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Article

Novel PtPd alloy nanoparticle-decorated g-C₃N₄ nanosheets with enhanced photocatalytic activity for H₂ evolution under visible light irradiation

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ABSTRACT

PtPd bimetallic alloy nanoparticle (NP)-modified graphitic carbon nitride (g-C₃N₄) nanosheet photocatalysts were synthesized via chemical deposition precipitation. Characterization of the photocatalytic H₂ evolution of the g-C₃N₄ nanosheets shows that it was significantly enhanced when PtPd alloy NPs were introduced as a co-catalyst. The 0.2 wt% PtPd/g-C₃N₄ composite photocatalyst gave a maximum H₂ production rate of 1600.8 μmol g⁻¹ h⁻¹. Furthermore, when K₂HPO₄ was added to the reaction system, the H₂ production rate increased to 2885.0 μmol g⁻¹ h⁻¹. The PtPd/g-C₃N₄ photocatalyst showed satisfactory photocatalytic stability and was able to maintain most of its photocatalytic activity after four experimental photocatalytic cycles. In addition, a possible mechanism for the enhanced photocatalytic activity was proposed and verified by various photoelectric techniques. These results demonstrate that the synergistic effect between PtPd and g-C₃N₄ helps to greatly improve the photocatalytic activity of the composite photocatalyst.

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1. Introduction

With increasing environmental pollution and depletion of traditional fossil energy reserves, it is imperative to explore new renewable energy resources to power a sustainable society and technology development. Semiconductor derived solar driven photocatalytic hydrogen production, which was discovered by Honda and Fujishima in 1972 [1], has shed light on one way to solve this challenge. Therefore, photocatalytic hydrogen production is considered one of the more promising technologies to provide renewable energy (i.e., hydrogen as an energy carrier) in an environmentally friendly approach. In the past

decade, various photocatalytic semiconductors have been discovered by researchers, such as metal oxides (e.g., TiO₂ [2,3], CuO [4]), and metal sulfides (e.g., CdS [5,6], ZnS [7,8], ZnIn₂S₄ [9], and Zn_{0.5}Cd_{0.5}S [10,11]). Compared to the reported inorganic photocatalysts, organic photocatalysts based on conjugated frameworks have attracted widespread attention recently because of their intrinsic advantages: low production cost, nontoxicity, and potential for functionality via molecular design. Among the novel organic photocatalysts now being developed, g-C₃N₄ exhibits the most excellent photocatalytic activity for H₂ production [12–15], water oxidation [16,17], organic pollutant degradation [18,19], and CO₂ reduction [20,21].

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However, pure g-C₃N₄ alone is not an ideal photocatalyst and shows poor photocatalytic activity. This is mainly attributed to the rapid recombination of the charges photogenerated. That is to say, much needs to be done in this field to improve further the photocatalytic activity of g-C₃N₄.

Compared to other strategies, co-catalyst modification provides a straightforward and efficient way to enhance the photocatalytic activities of photocatalysts. It is well known that noble metals (such as Pt [22], Pd [23], Ag [24,25], and Au [26]) are effective co-catalysts for efficient photocatalytic hydrogen production. With the ability to tune the electronic structure at atomic scale provided by noble metal alloy co-catalysts (such as AuPd [27], PtCo [28] and NiCo [29]), they have attracted great attention for their potential to achieve more satisfactory photocatalytic performance. Furthermore, arising from the synergistic effect between different active sites, bimetallic alloy nanoparticles (NPs), (composed of two different metal elements) usually exhibit superior electronic, optical, and photocatalytic properties. Such properties often cannot be achieved in the corresponding monometallic nanoparticles [30–32]; therefore, bimetallic alloy NPs offer the potential for more efficient co-catalysts [33,34].

Herein, we present a new strategy using the chemical deposition precipitation method to synthesize PtPd/g-C₃N₄ photocatalyst, which exhibits highly efficient visible-light activated H₂ production from water. The prepared PtPd/g-C₃N₄ composite photocatalysts showed remarkably enhanced photocatalytic H₂ evolution activity compared not only with monometallic Pt/g-C₃N₄ and Pd/g-C₃N₄, but also with pure g-C₃N₄. After full optimization of the loading ratio of PtPd alloy NPs, a photocatalytic H₂ evolution rate of 1600.8 μmol g⁻¹ h⁻¹ was achieved with a 0.2 wt% PtPd/g-C₃N₄ composite photocatalyst. This is 3.55 times higher than with Pt/g-C₃N₄ and 1.34 times higher than with Pd/g-C₃N₄. In addition, the most extraordinary result was that H₂ rapid precipitation occurred when K₂HPO₄ was added to the reaction system. To investigate the mechanism that enhances H₂ evolution activity in the PtPd/g-C₃N₄ composite photocatalyst, its structural characteristics and optical properties were analyzed. The photocatalytic H₂ evolution activity and stability of PtPd/g-C₃N₄ under visible light irradiation were also measured. Based on the characterization results and the photocatalytic activity, a possible photocatalytic mechanism for the enhanced H₂ evolution activity was proposed. Our experimental results demonstrate that PtPd alloy NPs can be effective co-catalysts for g-C₃N₄. This means that they may also have potential benefits for other semiconductor photocatalysts for H₂ evolution.

