SPECIAL TOPIC: Advanced Photocatalytic Materials

Triethanolamine-mediated photodeposition formation of amorphous Ni-P alloy for improved H₂-evolution activity of g-C₃N₄

Huogen Yu^{1,2*}, Jiachao Xu¹, Duoduo Gao¹, Jiajie Fan^{3*} and Jiaguo Yu⁴

ABSTRACT Developing efficient, stable, and low-cost novel electron-cocatalysts is crucial for photocatalytic hydrogen evolution reaction. Herein, amorphous Ni-P alloy particles were successfully modified onto g-C₃N₄ to construct the Ni-P/g-C₃N₄ photocatalyst through a simple and green triethanolamine (TEOA)-mediated photodeposition method. It was found that the TEOA could serve as an excellent complexing agent to coordinate with Ni²⁺ to form [Ni(TEOA)]²⁺ complex, which can promote the rapid and effective deposition of amorphous Ni-P alloy on the g-C₃N₄ surface. Photocatalytic tests suggest that the hydrogen-evolution performance of g-C₃N₄ can be greatly promoted through integrating amorphous Ni-P alloy. Especially, the Ni-P/g-C₃N₄ (5 wt%) exhibits the superior H₂-generation activity (118.2 μmol h⁻¹ g⁻¹), which is almost 35.8 times that of bare g-C₃N₄. Furthermore, the amorphous Ni-P alloy cocatalyst can also serve as the general hydrogen-production cocatalyst to greatly enhance the photocatalytic performance of traditional semiconductor materials such as TiO₂ and CdS. Based on the present results, the mechanism of the amorphous Ni-P alloy as the high-efficiency electron transfer medium was proposed for the boosted H₂-generation rate. The present facile route may broaden the horizons for the efficient development of highly active cocatalysts in photocatalytic field.

Keywords: photocatalysis, H₂ evolution, g-C₃N₄, amorphous Ni-P alloy, photodeposition

INTRODUCTION

The growing global energy demand has led to great efforts on the development of green and renewable energy

sources [1–5]. Clean hydrogen (H₂) has attracted much attention because the products of hydrogen combustion are non-toxic and harmless, and H₂ can be sustainably prepared by water electrolysis [6–9]. Recently, solar hydrogen production from water splitting over semiconductor photocatalysts has become an available technique [10–13]. However, a single semiconductor is often hardly to become the high-efficiency photocatalyst owing to the fast recombination of photo-generated carriers inside the photocatalytic material [14–16]. As a consequence, H₂-evolution cocatalysts have been demonstrated to be an ideal strategy to promote the photoexcited electron-hole pair separation, reduce the overpotentials for H₂ evolution, and subsequently enhance the interfacial catalytic efficiency of the photocatalysts [17–19]. It is well known that the noble metals (Au [20], Pt [21,22], Pd [23], etc.) are regarded as most-effective cocatalysts for photocatalytic H₂ evolution. Unfortunately, considering the rareness and high cost of these noble metals, it is necessary to develop efficient cocatalysts with excellent active and inexpensive earth-abundant elements [24,25]. Up to now, a variety of non-precious H₂-evolution catalysts, for instance, transition-metal hydroxides [26], carbides [27], nitrides [28], and sulfides [29,30], have been developed and shown promising performance. Especially, the transition metal phosphides (Ni-P [31], Mo-P [32], Co-P [33], Cu-P [34,35], etc.), alloys composed of metals and phosphorus, have been proven to be good candidates for photocatalytic H₂ evolution reactions.

Nickel phosphide (Ni-P) has aroused far-ranging at-

¹ Department of Chemistry, School of Chemistry, Chemical Engineering and Life Sciences, Wuhan University of Technology, Wuhan 430070, China

² State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, China

³ School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450002, China

⁴ State Key Laboratory of Advanced Technology for Material Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China

