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$Co_{1.4}Ni_{0.6}P$ cocatalysts modified metallic carbon black/g-C_3N_4 nanosheet Schottky heterojunctions for active and durable photocatalytic H_2 production

Rongchen Shen[a,b,1], Wei Liu[b,1], Doudou Ren[a,b], Jun Xie[a,b], Xin Li[a,b,*]

[a] *College of Forestry and Landscape Architecture, Key Laboratory of Energy Plants Resource and Utilization, Ministry of Agriculture, Key Laboratory of Biomass Energy of Guangdong Regular Higher Education Institutions, South China Agricultural University, Guangzhou 510642, PR China*
[b] *College of Materials and Energy, South China Agricultural University, Guangzhou 510642, PR China*

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ABSTRACT

Efficient separation and utilization of photogenerated electrons as well as holes play decisive roles in boosting photocatalytic hydrogen evolution reaction (HER). To reach this goal, we designed carbon black (CB) and $Co_{1.4}Ni_{0.6}P$ as dual cocatalysts co-modified graphitic carbon nitride for efficient and stable photocatalytic HER. This resulting ternary photocatalyst was synthesized by sonochemical loading and high-temperature phosphatizing. Impressively, the maximum photocatalytic hydrogen-production rate for the ternary photocatalysts could reach 405 $\mu mol h^{-1} g^{-1}$, which was 810, 2 and 1.7 times higher than those of pure g-C_3N_4 (0.5$\mu mol h^{-1} g^{-1}$), g-C_3N_4-$Co_{1.4}Ni_{0.6}P$ (195$\mu mol h^{-1} g^{-1}$) and g-C_3N_4-1% Pt (230 $\mu mol h^{-1} g^{-1}$), respectively. Through the test analysis, the enhanced hydrogen-evolution performance was attributed to the synergetic effect between the metallic CB and the low-cost $Co_{1.4}Ni_{0.6}P$ cocatalyst. More interestingly, the $Co_{1.4}Ni_{0.6}P$ cocatalyst could not only decrease the recombination of photogenerated electrons and holes, but also boost absorption in the visible region and the hydrogen-evolution kinetics. Furthermore, the formation of Schottky heterojunctions between metallic CB and g-C_3N_4 nanosheets could further accelerate the separation and transfer of photogenerated electrons. This work provides a simple and facile strategy to rationally design highly efficient photocatalyst using low-cost nanocarbon materials and high-activity metal phosphide.

1. Introduction

Hydrogen energy is considered as one of cleanest energy sources in comparison with currently used fossil fuels [1–3]. Photocatalytic hydrogen evolution reaction (HER), as an energy-saving and environment friendly method for hydrogen production, has been received a lot of attention in recent year [4–13]. As an organic semiconductor, g-C_3N_4 nanosheets were considered as a promising photocatalyst for various applications due to its suitable band gap and attractive physicochemical property [14–24]. However, fast recombination of photogenerated electron-hole pairs and sluggish surface hydrogen-production kinetics are two key factors limiting the photocatalytic HER over g-C_3N_4 nanosheets [25–27]. Loading cocatalyst is one of the easiest and most effective methods to improve the separation of photogenerated electrons and holes as well as hydrogen-generation kinetics to achieve efficient photocatalytic HER activity [25–27]. Although state-of-the-art Pt has been demonstrated to be an outstanding candidate, its application suffers from the disadvantages of low abundance and high price [28–30]. Thus, it is of great urgency to exploit high-performance and non-noble metal/metal-free cocatalyst toward HER [11,18,20,31–36]. Among the electrocatalysts, transition-metal phosphides (such as CoP_x, [37–43] Cu_3P [44] and NiP_x [21,45,46]) have been widely used as the H_2-evolution cocatalysts due to their low costs, stabilities and remarkable activities. Especially, $Ni_{2-x}Co_xP$ as a binary metal phosphide has been successfully used in electrocatalytic area, which exhibits the much lower overpotential and charge transfer impedance for elctrocatalytic H_2 evolution compared with the single metal phosphide [47–50]. Motivated by these works, it was proposed that the $Co_{1.4}Ni_{0.6}P$ (the molar ratio of Co/Ni approaches the value of 2:1 in the most of above elctrocatalysts) could also serve as an optimal cocatalyst to enhance photocatalytic HER for pure g-C_3N_4 nanosheets [51,52]. However, it is of great importance and challenge for designing and constructing the really robust, safe as well as active bi-metal phosphide-based photocatalytic hydrogen-evolution systems.