2. Experimental

2.1. Synthesis of the g-C₃N₄ nanosheets

All reagents were of analytical grade and were used without further purification. The g-C₃N₄ nanosheets were prepared according to a reference, with slight modification [35]. Two-dimensional (2D) g-C₃N₄ nanosheets were prepared by heating 10 g of urea in a covered crucible at 550 °C for 4 h with

a ramping rate of 5 °C/min. After that, the g-C₃N₄ nanosheets were fabricated by thermal oxidation etching of as-obtained bulk g-C₃N₄ powders at 500 °C for another 2 h under the same condition. After heating and cooling, a light-yellow powder product was obtained. Then, the powders were washed in deionized water with centrifugation several times. The final products were obtained by drying them at 60 °C for 8 h in a vacuum oven. The as-synthesized g-C₃N₄ was subsequently used to prepare the PtPd/g-C₃N₄ nanocomposites.

2.2. Synthesis of the PtPd/g-C₃N₄ nanocomposites

Preparation of the PtPd/g-C₃N₄ composite catalysts proceeded as follows. The 0.5 g of g-C₃N₄ nanosheet powder was dispersed ultrasonically in 40 mL of ethylene glycol for up to 1 h. The product was used as stock solution. Subsequently, a certain weight ratio of 2 g L⁻¹ H₂PtCl₆ (Pt) and 4 g L⁻¹ PdCl₂ (Pd) were added to the stock solution with continuous stirring (Pt: Pd = 0.5:0.5). After 5 min, 500 μL of 80% hydrazine hydrate was added to the reaction mixture and stirring was continued for another 4 h at room temperature. The product was washed and centrifuged with deionized water and ethanol several times, respectively, and then dried at 60 °C for 8 h in a vacuum oven [36]. The obtained samples of PtPd/g-C₃N₄ were further heated at 300 °C for 2 h under Ar flow in a tube furnace [37]. Finally, PtPd/g-C₃N₄ composite photocatalysts with different weight ratios were obtained. The weight percentages of the PtPd alloy NPs in the prepared composite photocatalysts were 0.0, 0.1, 0.2, 0.5, 1.0, and 2.0 wt%, respectively. Next, PtPd/g-C₃N₄ with other Pt/Pd ratios was synthesized under the same experimental conditions and same methods. These included Pt/g-C₃N₄, Pd/g-C₃N₄, Pt_{0.9}Pd_{0.1}/g-C₃N₄, Pt_{0.7}Pd_{0.3}/g-C₃N₄, Pt_{0.3}Pd_{0.7}/g-C₃N₄, and Pt_{0.1}Pd_{0.9}/g-C₃N₄ composite photocatalysts with 0.2 wt% loading.

2.3. Characterization

An X-ray diffractometer (XRD) using Cu K_α as radiation was applied to investigate the crystallographic texture of all samples, with 2θ ranges from 5° to 60°. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were carried out using an FEI Tecnai G2 F20 microscope. UV-vis diffuse reflection spectroscopy (DRS) of all samples was detected using a Hitachi UV-4100 spectrophotometer, and BaSO₄ was used as the reflectance standard. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250XI) was applied to analyze the element-valence state of the samples. The signal of carbon at 284.8 eV was used as a reference to calibrate the binding energies. A photoluminescence (PL) spectrum was provided by an FLS980 Series of fluorescence spectrometer.

2.4. Photocatalytic activity

The photocatalytic H₂ evolution test was performed in a Perfectlight Labsolar IIIAG system equipped with a 300 mL quartz reactor. The temperature of the system was maintained

at 4 °C by connecting it to a low-temperature thermostat in a bath of circulating water. The employed visible light source was a PLS-SXE 300W Xe arc lamp combined with a UV-cutoff (≥ 400 nm) filter. The light source was positioned 15 cm away from the reactor to trigger the photocatalytic reaction. The irradiation light intensity selected was 32 mW/cm² and was confirmed by a radiometer. In a typical procedure, 50 mg of catalyst was dispersed in 100 mL of mixed aqueous solution containing 10 mL of triethanolamine (TEOA) and 90 mL of deionized water. This was subjected to constant ultrasonic treatment for about 5 min before the reactor was installed in the system. In addition, 10 g of K₂HPO₄ was added to the above solution to promote photocatalytic performance. Moreover, before irradiation, the system was evacuated for at least 0.5 h to remove dissolved oxygen and ensure an anaerobic condition. The mixture was magnetically stirred meanwhile. The gas produced during the reaction was detected by a gas chromatograph (Beifen 3420A, China) using high purity argon as the carrier gas. The chromatograph was equipped with a 420 ± 5 nm band pass cut filter. The apparent quantum yield (AQY) was calculated using Eq. (1):

$$\begin{aligned} \text{AQY} &= \frac{\text{the number of reacted electrons}}{\text{the number of incident photons}} \times 100\% \\ &= \frac{\text{the number of evolved H}_2 \text{ molecules} \times 2}{\text{the number of incident photons}} \times 100\% \quad (1) \end{aligned}$$

2.5. SPV measurements

The surface photovoltage (SPV) measurements were carried out on a surface photovoltage spectroscope (PL-SPS/IPCE1000, Beijing Perfect Light Technology Co., Ltd.). The measurement system included a source of monochromatic light, a lock-in amplifier (SR830, Stanford Research Systems, Inc.), a light chopper (SR 540, Stanford Research Systems, Inc.), and a sample cell. The measurements were done under ambient conditions.