* Corresponding authors (emails: yuhuogen@whut.edu.cn (Yu H); fanjiajie@zhu.edu.cn (Fan J))

tention in hydrodenitrogenation (HDN) [36], hydrodesulfurization (HDS) [37], Li-S batteries [38] and water splitting [39], due to its high catalytic activity, excellent chemical stability and electrical conductivity. Based on previous reports, phosphorus can produce a “weak ligand” effect and ensemble effect in metal phosphides upon forming metal-P bonds, which facilitates the effective adsorption of H^+ (or H_2O) and the desorption of molecular hydrogen at the active sites [40]. Therefore, it is clear that the Ni-P can effectively promote the interfacial hydrogen production reaction. In fact, the above results for the effective electrocatalytic H_2 -evolution reaction of Ni-P have been experimentally proven, where the Ni-P can be used as efficient active sites to reduce the overpotential of interfacial H_2 -evolution reaction [41]. Considering a similar mechanism between electrocatalytic and photocatalytic hydrogen evolutions, the Ni-P could be hopefully regarded as a superior H_2 -evolution cocatalyst for promoting the hydrogen-evolution performance of various photocatalysts [42]. Recently, the Ni-P as an efficient H_2 -evolution cocatalyst has been widely reported in the photocatalytic field. Typically, Ni-P was widely and effectively prepared and deposited on various photocatalyst surfaces (such as TiO_2 , CdS and $\text{g-C}_3\text{N}_4$) through calcinating the nickel precursors and NaH_2PO_2 at 300°C , where the Ni-P was produced *via* the direct reduction of nickel precursors by the PH_3 (from NaH_2PO_2 decomposition) [43–45]. In addition, Liu *et al.* [46] synthesized a carbon-encapsulated Ni-P to improve the photocatalytic H_2 evolution of conjugated polymer *via* heating the mixing solution of nickel(II) acetylacetonate and tri-*n*-octylphosphine (TOP). Wang *et al.* [47] also reported the production of high H_2 -evolution $\text{Ni}_2\text{P/g-C}_3\text{N}_4$ photocatalyst *via* a hydrothermal method (140°C) of nickel chloride and red phosphorus. Obviously, the above results clearly suggest that the Ni-P can become an efficient H_2 -evolution cocatalyst. However, the above-described preparation procedures usually involve a relatively high temperature, toxic PH_3 or organophosphorus compounds, and flammable red phosphorus. Hence, it is highly desirable to explore a green, simple and safe process for the production of Ni-P cocatalyst to boost the hydrogen-generation activity of various photocatalytic semiconductors.

According to the previous reports, compared with crystalline cocatalyst materials, amorphous cocatalysts usually show a higher H_2 -evolution activity because of the highly irregular structure and abundant unsaturated or defected atoms, which can serve as the ideal H_2 -evolution active sites [48,49]. In this work, the Ni-P alloy with

amorphous structure, as a highly efficient H_2 -evolution cocatalyst, was efficiently deposited on the $\text{g-C}_3\text{N}_4$ surface through a Ni-P (TEOA)-mediated photodeposition method. Notably, it was found that the resulting Ni-P/ $\text{g-C}_3\text{N}_4$ (5 wt%) significantly displayed an improved H_2 -evolution rate ($118.2 \mu\text{mol g}^{-1} \text{h}^{-1}$), which is 35.8-fold increase compared with the performance of bare $\text{g-C}_3\text{N}_4$. Herein, *in-situ* X-ray photoelectron spectroscopy (XPS) technique was applied to clarify the electron-transfer mechanism between the Ni-P alloy cocatalyst and $\text{g-C}_3\text{N}_4$ for manifesting the boosted hydrogen-evolution efficiency of the Ni-P/ $\text{g-C}_3\text{N}_4$ photocatalyst. Moreover, the amorphous Ni-P alloy could also be used as the outstanding electron transfer medium to improve the H_2 -evolution activity of traditional titanium dioxide (TiO_2) and cadmium sulfide (CdS). Considering its simple, green and safe synthesis route, the present TEOA-mediated photodeposition approach may provide some novel ideas for the efficient preparation of various high-performance photocatalysts.

EXPERIMENTAL SECTION

Synthesis of blank $\text{g-C}_3\text{N}_4$

The blank $\text{g-C}_3\text{N}_4$ photocatalysts were prepared through a facial calcination process according to our previous reports [50]. Typically, melamine precursor was continuously calcined at 823 K in a muffle furnace for 4 h, and the resulting yellow solid was bulk $\text{g-C}_3\text{N}_4$.

Synthesis of Ni-P/ $\text{g-C}_3\text{N}_4$

The Ni-P alloy-modified $\text{g-C}_3\text{N}_4$ photocatalyst was obtained by a facile TEOA-mediated photo-induced deposition means. First, the obtained $\text{g-C}_3\text{N}_4$ (200 mg) powder was dissolved into 60 mL of distilled water under strong stirring, and 20 mL of NaH_2PO_2 (0.2 mol L^{-1}) was injected to form a homogeneous solution. Subsequently, a certain volume of 0.1 mol L^{-1} $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ solution (with 10% TEOA) was injected to the above system drop by drop. After that, the mixture was bubbled by pure N_2 for 20 min to create an anaerobic atmosphere. After four 420 nm light emitting diodes (LEDs) irradiation for 1 h, the formed sediments were collected and dried in oven at 60°C for 20 h to prepare the Ni-P/ $\text{g-C}_3\text{N}_4$ photocatalyst.

