

Article

Facile Fabrication of a Novel Au/Phosphorus-Doped g-C₃N₄ Photocatalyst with Excellent Visible Light Photocatalytic Activity

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Abstract: The intrinsic disadvantages of pristine graphitic carbon nitride (g-C₃N₄) significantly restrict its applications in photocatalysis field. Hence, we have demonstrated facile thermal copolymerization and in situ photodeposition methods to fabricate a novel Au/phosphorus-doped g-C₃N₄ (Au/P-g-C₃N₄) photocatalyst. The results showed that phosphorus was doped into the structure of g-C₃N₄ and that the surface deposition of gold was successfully accomplished. The H₂ generation rate of the optimal Au/P-g-C₃N₄ is 8.4 times compared with the pristine g-C₃N₄ under visible light irradiation. The enhancement of photocatalytic activity is due to the synergic effect between gold induced surface plasmon resonance and the modified structural and electronic properties of the g-C₃N₄ induced by the phosphorus dopant.

Keywords: g-C₃N₄; surface plasmon resonance effect; phosphorus doping; photocatalytic activity

1. Introduction

Photocatalytic hydrogen (H₂) generation using solar energy is the most promising strategy to solve the energy crisis [1–4]. To date, various semiconductors have been used for photocatalytic H₂ generation, such as ZnO, Ag₂S and BiVO₄. They are mainly inorganic semiconductors with poor photocatalytic activity [5–7]. Hence, photocatalysts with excellent activity for H₂ generation using solar energy are still unavailable, which remains a significant challenge [8].

Graphitic carbon nitride, g-C₃N₄, is a non-metal polymer semiconductor that has shown much promise as a visible light photocatalyst for a range of applications from H₂ generation to organic pollutant digestion [9]. It has a band gap of about 2.6 eV (urea thermal polymerization) [10]. g-C₃N₄ is an organic semiconductor showing the advantages of an environmentally friendly and sustainable material compared with other reported photocatalysts. Meanwhile, it consists of easily acquired elements from our planet (carbon and nitrogen) [11]. The previous research has clearly shown that the conjugated aromatic π -stacking g-C₃N₄ photocatalyst owns satisfactory chemical and thermal stability as well as good electronic properties. As a consequence, g-C₃N₄ becomes a promising material in the photocatalysis field [11,12]. However, some important problems still limit the application of g-C₃N₄ in the photocatalytic field, such as, the narrow absorption region, the poor surface area and low separation rate of the photogenerated electron-hole [13]. Thus, many strategies such as nonmetal or metal doping, coupling with noble metal materials (Pt, Au, Ag) or carbon materials, introducing vacancy have been employed [14–17].



In the above methods, doping with nonmetal atoms and coupling Au nanoparticles have been considered as an efficient strategy. Recently, Cheng et al. prepared Sulfur doped g-C₃N₄ via treated raw g-C₃N₄ at high temperature in H₂S atmosphere. However, it could pollute the surrounding environment and S-doped g-C₃N₄ exhibited unsatisfactory photocatalytic activity [18]. Zhang et al. employed ionic liquid and dicyandiamide as precursors to prepare phosphorus doped g-C₃N₄. The visible light utilization ability was obviously improved after phosphorus doping. Nevertheless, it is not a facile method because of the high cost of ionic liquid and complicated synthesis [19]. Furthermore, Qian et al. reported on Au nanoparticles modified on the surface of g-C₃N₄ through a complex method and surveyed the photocatalytic activity for H₂ generation [20]. Parida et al. dispersed Au nanoparticles on g-C₃N₄ to transfer photogenerated electrons and to improve the light absorption [11]. The photocatalytic activity of g-C₃N₄ could be partly improved with the existence of Au nanoparticles. However, the deposition and combination of Au nanoparticles on the surface of g-C₃N₄ were not good. In general, the early studies did not reflect the benefit of the synergic effect between doping and surface plasmon resonance. As a consequence, the reinforcement of photocatalytic performance in the above works was not marked.

Hence, we fabricated Au/phosphorus-doped g- C_3N_4 (Au/P-g- C_3N_4) photocatalyst by facile thermal copolymerization and in situ photodeposition methods. A series of analyses evidenced the good electronic structures and texture of Au/P-g- C_3N_4 . Subsequently, the reasons for enhanced photocatalytic activity are discussed and a possible mechanism is proposed based on our experimental results.