2.6. Electrochemical measurements

The photocurrent measurements were conducted on an electrochemical workstation (CHI, China) in a standard three electrode framework with a 0.5 mol/L Na₂SO₄ electrolyte solution. A Pt sheet was used as the counter electrode and an Ag/AgCl electrode as the reference electrode. The work electrode was prepared as follows. The photocatalyst (10 mg) was dispersed in a solution of 500 μ L of absolute ethanol and 15 μ L of Nafion solution. The obtained slurry was then dripped onto pretreated FTO glass with a controlled area of 1 cm $\times$ 1 cm. It was then dried in air at 150 °C for 2 h to form a film electrode. Photocurrents were obtained using a 300 W xenon arc lamp with light passing through an AM 1.5 G filter.

3. Results and discussion

3.1. Characterization of the PtPd/g-C₃N₄ composite samples

The chemical composition and crystal structure of the

as-prepared photocatalysts were investigated by X-ray diffraction (XRD), and the results are shown in Fig. 1. The pure g-C₃N₄ nanosheets have two diffraction peaks located at 12.8° and 27.4°, corresponding to the (100) and (002) lattice planes of g-C₃N₄, respectively [38]. Aside from the diffraction peaks of g-C₃N₄, the PtPd/g-C₃N₄ sample has two additional diffraction peaks at 40.1° and 46.6°. These were indexed to the (111) and (200) crystal planes of PtPd (JCPDS 65-6418), indicating the existence of PtPd alloy. The co-existence of PtPd and g-C₃N₄ in the as-prepared PtPd/g-C₃N₄ composites indicates that the PtPd/g-C₃N₄ composites were successfully synthesized. The clear crystal diffraction pattern of g-C₃N₄ demonstrates that its crystal structure was not destroyed during the coupling of the PtPd phase.

To confirm the presence of PtPd NPs in the PtPd/g-C₃N₄ composite sample, the morphology and crystallography information of the samples were investigated using TEM and HRTEM. From the TEM images shown in Fig. 2, it can be seen that the pure g-C₃N₄ nanosheets are thin film and that the PtPd/g-C₃N₄ composite sample has a typical thin film morphology with black nanoparticles distributed on the surface. The thin film observed in TEM can be attributed to g-C₃N₄ due to its intrinsic 2D molecular structure. To determine the composition of the black nanoparticles observed on the surface of g-C₃N₄, a close investigation of the sample was done using HRTEM. When the HRTEM focus was on the black nanoparticles, a set of clear lattice fringes could be seen in the image, from which a lattice spacing of 0.225 nm was determined. The lattice spacing revealed by HRTEM matches well with the interplanar crystal spacing of the (111) crystal plane of the PtPd alloy (JCPDS 65-6418), which provides additional support for the successful synthesis of the PtPd/g-C₃N₄ composites. Fig. 2(d) shows the element-distribution maps of Pt and Pd, illustrating the composition of Pt and Pd in the bimetallic catalysts.

X-ray photoelectron spectroscopy (XPS) was further utilized to investigate the surface chemical composition and electronic states of the PtPd/g-C₃N₄ composite sample. The XPS spectra of C 1s, and N 1s, Pt 4f, and Pd 3d are shown in Fig. 3. The results

Fig. 1. XRD patterns of PtPd/g-C₃N₄ samples with different weight ratios.

Fig. 2. (a) TEM image of pure g-C₃N₄ nanosheets; (b) TEM image, (c) HRTEM image, and (d) EDS mapping image of the 0.2 wt% PtPd/g-C₃N₄ composite sample.

of the survey scan of the PtPd/g-C₃N₄ composite show the presence of C, N, Pt, and Pd in the composite (Fig. 3a). Fig. 3(b) displays the XPS spectra of C 1s: the two peaks located at 284.8 and 288.4 eV were related to C–C and N–C=N, respectively [27]. There were no differences between the pure g-C₃N₄ nanosheets and the PtPd/g-C₃N₄ composite sample, which means that there was no obvious effect on their chemical bonding after