In order to clearly demonstrate the effect of Ni-P amounts on the photocatalytic performances of the Ni-P/ $\text{g-C}_3\text{N}_4$ samples, the ratio of Ni to $\text{g-C}_3\text{N}_4$ was regulated to be 0, 1, 3, 5 and 8 wt%. In this study, the corresponding catalysts were marked as Ni-P/ $\text{g-C}_3\text{N}_4$ ($X \text{ wt\%}$), where X means the amount of Ni to $\text{g-C}_3\text{N}_4$. As a contrast ex-

periment, the Ni/g-C₃N₄ and P/g-C₃N₄ samples were also synthesized through a same route as Ni-P/g-C₃N₄ without adding NaH₂PO₂ solution or NiCl₂·6H₂O solution, respectively.

Characterization

The X-ray diffraction (XRD) patterns were acquired on a Rigaku D/Max-2250 diffractometer. The morphological features were collected by using field-emission scanning electron microscope (FESEM) (JEOL, JSM-7500, Japan) and transmission electron microscope (TEM) (JEM-2100F, Japan). XPS measurements (KRATOA XSAM800) were used to detect the surface information of the samples. The accurate amounts of Ni and P elements could be attained by inductively coupled plasma optical emission spectrometer (ICP-OES) (Agilent 730, USA). Ultraviolet-visible diffuse reflectance spectrum (UV-vis DRS) data were acquired *via* applying a UV-2450 spectrophotometer (Shimadzu, Japan). *In-situ* XPS measurement was detected on ESCALAB 210 (VG, UK) with 365 nm LED as the light source. Steady-state photoluminescence (PL) and time-resolved PL were measured on the F-7000 fluorescence and FLS920 fluorescence spectrophotometer (365 nm, Edinburgh Instruments, UK), respectively.

The H₂-generation activity of the Ni-P/g-C₃N₄ sample

was carried on the basis of our previous report [51], and the details are shown in the Supplementary information SI-1.

RESULTS AND DISCUSSION

Formation route of Ni-P/g-C₃N₄ photocatalyst

The formation route of the Ni-P/g-C₃N₄ samples could be briefly explained through the TEOA-mediated photodeposition method, as shown in Fig. 1. It is well known that TEOA can serve as an excellent complexing agent to coordinate with Ni²⁺, forming the [Ni(TEOA)]²⁺ complex [52], which can not only effectively suppress the hydrolysis of metal ions to obtain a uniform and stable solution system, but also promote the rapid formation of metallic Ni by the following photo-induced deposition method (a smaller reduction potential of [M(TEOA)]²⁺ complex and a higher reduction current are clearly observed than in the pure Ni²⁺, as shown in Fig. S1). In this work, to ensure the sufficient complex of Ni²⁺ ions with TEOA, excess TEOA was added to NiCl₂ solution (molar ratio = 7:1) to produce a darkblue [Ni(TEOA)]²⁺ solution, which caused an improved UV-vis light absorption (Equation (1), Fig. S2). When the [Ni(TEOA)]²⁺ complex was injected into the g-C₃N₄-NaH₂PO₂ suspension solution, the posi-

Figure 1 (a) Schematic diagram illustrating the TEOA-mediated photodeposition formation of Ni-P/g-C₃N₄ and (b) its corresponding color changes: ① the addition of [Ni(TEOA)]²⁺ complex solution into the g-C₃N₄/NaH₂PO₂ suspension; ② the preferential reduction of the adsorbed [Ni(TEOA)]²⁺ complex; ③ the transformation of Ni/g-C₃N₄ into Ni-P/g-C₃N₄ photocatalyst with a simultaneous H₂ evolution; (c) the detailed formation mechanism in step ③ for Ni-P alloy; (d) the amount of released hydrogen during the photodeposition of Ni-P alloy with different loadings.

