramic crucible and heated in a muffle furnace to 550°C , $2.5^\circ\text{C}/\text{min}$, and maintained for 4 h. Then, the powder was loaded into an uncovered ceramic crucible and continued to heat at 500°C , $5^\circ\text{C}/\text{min}$, and maintained for 2 h. When it falls to the normal temperature, the obtained ultrathin CNNS was collected and rinsed through deionized water, dried via a vacuum freeze dryer.

2.3. Preparation of $Ni_2(\text{OH})_2\text{CO}_3 \cdot 4\text{H}_2\text{O}/\text{CNNS}$ composites

Typically, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (1 mmol) was dispersed into ethanol

(150 mL). Then, pure CNNS were dispersed into the solution with sonication until it was dispersed evenly. Finally, 3 mmol NH_4HCO_3 was dispersed into the solution and continued to stir for 6 h. The obtained samples were washed by ethanol, dried by a vacuum freeze dryer. The $\text{Ni}_2(\text{OH})_2\text{CO}_3 \cdot 4\text{H}_2\text{O}/\text{CNNS}$ composite materials with different weights of CNNS (700, 900, 1100 and 1300 mg) were denominated as $\text{Ni}_2(\text{OH})_2\text{CO}_3 \cdot 4\text{H}_2\text{O}/\text{CNNS}-700$, $\text{Ni}_2(\text{OH})_2\text{CO}_3 \cdot 4\text{H}_2\text{O}/\text{CNNS}-900$, $\text{Ni}_2(\text{OH})_2\text{CO}_3 \cdot 4\text{H}_2\text{O}/\text{CNNS}-1100$, and $\text{Ni}_2(\text{OH})_2\text{CO}_3 \cdot 4\text{H}_2\text{O}/\text{CNNS}-1300$, respectively. In addition, $\text{Co}(\text{CO}_3)0.5(\text{OH}) \cdot 0.1\text{H}_2\text{O}/\text{CNNS}-900$ and $\text{Fe}_6(\text{OH})_{12}\text{CO}_3 \cdot 2\text{H}_2\text{O}/\text{CNNS}-900$ were prepared using the same method. All of these composites were abbreviated as $M_x(\text{OH})_y(\text{CO}_3)_z \cdot a\text{H}_2\text{O}/\text{CNNS}$.

2.4. Preparation of nickel phosphide/g- C_3N_4 nanosheets composites (NiP_x/CNNS)

$M_x(\text{OH})_y(\text{CO}_3)_z \cdot a\text{H}_2\text{O}/\text{CNNS}$ in square ceramic crucible was placed in the downstream end of the tube furnace and NaH_2PO_2 in square ceramic crucible was placed in the upstream end of it. Then, these materials were heated at 350°C , $2^\circ\text{C}/\text{min}$, and maintained for 2 h under Ar atmosphere. After that, these materials dropped to normal temperature with the protection of Ar. Finally, NiP_x/CNNS composites supported on $\text{Ni}_2(\text{OH})_2\text{CO}_3 \cdot 4\text{H}_2\text{O}/\text{CNNS}$ were fabricated. Other metal phosphide/g- C_3N_4 nanosheets composites (MP_x/CNNS) were prepared by the same method.

2.5. Characterization methods

D/MAX2500 V diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) used to measure XRD (Powder X-ray diffraction) data. UV–vis diffuse reflection spectroscopy of samples was measured by Shimadzu UV-2500 spectrophotometer with BaSO_4 as the reference. Thermogravimetric analysis was measured through TG-DTA 8121. The structural info was achieved by FT-IR (Fourier transform spectrophotometer, Avatar 370, Thermo Nicolet) via the standard KBr disk method. XPS (X-ray photoelectron spectroscopy) was achieved by ESCALAB250 with $\text{Mg K}\alpha$ as the source and the C 1s peak at 284.6 eV as an internal standard. Samples' morphologies and compositions were measured using JEOL JSM-6330F scanning electron microscopy (SEM) and JEOL-2100 field emission transmission electron microscope (FETEM) at an accelerating voltage of 200 kV. SHIMADZU RF-6000 was used to measured the photoluminescence spectra. CHI 660E electrochemical workstation biased at 0.8 V with a 50 mW LED as light source was used to measured Transient photocurrent responses in three-electrode cell system. The carbon fiber paper deposited with photocatalysts, Pt flake, and a saturated calomel electrode were, respectively, used as working electrodes, counter electrode, and reference electrode. The electrolyte was 1.0 M Na_2SO_4 aqueous solution

2.6. Photocatalytic H_2 production

The reaction of photocatalytic H_2 production was carried out in the 500 mL Pyrex glass cell. The visible-light source is a 300 W Xe lamp with a 400 nm cutoff optical filter. In general, NiP_x/CNNS and other MP_x/CNNS photocatalysts (10 mg) were dispersed in mixed aqueous solution containing water (100 mL) and TEOA (20 mL) served as sacrificial agents by a constant stirring. In addition, Pt/CNNS was also measured (10 mg CNNS, 300 μL H_2PtCl_6 (0.0244 M), 100 mL water and 20 mL TEOA). During the whole experiment, the photocatalyst was suspended by continuous magnetic stirring. Before visible-light illumination, the whole system was vacuumed and guaranteed the reaction system in the vacuum state. The H_2 -solar system with a gas chromatogram (Beijing Aulight Co., Ltd.), contained a thermal conductivity detector, TDX-01 column, and N_2 as carrier gas, was used to collect and online-detect evolved H_2 . The measurement of H_2 evolution rate on NiP_x/CNNS and other MP_x/CNNS composites were obtained by the

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