loading the PtPd alloy NPs onto the surface of the g-C₃N₄ nanosheets. The N 1s XPS spectra were deconvoluted into three peaks at 398.51, 399.25, and 400.65 eV (Fig. 3c and 3d), which represent *sp*²-bonded N in C=N–C, tertiary nitrogen N–C₃, and nitrogen, respectively, in the C–N–H functional group in the polymeric g-C₃N₄ structure [18,28]. A slight shift can be observed for N 1s toward higher binding energy compared with pure g-C₃N₄, which is attributed to changes in the surface electron density. The XPS spectra of Pt 4f for the Pt/g-C₃N₄ and PtPd/g-C₃N₄ sample are shown in Fig. 3(e). The Pt 4f XPS spectra have two peaks at 70.62 and 73.92 eV in the Pt/g-C₃N₄ sample, which correspond to Pt 4f_{7/2} and Pt 4f_{5/2}, respectively [39]. However, the PtPd/g-C₃N₄ sample shows two peaks at 71.45 and 74.74 eV in the Pt 4f XPS spectra, which exhibit a positive upshift (~ 0.83 eV) compared to that of the Pt/g-C₃N₄ sample. This positive upshift in the binding energies for Pt 4f can be attributed to the alloying effect between Pt and Pd. Similarly, in Fig. 3(f) the two Pd 3d XPS peaks in the PtPd/g-C₃N₄ sample correspond to Pd 3d_{5/2} at 336.20 and Pd 3d_{3/2} at 341.35 eV, and also show a 0.83 eV shift compared to the Pd/g-C₃N₄ sample (335.37 and 340.52 eV) [37]. From the shift of binding energy for Pt 4f and Pd 3d in the PtPd/g-C₃N₄ sample, we can conclude that the PtPd alloy NPs were successfully synthesized and deposited on the surface of the g-C₃N₄ nanosheets.

The UV-vis diffuse reflectance spectra (DRS) of the as-prepared samples were recorded to investigate their optical properties and the results are shown in Fig. 4. Compared to pure g-C₃N₄, the optical absorption of the PtPd/g-C₃N₄ composite samples was substantially enhanced in the wavelength range 350–800 nm. This is consistent with the change of color observed in the prepared samples from yellow (pure g-C₃N₄) to

Fig. 3. XPS spectra of pure g-C₃N₄, PtPd/g-C₃N₄, Pt/g-C₃N₄, and Pd/g-C₃N₄ composite samples. (a) Survey of PtPd/g-C₃N₄; (b) C 1s; (c) N 1s of pure g-C₃N₄; (d) N 1s of PtPd/g-C₃N₄; (e) Pt 4f; (f) Pd 3d.

Fig. 4. UV-visible diffuse reflectance spectra of pure g-C₃N₄ and PtPd/g-C₃N₄ composites with different weight ratios of PtPd alloy NPs.

gray (PtPd/g-C₃N₄) [11]. With increasing loading ratio of PtPd alloy NPs, the absorption of PtPd/g-C₃N₄ in the visible range also increased. The enhanced light absorption efficiency of these composite photocatalysts indicates that they have the potential to harvest more photons to drive photocatalytic reactions, which would be expected to deliver improved photocatalytic activity [38]. The band gap of the as-prepared samples was derived using Eq. (2):

$$a = \frac{A(h\nu - E_g)^{n/2}}{h\nu} \quad (2)$$

where A is the proportionality constant, h is Planck's constant, ν is the incident light frequency, and E_g represents the band gap energy. The value of n is related to the type of band gap. Here, a value of '1' was used for n because g-C₃N₄ is reported to have a direct band gap [35]. The band gap of pure g-C₃N₄ was estimated to be 2.69 eV using Eq. (2), as shown in the Fig. 4 inset. This is consistent with the results in previous studies [27,37]. The DRS results indicate that the PtPd alloy NPs chemically deposited in situ had considerable effect on the g-C₃N₄ and resulted in more efficient utilization of visible light.

3.2. Photocatalytic H₂ evolution activity

The photocatalytic H₂ evolution activities of the prepared samples were characterized and the results are shown in Fig. 5. The pure g-C₃N₄ sample shows a relatively low H₂ production rate of 2.2 μmol g⁻¹ h⁻¹. After loading the PtPd alloy NPs onto the surface of the g-C₃N₄ nanosheets, the photocatalytic activity of the sample for hydrogen production was significantly enhanced. After loading only 0.1 wt% PtPd alloy NPs, the rate of H₂ production was remarkably increased to 1207.1 μmol g⁻¹ h⁻¹; nearly 600 times higher than that of pure g-C₃N₄. Along with the gain from increase of the PtPd alloy NP weight ratios, the H₂ evolution activity of the PtPd/g-C₃N₄ composite sample was also improved when the weight fraction of the PtPd alloy was increased to 0.2 wt%. The 0.2 wt% PtPd/g-C₃N₄ sample gave the highest H₂ evolution activity (rate of 1600.8 μmol g⁻¹ h⁻¹), 800 times higher than that of pure g-C₃N₄. It can be seen

Fig. 5. Photocatalytic H₂ evolution over PtPd/g-C₃N₄ composite samples with different weight contents of PtPd alloy NP loading. (1) Pure g-C₃N₄; (2) 0.1 wt%; (3) 0.2 wt%; (4) 0.5 wt%; (5) 1.0 wt%; (6) 2.0 wt%; (7) 0.2 wt% with K₂HPO₄ solution.