tively charged $[\text{Ni}(\text{TEOA})]^{2+}$ complex molecules could be uniformly anchored on the negative $\text{g-C}_3\text{N}_4$ surface because of the higher pH value of the above system than the isoelectric point of $\text{g-C}_3\text{N}_4$ (ca. 5) (Fig. 1a) [53,54]. When the reaction system was exposed to light irradiation, the photo-induced electrons of $\text{g-C}_3\text{N}_4$ could effectively reduce the adsorbed $[\text{Ni}(\text{TEOA})]^{2+}$ molecules to *in-situ* form metallic nickel, which could induce the following deposition of Ni-P alloy (Fig. 1b, Equations (2) and (3)). Herein, the firstly produced metallic Ni on the $\text{g-C}_3\text{N}_4$ surface could work as the adsorption site of hydrogen ions (H^+) in solution, which would further be reduced by the photogenerated electrons to produce highly active hydrogen atom ($[\text{H}]$) (Fig. 1c, Equation (4)). Subsequently, the highly active $[\text{H}]$ could simultaneously induce the rapid reduction reaction of $[\text{Ni}(\text{TEOA})]^{2+}$ complex and H_2PO_2^- ions, resulting in the codeposition of metallic Ni and P elements to form Ni-P alloys onto $\text{g-C}_3\text{N}_4$, similar to the conventional electroless plating method [55,56]. Furthermore, the formation mechanism of Ni-P alloys could be evidently demonstrated by the rapid and drastic formation of a large amount of H_2 , as shown in Fig. 1d. It was found that as the amount of Ni-P alloy cocatalyst gradually increased (from 1% to 8%), the amount of the released hydrogen during photodeposition remarkably increased due to the rapid and effective reduction of H_2PO_2^- by highly active $[\text{H}]$ (Equation (5)). In addition, the above mechanism can further be proved by a series of contrast experiments, as shown in Table S1. It was found that only in the simultaneous presence of $\text{g-C}_3\text{N}_4$, $[\text{Ni}(\text{TEOA})]^{2+}$ complex, H_2PO_2^- ions and visible-light irradiation in this system, the Ni-P alloy could be produced and deposited on the photocatalyst surface. Obviously, the Ni-P alloy with a controllable amount could be effectively modified on the $\text{g-C}_3\text{N}_4$ surface through the present mild, green, facile and TEOA-mediated photodeposition method.

Characterizations of the Ni-P/g- C_3N_4 photocatalysts

The XRD and FESEM data were first applied to confirm the successful synthesis of the Ni-P/g- C_3N_4 photocatalyst, as shown in Fig. 2 and Fig. S3. From the XRD results, it is

Figure 2 XRD patterns of various samples. (a) $\text{g-C}_3\text{N}_4$, (b) Ni-P/g- C_3N_4 (1 wt%), (c) Ni-P/g- C_3N_4 (5 wt%) and (d) Ni-P/g- C_3N_4 (8 wt%).

obvious that the distinct diffraction peaks of pure $\text{g-C}_3\text{N}_4$ locate at 27.8° (002) and 13.0° (100), which are indexed to the inter-planar stacking and in-planar packing of the tri-s-triazine units inside $\text{g-C}_3\text{N}_4$, respectively [57]. Meanwhile, the corresponding FESEM image (Fig. S3a) indicates that the pure $\text{g-C}_3\text{N}_4$ sample is in a lamellar and porous structure due to the calcination of melamine. For the Ni-P/g- C_3N_4 samples, a new XRD peak at ca. 44.5° can be found apart from the $\text{g-C}_3\text{N}_4$ phase, which can be assigned to the Ni-P alloy (the inset of Fig. 2). Considering the excellent insertion of phosphorus atom into the metallic Ni, the resulting Ni-P alloy exhibits a broad and weak diffraction peak, in agreement with previous reports [58,59]. Meanwhile, based on their energy-dispersive X-ray spectroscopy (EDS) results, the signal of Ni and P elements are well observed, except the primary C and N elements (Fig. S3b–d). Moreover, with the introduction of Ni^{2+} from 1 to 5 wt%, the amount of Ni and P elements gradually increase from ca. 0.12 to 2.02 at% and 0.12 to 0.29 at% in the Ni-P/g- C_3N_4 photocatalysts, respectively. Hence, the above characterization data evidently suggest that the Ni-P alloy could be efficiently modified on $\text{g-C}_3\text{N}_4$ surface *via* the present facial method.