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[*] Corresponding author at: College of Forestry and Landscape Architecture, South China Agricultural University, Guangzhou 510642, PR China.
E-mail address: Xinliscau@yahoo.com (X. Li).

[1] These authors contributed equally.

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Our previous works have confirmed that optimizing the interface between semiconductor photocatalysts and cocatalyst could significantly improve the photocatalytic HER performance. The metallic nanocarbon materials have been extensively employed as the common conductive additives to effectively boost photocatalytic hydrogen-evolution activity of the earth-abundant cocatalysts over the semiconductor photocatalysts, due to their superior electrical conductivity and stability, [53,54]. In general, the metallic nanocarbon materials could create the favorable Schottky-based heterojunctions over the semiconductor, thus prolonging the lifetime of photogenerated electrons and resulting in an enhancement of the photocatalytic hydrogen-evolution performance as well as stability over the earth-abundant cocatalyst [30,54–57]. According to the previous report, there are no reports about engineering the interface between TMP cocatalyst and semiconductor photocatalyst. Motivated by the above efforts, a new strategy will be developed to extend the lifetime of photogenerated electrons and improve the stable of the g-C_3N_4-$Co_{1.4}Ni_{0.6}P$ through inserting a conductive nanocarbon interface layer. Consequently, we innovatively loaded low-cost $Co_{1.4}Ni_{0.6}P$ cocatalysts on the metallic carbon black/g-C_3N_4 nanosheet Schottky heterojunctions, which can simultaneously improve the stability of $Co_{1.4}Ni_{0.6}P$ and accelerate the transfer of electrons from g-C_3N_4 nanosheets to $Co_{1.4}Ni_{0.6}P$. As a result, an improvement of the photocatalytic hydrogen-production performance and stability over the g-C_3N_4-$Co_{1.4}Ni_{0.6}P$ will be accomplished.

Herein, we report noble metal free $Co_{1.4}Ni_{0.6}P$ and metallic CB co-modified g-C_3N_4 nanosheets for highly improved photocatalytic HER from water splitting. The ternary photocatalysts was synthesized by a convenient method. The synergetic effect between the $Co_{1.4}Ni_{0.6}P$ cocatalysts and metallic conductive layer CB could significantly boost the photocatalytic HER performance by improving the separation of photogenerated electron-hole pairs, visible light absorption and the hydrogen-evolution kinetics. The maximum photocatalytic hydrogen-production rate for the ternary photocatalysts could reach 405 $umolh^{-1}g^{-1}$, which was 810 and 1.75 times higher than that of pure g-C_3N_4 (0.5$umolh^{-1}g^{-1}$) and g-C_3N_4-Pt (230 $umolh^{-1}g^{-1}$) photocatalysts. This study may provide a new strategy to develop efficient and stable non-noble metal systems for photocatalytic HER.

2. Experimental section

2.1. Synthesis g-C_3N_4-CB-$Co_{1.4}Ni_{0.6}P$ ternary photocatalysts

The g-C_3N_4 nanosheets were prepared by directly calcining urea at 550 °C for 4 h under air. Then, the as-obtained yellow bulk C_3N_4 powders were heated for another 2 h at 500 °C to obtain the ultrathin g-C_3N_4 nanosheets.

The g-C_3N_4-CB was synthesized though a sonochemical method. g-C_3N_4 (500 mg) and CB (2.5 mg) were ultrasonicated in ethyl alcohol (40 mL) for 2 h. The final composites were collected by filtration and dried at 60 °C overnight.

The ternary g-C_3N_4-CB-$Co_{1.4}Ni_{0.6}P$ was synthesized as follows: 0.3 g of as-prepared g-C_3N_4-CB, 7 mg of $Co(NO)_3.6H_20$ and 3 mg of Ni $(NO)_3.6H_20$ were dispersed in 50 mL of distill water. Then, the slurry was ultrasonicated for 1 h. Next, 10 mg of NaOH were added into the solution to obtained g-C_3N_4-CB-$CoNi(OH)_X$. The g-C_3N_4-CB-$Co_{1.4}Ni_{0.6}P$ was prepared by heating g-C_3N_4-CB-$CoNi(OH)_X$ and NaH_2PO_2 at 300 °C for 1 h.