that deposition of the PtPd alloy NPs can remarkably improve the hydrogen evolution activity of pure g-C₃N₄. However, further increase in the deposition ratio of PtPd alloy NPs to higher than 0.2 wt% results in a decrease in the H₂ production rate. The degraded photocatalytic H₂ evolution activity might be caused by the light shielding effect of the excess black PtPd alloy NPs, which would attenuate the light intensity at the surface of the g-C₃N₄. To explore the conditions needed to provide the greatest potential of the PtPd/g-C₃N₄ composite sample for photocatalytic H₂ evolution, K₂HPO₄ was added to the electrolyte as a sacrificial agent. When 10 g of K₂HPO₄ was added to the photocatalytic system, the H₂ production rate of the PtPd/g-C₃N₄ composite sample reached 2885.0 μmol g⁻¹ h⁻¹. The explanation of this enhancement is that HPO₄²⁻ can act as a mediator that directly takes part in the photocatalytic H₂ production [27,40]. From Table 1, it can be noted that better hydrogen production rates were obtained in this study than with the other monometallic and bimetallic photocatalysts reported in the literature.

In addition, the atomic ratio between Pt and Pd in the PtPd alloy NPs greatly influenced the photocatalytic activity of the PtPd/g-C₃N₄ composite sample. As shown in Fig. 6, the rate of H₂ production was only 450.1 μmol g⁻¹ h⁻¹ for the 0.2 wt% Pt/g-C₃N₄ sample. By increasing the atomic ratio of Pd in the PtPd bimetallic alloy NPs, the photocatalytic hydrogen evolution of PtPd/g-C₃N₄ was significantly enhanced. The optimal atomic ratio of Pt: Pd in the PtPd bimetallic alloy NPs to achieve the highest photocatalytic activity in the PtPd/g-C₃N₄ composite sample was demonstrated to be 1:1. The 0.2 wt% Pt_{0.5}Pd_{0.5}/g-C₃N₄ sample showed the highest H₂ evolution rate (1600.8 μmol g⁻¹ h⁻¹): about 3.6 and 1.5 times higher than that of Pt/g-C₃N₄ (450.1 μmol g⁻¹ h⁻¹) and Pd/g-C₃N₄ (1040.5 μmol g⁻¹ h⁻¹), respectively. The enhanced activity observed with Pd might be related to the following properties [41]. (1) Pd has a higher density of states in the vicinity of the semiconductor's Fermi level than Pt does. The Fermi level of Pd is around 0.2 eV higher than that of Pt (~10.8 eV) [49]. (2) Pd has a much lower electron affinity (hence electron trapping capability), which

Table 1Comparison of photocatalytic H₂ evolution of metal/g-C₃N₄ photocatalysts reported in the literature with that of the present study.

Photocatalyst	Metal loading method	Reactant solution	Total mass of catalysts (mg)	Irradiation source wavelength (nm)	AQY	H ₂ production rate	Ref.
0.2 wt% PtPd/g-C ₃ N ₄	Chemical deposition precipitation	100 mL of 10 vol% triethanolamine aqueous solution	50	300 W Xe lamp $\lambda \geq 400$ nm	5.5% (420 nm)	1600.8 $\mu\text{mol g}^{-1} \text{h}^{-1}$	This work
0.2 wt% PtPd/g-C ₃ N ₄	Chemical deposition precipitation	100 mL of 10 vol% triethanolamine K ₂ HPO ₄ solution	50	300 W Xe lamp $\lambda \geq 400$ nm	—	2885.0 $\mu\text{mol g}^{-1} \text{h}^{-1}$	This work
0.5 wt% AuPd/g-C ₃ N ₄	PVA assisted chemical reduction	100 mL of 10 vol% triethanolamine aqueous solution	50	300 W Xe lamp $\lambda \geq 400$ nm	—	326 $\mu\text{mol g}^{-1} \text{h}^{-1}$	Han 2015 [37]
1.0 wt% AuPd/g-C ₃ N ₄	PVA assisted chemical reduction	100 mL of 10 vol% triethanolamine K ₂ HPO ₄ solution	50	300 W Xe lamp $\lambda \geq 400$ nm	—	107 $\mu\text{mol g}^{-1} \text{h}^{-1}$	Han 2017 [27]
Pd _{0.7} Ag _{0.3} /g-C ₃ N ₄	Chemical reduction	25 mL of 10 vol% triethanolamine aqueous solution	10	Direct solar irradiation	8.7% (460 nm)	1250 $\mu\text{mol g}^{-1} \text{h}^{-1}$	Majeed 2018 [41]
Au ₅₀ Pt ₅₀ /g-C ₃ N ₄	Laser ablation	10 vol% triethanolamine aqueous solution	40	300 W Xe lamp $\lambda \geq 420$ nm	—	64.1 $\mu\text{mol g}^{-1} \text{h}^{-1}$	Xu 2018 [30]
1.0 wt% PtCo/g-C ₃ N ₄	PVA assisted chemical reduction	100 mL of 10 vol% triethanolamine aqueous solution	50	300 W Xe lamp $\lambda \geq 420$ nm	—	960 $\mu\text{mol g}^{-1} \text{h}^{-1}$	Han 2015 [28]
5.0 wt% Ni/SCN	Photo-deposition	200 mL of 20 vol% triethanolamine aqueous solution	200	300 W Xe lamp $\lambda \geq 420$ nm	3.2% (405 nm)	2021.3 $\mu\text{mol g}^{-1} \text{h}^{-1}$	Sun 2018 [42]
0.16 wt% Pt/g-C ₃ N ₄	Anneal in Ar	200 mL of 10 vol% triethanolamine aqueous solution	50	300 W Xe lamp $\lambda \geq 420$ nm	—	318 $\mu\text{mol g}^{-1} \text{h}^{-1}$	Li 2016 [43]
10 wt% Zn/g-C ₃ N ₄	Anneal in N ₂	50 mL of CH ₃ OH + 220 mL of H ₂ O	200	200 W Xe lamp $\lambda \geq 420$ nm	3.2% (420 nm)	59.5 $\mu\text{mol g}^{-1} \text{h}^{-1}$	Yue 2011 [44]
0.25 wt% Rh/g-C ₃ N ₄	Photo-deposition	100 mL of 10 vol% methanol aqueous solution	100	Xe Arc lamp $\lambda \geq 420$ nm	—	15 $\mu\text{mol g}^{-1} \text{h}^{-1}$	Zhang 2014 [45]
3.0 wt% Pt/g-C ₃ N ₄	Photo-deposition	270 mL of 10 vol% triethanolamine K ₂ HPO ₄ solution	50	300 W Xe lamp $\lambda \geq 420$ nm	26.1% (420 nm)	947 $\mu\text{mol g}^{-1} \text{h}^{-1}$	Liu 2015 [40]
0.3 mmol/L Ag-SCN/g-C ₃ N ₄	Photo-deposition	80 mL of 10 vol% lactic acid and potassium thiocyanate solution	50	LED 3 W $\lambda \geq 420$ nm	—	3.89 $\mu\text{mol g}^{-1} \text{h}^{-1}$	Chen 2017 [46]
1% Au/monolayer g-C ₃ N ₄	Oil bath	100 mL of 10 vol% hole Sacrificial agent aqueous solution	50	300 W Xe lamp $\lambda \geq 400$ nm	—	565 $\mu\text{mol g}^{-1} \text{h}^{-1}$	Mo 2018 [47]
Ag/g-C ₃ N ₄ -2	Supramolecular hydrogel	100 mL of 10 vol% triethanolamine aqueous solution	50	300 W Xe lamp $\lambda \geq 420$ nm	—	625 $\mu\text{mol g}^{-1} \text{h}^{-1}$	Wang 2017 [48]