The formation of Ni-P alloy cocatalyst can further be proven by TEM results, as displayed in Fig. 3. Distinctly, the Ni-P alloy particle sizes are about 80–200 nm and evenly anchored on the $\text{g-C}_3\text{N}_4$ surface (Fig. 3a). The corresponding line-scan electron energy loss spectroscopy (EELS) data indicate that both the nickel and phosphorus elements are evenly dispersed in the whole Ni-P particle and exhibit the same growth trend, strongly indicating the formation of Ni-P alloy structure (Fig. 3b). High-resolution TEM image shows that those Ni-P alloy par-

Figure 3 (a, b) TEM and (c) HRTEM images, (d) HAADF-STEM image and (d₁–d₄) EDS mapping images of the Ni-P/g-C₃N₄ (5 wt%) photocatalyst. Inset of (b) is the line-scan EELS data of a single Ni-P alloy particle.

ticles are not obvious lattice streaks, suggesting the Ni-P alloy is in an amorphous state owing to a relatively mild preparation condition (Fig. 3c). The EDS-mapping results show the Ni and P elements have exactly the same distribution position except the primary C and N elements, indicating the successful preparation of amorphous Ni-P alloy-modified g-C₃N₄ photocatalyst (Fig. 3d).

The surface information of the amorphous Ni-P alloy-modified g-C₃N₄ photocatalyst can be studied *via* XPS. Fig. 4a exhibits the XPS spectra of g-C₃N₄ before and after deposition of amorphous Ni-P alloy. Obviously, the primary XPS peaks of C and N elements can be ascribed to the g-C₃N₄, while the O element comes from the H₂O in the air [60]. Moreover, the characteristic peaks of Ni and

P elements appear in the Ni-P/g-C₃N₄ samples, indicating that the Ni-P alloy cocatalyst can be effectively integrated with g-C₃N₄. To further reveal the exact chemical states of the above mentioned elements, their high-resolution XPS survey spectra are displayed in Fig. 4b–f. Distinctly, in comparison with blank g-C₃N₄, the primary peaks of C 1s and N 1s in all the Ni-P/g-C₃N₄ samples exhibit similar binding energies (Fig. 4b and c) after the Ni-P alloy cocatalyst is deposited on its surface [61]. The core-level XPS spectra of Ni 2p and P 2p are presented in Fig. 4d and e. It is obvious that with increasing content of Ni-P alloy cocatalyst, the intensity for the peaks of Ni and P elements also increase, suggesting that more amorphous Ni-P alloy cocatalysts have been modified onto g-C₃N₄.

Figure 4 (a) XPS survey spectra and (b–f) high-resolution XPS spectra of (b) C 1s, (c) N 1s, (d) Ni 2p, (e, f) P 2p for various samples.

Further observation indicates that the Ni element shows two peaks at 856.1 eV (Ni 2p_{3/2}) and 873.8 eV (Ni 2p_{1/2}), and the P element exhibits an obvious peak at 129.7 eV in addition to the well-known PO₄^{3−} (two peaks at 132.8 and 134.3 eV) [62,63]. Compared with the typical metallic Ni and red phosphorus, the spectrum of Ni element shows a positive shift while that of the P element shows a negative shift, strongly indicating that Ni and P have a partial positive (Ni^{δ+}) and a partial negative charge (P^{δ−}) separately, owing to their strong interactions inside the Ni-P alloy cocatalyst [64]. In addition, ICP-OES measurement was used to further investigate the exact amount of Ni-P

alloy in the Ni-P/g-C₃N₄ photocatalyst, and their data are shown in Table S2. It can be found that the amounts of Ni and P elements in the Ni-P/g-C₃N₄ (5 wt%) sample are 4.67 and 0.21 wt%, respectively. Thus, the above data evidently prove that the Ni-P alloy could be controllably and efficiently modified onto g-C₃N₄ via the simple TEOA-mediated photodeposition method.

The successful modification of the amorphous Ni-P alloy on g-C₃N₄ could also be illustrated by UV-vis DRS (Fig. 5). Notably, the pristine g-C₃N₄ exhibits a typical absorption at ca. 460 nm [65]. After modification with amorphous Ni-P alloy, the obtained Ni-P/g-C₃N₄ pho-

Figure 5 UV-Vis absorption spectra for (a) g-C₃N₄, (b) Ni-P/g-C₃N₄ (1 wt%), (c) Ni-P/g-C₃N₄ (5 wt%) and (d) Ni-P/g-C₃N₄ (8 wt%). Inset shows the color change of various samples.

tocatalyst displays an enhanced light-absorbing capability than pristine g-C₃N₄. Moreover, upon the increasing amount of the amorphous Ni-P alloy cocatalyst, the above absorption is greatly increased for the Ni-P/g-C₃N₄ photocatalysts, which strongly demonstrates the effective integration of more Ni-P alloy with g-C₃N₄.