2.2. Characterization

XRD (MSAL-XD2) and XPS (VG ESCALAB250) used to analyze the chemical composition and crystalline structures of g-C_3N_4-$Co_{1.4}Ni_{0.6}P$. The surface morphologies of g-C_3N_4-$Co_{1.4}Ni_{0.6}P$ were observed with TEM and HRTEM (JEM-2100HR, 200 kV, Japan). The diffuse reflection spectra were obtained by UV–vis spectrometer (Shimadzu UV-2550). The steady-state photoluminescence (PL) spectra were measured at 385 nm (LS 50B, Perkin Elmer, Inc., USA). The specific surface area and pore size distribution were analyzed by Brunauer–Emmett–Teller (BET) method and Barrett–Joyner–Halenda (BJH), respectively.

2.3. Photocatalytic and electrocatalytic test

The photocatalytic HER was performed in three-neck Pyrex glass photoreactor at ambient atmosphere. Visible light was generated by 350 W Xe lamp (PLS-SXE300, Beijing Perfect Light Technology Co., Ltd, with the intensity ca. 160 $mWcm^{-2}$). g-C_3N_4-$Co_{1.4}Ni_{0.6}P$ photocatalysts (0.05 g) in 15 vol% TEOA (80 mL) aqueous solution were bubbled with N_2 for 30 min to ensure vacuum conditions before illuminating. The produced hydrogen was determined using a GC-9500 chromatograph. The repeating experiments were measured under the same condition. The electrocatalytic hydrogen evolution was similar to our previous method [30,58].

3. Results and discussion

3.1. The structures and compositions of photocatalysts

The chemical composition and crystal structures of the as prepared samples were measured by XRD measurements. As showed in Fig. 1, two observed diffraction peaks of g-C_3N_4 at around 13.1° and 27.3° could be indexed as the (1 0 0) and (0 0 2) planes of g-C_3N_4 (JCPDS # 87-1526), respectively [57]. The peak at 13.1° is related to in-plane structural packing motif, while the peak at 27.3° is related to tris-s-triazine composites. Additionally, for NiCoP sample, four main diffraction peaks at around 33.3°, 41.2°, 44.8° and 55.3° are attributed to the (1 1 1), (1 0 2), (1 0 3), (0 0 6) and (1 1 0) diffraction plans of NiCoP (JCPDS # 71-2336) [59]. However, no obvious peaks of $Co_{1.4}Ni_{0.6}P$ and CB were detected in g-C_3N_4-CB-$Co_{1.4}Ni_{0.6}P$. This is largely due to the uniform dispersion of loading cocatalysts on the surface of g-C_3N_4 nanosheets.

As showed in Fig. 2A–C, it could be found that g-C_3N_4 shows porous and 2D nanosheet structures. Furthermore, from Fig. 2C, it could be found that the CB (mean diameter of about 30–50 nm) and $Co_{1.4}Ni_{0.6}P$ (mean diameter of about 40–60 nm) were dispersed homogeneously on the surface of g-C_3N_4 nanosheets. In Fig. 2D, the lattice distance of 0.22 nm corresponded to the (1 1 1) plane of $Co_{1.4}Ni_{0.6}P$, while the lattice distance of 0.374 nm corresponded to the (3 0 1) plane of g-C_3N_4 nanosheets. Furthermore, for the reason of amorphous structures, we did not detect the lattice fringes of CB through testing HRTEM [54]. To further investigate the element distribution, the C, N, Co, Ni and P elements were measured by EDS mapping (Fig. 2E–J), further confirming the homogeneous distribution of various elements.

X-ray photoelectron spectra (XPS) was used to confirm the surface chemical composition and valence state of the g-C_3N_4-CB-$Co_{1.4}Ni_{0.6}P$. The XPS survey spectrum of the g-C_3N_4-CB-$Co_{1.4}Ni_{0.6}P$ and

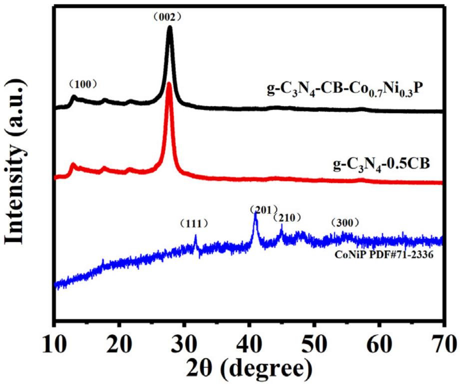

Fig. 1. XRD images of as prepared samples.