may enable more facile electron transfer from Pd to protons [50]. This suggests that alloy NPs have the potential for much higher photocatalytic activity compared to their monometallic counterparts.

The AQY of the PtPd/g-C₃N₄ composite sample for photocatalytic H₂ production was measured at 420±5 nm. One molecule of H₂ was assumed to be generated by absorption of two photons. The AQY characterization result is shown in Fig. 7.

From the measured light intensity and the average rate H₂ evolution rate of 527.4 $\mu\text{mol g}^{-1} \text{h}^{-1}$, the AQY of the PtPd/g-C₃N₄ composite sample at 420 nm was determined to be 5.5%. This high AQY for photocatalytic H₂ evolution indicates efficient conversion of visible light energy, suggesting that the PtPd/g-C₃N₄ composite photocatalyst is highly active in electron-hole pair generation and separation. Thus, it can be seen that PtPd/g-C₃N₄ is an efficient photocatalyst for visi-

Fig. 6. Photocatalytic H₂ evolution over bulk 0.2 wt% Pt_{1-x}Pd_x/g-C₃N₄ composite samples with different Pt/Pd percentage. **Fig. 7.** Photocatalytic H₂ evolution and quantum efficiency in the presence of 0.2 wt% PtPd/g-C₃N₄ composite under 400 nm light irradiation.

Fig. 8. Cycling runs of the photocatalytic H₂ evolution for 0.2 wt% PtPd/g-C₃N₄ nanosheet photocatalyst under 420 nm light irradiation.

ble-light-driven photocatalytic H₂ evolution.

Stability is an important parameter by which to define the performance of a photocatalyst. The stability of the photocatalyst with optimal 0.2 wt% PtPd/g-C₃N₄ was evaluated by performing cycle runs of photocatalytic H₂ evolution, and the results are displayed in Fig. 8. It can be seen clearly that there is no substantial decrease in the H₂ evolution rate after four successive runs of photocatalytic reaction, which demonstrates the high durability of 0.2 wt% PtPd/g-C₃N₄ for photocatalytic H₂ production.