Photocatalytic activity and mechanism

The H₂-evolution rates for various samples were accessed under visible light (Fig. 6a). It is clear that the blank g-C₃N₄ photocatalyst exhibits an insignificant hydrogen-evolution performance (ca. 3.3 μmol h⁻¹ g⁻¹), which can be ascribed to the lack of enough active sites. After the Ni-P alloy cocatalyst is modified on the g-C₃N₄ surface, all the resultant Ni-P/g-C₃N₄ samples show a notably increased hydrogen-evolution performance compared with the blank g-C₃N₄. In particular, when the Ni content reaches 5 wt%, the obtained Ni-P/g-C₃N₄ (5 wt%) sample has the maximum hydrogen production rate

(118.2 μmol h⁻¹ g⁻¹) with an apparent quantum efficiency (AQE) of 0.66% (the details are shown in Supplementary information SI-3), and the performance is 35.8-fold increased than that of the blank g-C₃N₄ samples. It is found that the as-prepared Ni-P/g-C₃N₄ photocatalyst in this work usually shows a higher AQE than the usual cocatalyst-modified g-C₃N₄ photocatalysts (Table S3). However, further loading of the Ni-P alloy cocatalyst would result in the slowly reduced photocatalytic activity. The cycling test was applied to access the H₂-production stability of the Ni-P/g-C₃N₄ photocatalyst, as shown in Fig. 6b. It can be seen that the Ni-P/g-C₃N₄ (5 wt%) sample maintains an effective H₂-evolution stability during repeating tests. Therefore, based on the above results, it is obvious that TEOA-mediated photodeposited amorphous Ni-P alloy could work as an high-efficiency hydrogen-production cocatalyst to remarkably enhance the interfacial H₂-evolution rate.

To illustrate the improved photocatalytic activity mechanism of the amorphous Ni-P alloy-modified g-C₃N₄, *in situ* XPS characterization was conducted and displayed in Fig. 7. For the bare g-C₃N₄ sample, the C 1s shows a binding energy of 288.21 eV. After the integration of the Ni-P alloy cocatalyst with the g-C₃N₄, the binding energy of C 1s shifts toward a lower value (288.06 eV) (Fig. 7a), implying the effective electron transfer from Ni-P alloy to g-C₃N₄ when they are connected. Actually, the above result is reasonable because the work function of the g-C₃N₄ (5.32 eV) is higher compared with the value of Ni-P (4.94 eV), which can induce the free-electron transfer from the Ni-P alloy cocatalyst to g-C₃N₄ until their Fermi levels are identical (Fig. 7c) [66–68]. Herein, the above electron transfer between the Ni-P alloy and g-C₃N₄ can create an internal electric field pointing from the Ni-P alloy to g-C₃N₄, which can greatly induce the orientation shift of photo-induced electrons from the conduction band (CB) of g-C₃N₄ to the Ni-P alloy cocatalyst (Fig. 7d)

Figure 6 (a) The photocatalytic H₂-evolution activity for (1) g-C₃N₄, (2) P/g-C₃N₄ (5 wt%), (3) Ni/g-C₃N₄ (5 wt%), (4) Ni-P/g-C₃N₄ (1 wt%), (5) Ni-P/g-C₃N₄ (3 wt%), (6) Ni-P/g-C₃N₄ (5 wt%) and (7) Ni-P/g-C₃N₄ (8 wt%); (b) the cycling performance of the Ni-P/g-C₃N₄ (5 wt%) sample.

Figure 7 (a, b) *In situ* XPS spectra of (a) C 1s and (b) Ni 2p for g-C₃N₄ and Ni-P/g-C₃N₄; (c-e) schematic diagrams for the electron transfer of Ni-P/g-C₃N₄: (c) before contact, (d) after contact and (e) under visible-light irradiation.