3.3. Investigation of the photocatalytic mechanism

In order to determine the reason for the enhancement of photocatalytic activity by the PtPd decorated g-C₃N₄ sample, steady-state PL spectroscopy of the 0.2 wt% PtPd/g-C₃N₄ composite photocatalyst was performed to investigate the interfacial charge transfer process. As shown in Fig. 9(a), pure g-C₃N₄ nanosheets exhibit a strong emission peak at approximately 460 nm, indicating a high rate of recombination of the photogenerated electron-hole pairs. This generally results in low photocatalytic activity [51]. Obviously, after loading the PtPd alloy NPs, the PL emission intensity decreased, demonstrating more efficient charge separation and slower rate of

recombination of the photogenerated electron-hole pairs in the PtPd/g-C₃N₄ composite sample. Time-resolved fluorescence decay spectra were captured to evaluate the kinetic properties of the photo-generated charge carriers in the PtPd/g-C₃N₄ composite sample (Fig. 9b and 9c). The average lifetime of the photogenerated hole-electron pairs could be calculated using Eq. (3):

$$\tau_a = \frac{A_1 \times \tau_1^2 + A_2 \times \tau_2^2}{A_1 \times \tau_1 + A_2 \times \tau_2} \quad (3)$$

where A is the corresponding amplitude and τ is the PL emission lifetime [35,52,53]. The average charge lifetime τ_a of pure g-C₃N₄ and the PtPd/g-C₃N₄ composites was found to be 5.0920 and 5.5392 ns, respectively. The longer charge lifetime of the PtPd/g-C₃N₄ composites could improve the potential for the involvement of photo-generated charge carriers in photocatalytic reactions before they recombine, which leads to enhanced photocatalytic activity [54].

Furthermore, surface photovoltage (SPV) spectra were used to investigate the separation efficiency of the photo-generated charge carriers. It is well known that a stronger SPV peak represents higher separation efficiency of the electron-hole pairs [55]. As shown in Fig. 10, both the pure g-C₃N₄ nanosheets and PtPd/g-C₃N₄ composite photocatalysts exhibit positive photovoltage response in the wavelength range between 300 and 400 nm. This matches the photo-active wavelength range of DRS. Thus, the photovoltage values are only noise in the range 400–600 nm, which means that the light in this wave band is unused in both pure g-C₃N₄ and PtPd/g-C₃N₄. In addition, the PtPd/g-C₃N₄ composite shows a much stronger SPV response than pure g-C₃N₄ does. This result demonstrates higher charge separation efficiency after loading the PtPd alloy NPs onto the surface of the g-C₃N₄ nanosheets. High photocatalytic activity benefits from the high charge separation rate. This result is consistent with the results on photocatalytic performance.

The transient photocurrent response of a photoelectrochemical system under chopped light illumination can give information about the kinetics of the photo-generated carriers from a different perspective. For this reason, the transient photocurrent response of the samples was recorded, and is shown in Fig. 11. It can clearly be seen that the photoelectrode composed of the PtPd/g-C₃N₄ composite photocatalyst shows higher photocurrent than the pure g-C₃N₄ nanosheets do, which

Fig. 9. (a) PL spectra (pure g-C₃N₄ and 0.2 wt% PtPd/g-C₃N₄ samples) and time-resolved fluorescence spectra of (b) pure g-C₃N₄ and (c) 0.2 wt% PtPd/g-C₃N₄ samples.

Fig. 10. SPV spectra of pure g-C₃N₄ and 0.2 wt% PtPd/g-C₃N₄ samples.

suggests improved charge separation efficiency in the g-C₃N₄ decorated with PtPd alloy NPs. Both the low photocurrent value and the rapid decay characteristic of pure g-C₃N₄ can be assigned to fast recombination kinetics [56].

Based on the characterization analysis and photocatalysis experimental results, a possible photocatalytic mechanism for overall water splitting over PtPd/g-C₃N₄ photocatalyst is proposed (Fig. 12). Under visible light irradiation, g-C₃N₄ absorbs photons and excites electron (e⁻)-hole (h⁺) pairs. The electrons transfer from the valence band (VB) to the conduction band (CB), leaving the holes in the VB. However, without co-catalyst, the photo-generated e⁻ and h⁺ are likely to recombine rapidly, which results in low photocatalytic H₂ production activity. The PtPd alloy NPs on the g-C₃N₄ nanosheet surfaces act as electron traps and provide protons reduction sites for H₂ production. At the same time, the h⁺ diffuse to the semiconductor/electrolyte interface and take part in another half-redox reaction for H₂ evolution, that is, oxidizing TEOA to TEOA⁺. Moreover, using K₂HPO₄ as sacrificial agent is an effective way to enhance the photocatalytic H₂ production rate even further. In the presence of K₂HPO₄, HPO₄²⁻ acts as a mediator that participates directly in the photocatalytic reaction, such that H⁺ from HPO₄²⁻ instead

Fig. 11. Transient photocurrent responses of pure g-C₃N₄ and 2 wt% PtPd/g-C₃N₄ samples.

Fig. 12. Schematic illustration of charge transfer and H₂ evolution mechanism involving HPO₄²⁻ for PtPd/g-C₃N₄ photocatalyst under visible light irradiation.

of H₂O combines with the photogenerated electrons to produce H₂. After H₂ evolution from HPO₄²⁻, the newly formed PO₄³⁻ immediately combines with H⁺ from H₂O to regenerate HPO₄²⁻ and complete the proton-reduction cycle [40].

4. Conclusions

We successfully synthesized a series of PtPd/g-C₃N₄ composites *via* the chemical deposition precipitation method. The decoration with PtPd NPs did not result in damage to the morphology or crystal structure of the g-C₃N₄ photocatalyst. Compared to pure g-C₃N₄, the PtPd/g-C₃N₄ composite photocatalysts exhibited enhanced photocatalytic activity for H₂ production. The 0.2 wt% PtPd/g-C₃N₄ sample exhibited the highest photocatalytic activity. An even higher H₂ evolution rate of 2885.0 μmol·g⁻¹·h⁻¹ was achieved when K₂HPO₄ was used as a sacrificial agent. In addition, the 0.2 wt% PtPd/g-C₃N₄ sample also showed good photocatalytic stability in the time-circle experiments. In order to explain the observed H₂ evolution activity enhancement in PtPd alloy-NP decorated g-C₃N₄ nanosheets, a possible mechanism based on suppressed charge recombination and promoted charge transfer at the PtPd/g-C₃N₄ interface is proposed. This was confirmed by the SPV, PL, and time-resolved fluorescence characterizations. Therefore, our experimental results demonstrated that PtPd alloy NPs are a promising co-catalyst for g-C₃N₄, which can also be regarded as a potential functional co-catalyst for enhancement of the photocatalytic H₂ production activities of other semiconductor photocatalysts.

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Graphical Abstract

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Novel PtPd alloy nanoparticle-decorated g-C₃N₄ nanosheets with enhanced photocatalytic activity for H₂ evolution under visible light irradiation

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PtPd/g-C₃N₄ photocatalysts were used as a photosensitizer and coupled with PtPd alloy nanoparticles for photocatalytic H₂ production under visible light. The H₂ production rate was ~800 times higher than with pure g-C₃N₄. This enhancement is probably due to a semiconductor/co-catalyst interface interaction between the PtPd alloy nanoparticles and the g-C₃N₄ nanosheets that increases the charge transfer process efficiency.

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新型PtPd合金纳米颗粒修饰g-C₃N₄纳米片以提高可见光照射下光催化产氢活性

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摘要: 石墨相氮化碳(g-C₃N₄)纳米片因其廉价、易得、无毒等优点而在光催化领域被广泛应用和研究。但单一的g-C₃N₄存在光生电子与空穴易复合等缺陷, 而助催化剂的存在可以促进电荷转移, 延长载流子寿命, 从而提高光催化性能。本文通过合成PtPd双金属合金纳米颗粒作为助催化剂, 对g-C₃N₄纳米片光催化剂进行修饰以提高可见光照射下的光催化产氢速率。

g-C₃N₄是以尿素为原材料, 通过高温热缩聚和热刻蚀的方法合成, PtPd/g-C₃N₄复合光催化剂通过化学还原沉积法合成。对所获得的复合光催化剂进行了XRD测试并将结果与PdPt标准卡片进行了对比, 结果表明, 各峰的位置都能有较好的对应, 说明成功合成了PdPt。采用TEM对PtPd/g-C₃N₄的形貌进行观察, 发现g-C₃N₄呈薄片状, 且PdPt颗粒较为均匀地分布在其表面。XPS测试发现, PtPd/g-C₃N₄复合样品中Pt和Pd元素的峰值较Pt/g-C₃N₄和Pd/g-C₃N₄均发生0.83 eV的偏移, 进一步说明合成了PtPd双金属合金纳米颗粒。DRS测试表明, g-C₃N₄的带隙宽度为2.69 eV, 而PtPd双金属合金纳米颗粒的负载有效地减小了禁带宽度, 从而提高了光催化剂对光的利用率。

光催化产氢性能实验发现, 当g-C₃N₄负载PtPd双金属合金纳米颗粒后, 光催化产氢速率大幅度提高, 其中负载量为0.2 wt%的PtPd/g-C₃N₄复合光催化剂的产氢速率最高, 为1600.8 μmol g⁻¹ h⁻¹, 是纯g-C₃N₄纳米片的800倍。向光催化体系中添加10 g K₂HPO₄后, 产氢速率提高到2885.0 μmol g⁻¹ h⁻¹。当二元合金中Pt: Pd比为1:1时, PtPd/g-C₃N₄复合光催化剂上的产氢速率最高, 分别是Pt/g-C₃N₄和Pd/g-C₃N₄上的3.6倍和1.5倍。另外, 在420 nm处量子效率为5.5%。PtPd/g-C₃N₄复合光催化剂还表现出很好的稳定性, 能够在完成4次光催化实验循环后仍然保持其良好的光催化活性。

对PtPd/g-C₃N₄复合光催化剂进行了一系列光电化学表征。PL结果表明, PtPd/g-C₃N₄复合光催化剂与纯g-C₃N₄相比荧光强度减弱, 说明PtPd/g-C₃N₄复合光催化剂有较慢的光生电子-空穴复合速率, 这可以更有效地使电荷分离, 从而提高光催化活性。根据光催化反应和表征分析结果提出了复合光催化剂上水分解产氢可能的机理, 即PtPd/g-C₃N₄之间的协同作用有助于提高复合光催化剂的光催化活性。

关键词: g-C₃N₄纳米片; PtPd合金纳米颗粒; 产氢; 光催化

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