[69,70]. In this case, when exposed to visible light, it is entertaining to detect that the binding energy of C 1s for the Ni-P/g-C₃N₄ shifts to a higher binding energy (288.38 eV, as shown in Fig. 7a), while that of Ni 2p shifts to a lower value (855.94 eV, as shown in Fig. 7b). Thus, the present data evidently suggest that the photo-induced electrons of g-C₃N₄ surface can swiftly shift to the Ni-P alloy through the promotion of internal electric field during photocatalytic reactions (Fig. 7e). After rapidly seizing the photo-induced electrons from the CB of g-C₃N₄, the Ni-P alloy cocatalyst could work as the high-efficiency H₂-production active sites to greatly promote the interfacial catalytic reaction. Herein, the Ni^{δ+} can serve as the electron capture center from g-C₃N₄ photocatalyst, while the P^{δ-} can adsorb the H⁺ from aqueous solution and serve as the molecular hydrogen desorption sites. As a consequence, the excellent synthetic effect of Ni^{δ+} and P^{δ-} in the amorphous Ni-P alloy cocatalyst greatly improves the H₂-generation performance of the Ni-P/g-C₃N₄ photocatalyst [71].

The enhanced photocatalytic activity of the amorphous

Ni-P/g-C₃N₄ photocatalyst can be further verified *via* a series of photo- and electro-chemical characterizations (the details are shown in the Supplementary information SI-2). Fig. 8a indicates that the remarkable fluorescence quenching of the Ni-P/g-C₃N₄ sample, manifesting that the formation of amorphous Ni-P alloy can effectively reduce the recombination rate of photo-induced electron-hole pair. Moreover, Fig. 8b displays the time-resolved PL spectra of the g-C₃N₄ samples before and after loading Ni-P alloy cocatalyst, which probes the charge transport between the Ni-P alloy cocatalyst and g-C₃N₄. Here, the emission decay spectra of the samples are fitted by tri-exponential kinetics function (Table S4). The average emission lifetime, which reflects the overall fluorescence decay dynamics of the sample, has also displayed a distinct decrease for Ni-P/g-C₃N₄ (10.62 ns) than that of the bulk g-C₃N₄ (12.43 ns). Notably, shorter decay lifetime clearly indicates faster interfacial electron transfer occurring at the Ni-P/g-C₃N₄ sample [72]. The reduction of the fluorescence intensity and lifetime demonstrates that the construction of an electron shift path

Figure 8 (a) Steady-state and (b) transient-state PL spectra, (c) linear sweep voltammetry curves, and (d) EIS of various samples.

from $g-C_3N_4$ to the Ni-P alloy cocatalyst can greatly facilitate the transfer of photogenerated electrons, thus inducing more available electrons to participate in the subsequent interfacial catalytic reaction. The H_2 -generation reaction polarization curves of different samples under dark are exhibited in Fig. 8c. Obviously, the Ni-P/ $g-C_3N_4$ photocatalyst shows improved cathodic current compared with the blank $g-C_3N_4$, manifesting that the amorphous Ni-P alloy cocatalyst can work as high-efficiency active centers to enhance the hydrogen-generation performance. In addition, as revealed in Fig. 8d, the electrochemical impedance spectroscopy (EIS) was also measured. It is clear that, compared with the blank $g-C_3N_4$, the Ni-P/ $g-C_3N_4$ samples exhibit smaller arc radius, indicating the smaller impedance, which can induce a faster charge-transfer rate inside the Ni-P/ $g-C_3N_4$ photocatalysts due to the existence of Ni-P alloy cocatalyst [73]. Therefore, the above results strongly confirm that the introduction of amorphous Ni-P alloy could greatly facilitate the H_2 -generation rate of pure $g-C_3N_4$ photocatalyst.

As an ideal cocatalyst for photocatalytic materials, the universality of amorphous Ni-P alloy cocatalyst is also very important. Therefore, the traditional hydrogen-

generation photocatalysts such as TiO_2 and CdS were modified with the amorphous Ni-P alloy cocatalyst and their corresponding photocatalytic performances were also evaluated, as shown in Fig. 9. Based on their corresponding EDX results, the amorphous Ni-P alloy cocatalyst has been successfully modified onto TiO_2 and CdS (Fig. 9a and b, Fig. S4). Furthermore, compared with the pristine TiO_2 (or CdS), the UV DRS illustrate that, the resulting Ni-P modified TiO_2 (or CdS) sample exhibits an improved visible-light absorption (Fig. 9c and d), further demonstrating the efficient preparation of Ni-P alloy cocatalyst on the photocatalyst surface. Photocatalytic performances indicate that both Ni-P/ TiO_2 and Ni-P/CdS photocatalysts exhibit distinctly boosted H_2 -generation efficiency (Fig. 9e and f), evidently implying that the amorphous Ni-P alloy could work as an effective and universal cocatalyst for promoting the H_2 -production activity of different photocatalytic materials.

CONCLUSIONS

In conclusion, the amorphous Ni-P alloy cocatalyst was successfully produced on $g-C_3N_4$ surface via the TEOA-mediated photodeposition approach. It is distinct that the Ni-P alloy particles have no obvious lattice fringes and are

Figure 9 (a, b) FESEM/EDS results of Ni-P/TiO₂ (5 wt%) and Ni-P/CdS (5 wt%); (c, d) UV-vis absorption spectra and (e, f) hydrogen-production rates for various samples.

well distributed on the g-C₃N₄ surface. Furthermore, H₂-generation test exhibits that the amorphous Ni-P alloy cocatalyst can effectively boost the H₂-generation of g-C₃N₄, and the obtained Ni-P/g-C₃N₄ (5 wt%) photocatalyst acquires the optimum hydrogen-production activity (118.2 μmol h⁻¹ g⁻¹). Notably, the amorphous Ni-P alloy can also act as a superior cocatalyst to greatly facilitate the hydrogen-evolution activity for other conventional photocatalysts such as TiO₂ and CdS. Based on the present data, the mechanism of the amorphous Ni-P alloy cocatalyst as the highly active site to facilitate the interfacial hydrogen-evolution rate of g-C₃N₄ is proposed.

Considering its advantages of high efficiency, low consumption and simple preparation, the amorphous Ni-P alloys can provide promising strategies for the development of superiorly active photocatalysts.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

Huogen Yu was born in 1978 and received his PhD in 2007 from Wuhan University of Technology (WHUT). He worked as a post-doctoral fellow for two years at the University of Tokyo, from 2008 to 2010. He then returned to the WHUT and was promoted to be a full professor in 2010. His research interests mainly focus on the high-performance photocatalytic materials and their photocatalytic mechanisms for water splitting and environmental purification. Prof.

Yu is the author or co-author of more than 100 peer-reviewed papers with over 7000 citations and his H-index is about 50. He was selected as the Most Cited Chinese Researchers in 2014–2018, based on the Scopus database from Elsevier.

Jiajie Fan was born in 1985 and received her PhD degree in 2012 from WHUT. She currently works as an associate professor at the State Centre for International Cooperation on Designer Low-carbon and Environmental Materials (CDLCEM), and the UK-China Centre for Multifunctional Nanomaterials, School of Materials Science and Engineering, Zhengzhou University, China. Her research interests include photocatalytic hydrogen production, thin film solar cells, hydrogen sensors, dye-sensitized solar cells; nanostructure metal oxide semiconductors, TiO_2 , $\text{CuO/Cu}_4\text{O}_3/\text{Cu}_2\text{O}$, thin films; graphene, nano-carbons, and related process technology. Her H-index is 14.

非晶镍磷合金助剂的三乙醇胺调控光沉积制备及其增强氮化碳光催化产氢活性

余火根^{1,2*}, 许家超¹, 高朵朵¹, 范佳杰^{3*}, 余家国⁴

摘要 开发高效、稳定且低成本的新型助催化剂对于光催化制氢反应至关重要。本文通过简单、绿色的三乙醇胺(TEOA)诱导的光沉积方法, 将非晶态Ni-P合金颗粒成功修饰到石墨相氮化碳($\text{g-C}_3\text{N}_4$)上, 以构建Ni-P/ $\text{g-C}_3\text{N}_4$ 光催化剂。TEOA是一种可以与 Ni^{2+} 配位形成 $[\text{Ni}(\text{TEOA})]^{2+}$ 络合物的优良络合剂, 在光照下能够促进非晶态Ni-P合金在 $\text{g-C}_3\text{N}_4$ 表面快速有效沉积。光催化产氢测试表明, 非晶态Ni-P合金的负载可以显著提高 $\text{g-C}_3\text{N}_4$ 的光催化产氢性能, 其中Ni-P/ $\text{g-C}_3\text{N}_4$ (5 wt%)样品具有最佳产氢性能($118.2 \mu\text{mol h}^{-1} \text{g}^{-1}$), 是纯 $\text{g-C}_3\text{N}_4$ 的35.8倍。此外, 非晶态Ni-P合金还可以作为具有通用性的制氢助催化剂, 可显著提高传统半导体材料(如 TiO_2 和 CdS)的光催化产氢性能。基于相关表征结果, 本文提出了非晶态Ni-P合金作为高效电子传递介质以提高产氢速率的机理。该三乙醇胺调控的光沉积方法为新型高效助催化剂的合成与开发提供了新的思路。