2. Results and Discussion

The crystal structure of as-prepared g-C₃N₄, P-g-C₃N₄, 3% Au/g-C₃N₄ and different Au/P-g-C₃N₄ samples were analyzed by XRD. As shown in Figure 1, the XRD pattern of g-C₃N₄ revealed two distinct reflections at 13.47 and 27.25°, which could be easily indexed that the g-C₃N₄ belonged to hexagonal phase (JCPDS 87-1526). The diffraction peak at 27.25° was assigned to the (002) plane of graphitic g-C₃N₄, which resulted from the conjugated aromatic system's stacking. Another minor peak at 13.47° was indexed for the (100) plane of $g-C_3N_4$ derived from the repeated units of melem (1,3,4,6,7,9,9b-Heptaazaphenalene-2,5,8-triamine) [21]. For P-g-C₃N₄, the above peaks were still maintained. This meant the phosphorus doping process did not change the structure of g-C₃N₄. Additionally, the peak position of the (002) plane shifted from 27.25 to 26.65°, which could probably be ascribed to the P doped into the structure of g-C₃N₄, indicating the interlayer stacking distance of $P-g-C_3N_4$ was increased [1]. This meant that $g-C_3N_4$ was exfoliated (larger surface area). The overall weakening intensity of the peaks concluded that P-g-C₃N₄ have poorer crystallinity, also resulting from the marginally doping of P which inhibited the growth of the g-C₃N₄ [22]. For Au nanoparticles loaded all samples, the XRD patterns revealed four separate reflections at 38.3, 44.5, 64.5, and 77.7°, corresponding to (111), (200), (220), (311) planes of metallic Au, respectively. The observed peaks were well matched with the featured reflections of Au (JCPDS 01-1174) [11]. The peaks of the above mentioned gradually increased with increasing the Au loading percentage on P-g-C₃N₄. The four peaks indicated the composition of Au on the P-g-C₃N₄, which was not discovered in the raw g-C₃N₄. The presence of both Au planes and P-g- C_3N_4 confirmed the formation of nanocomposites. Meanwhile, it could be concluded that impurities or any other phases did not exist in the composites because no significant other diffraction reflections could be observed, which showed that the introduction of Au particles and P doping did not change the crystal structure of g-C₃N₄.

The valence states and chemical composition of P-g-C₃N₄ and 3% Au/P-g-C₃N₄ were analyzed by XPS. Figure 2a shows the survey spectrum of P-g-C₃N₄. The spectrum manifested the presence of C, N, P and surface absorption O, which meant the thermal copolymerization process introduced P into g-C₃N₄ structure. Figure 2b shows the survey spectrum of 3% Au/P-g-C₃N₄, the peaks belonging to C, N, P and Au indicated the deposition of Au had been accomplished. More importantly, the P 2p signal (Figure 2c) could be fitted as two peaks located in 133.1 eV and 133.9 eV. These peaks were attributed to the P-N species, indicating P replaced C atoms in the g-C₃N₄ structure [23]. The high-resolution XPS

data was clear proof that P marginally doped into the structure of $g-C_3N_4$. Meanwhile, the two distinct peaks located in 79.8 eV and 83.6 eV (Figure 2d) originated from Au $4f_{5/2}$ and $4f_{7/2}$ electrons of metallic Au [24]. Therefore, it could be confirmed that the photodeposition process effectively generated metallic Au⁰ species on the surface of P-g-C₃N₄. As shown in Table 1, the P external element content was determined to be 0.66 wt.% and Au external element content was determined to be 2.96 wt.% (close to nominal Au content) by XPS analysis for 3% Au/P-g-C₃N₄, also the corresponding C/N atomic ratio (0.74) was close to the theoretical value of raw g-C₃N₄ (0.75) [25]. These results showed that the deposition of Au and doping of phosphorus into the texture of g-C₃N₄ had been accomplished. This was also supported by XRD studies.



Figure 1. XRD spectrograms of g-C₃N₄, P-g-C₃N₄, 3% Au/g-C₃N₄ and different Au/P-g-C₃N₄ samples.



Figure 2. XPS survey spectra of P-g-C₃N₄ (**a**) and 3% Au/P-g-C₃N₄ (**b**), P 2p high-resolution spectrum (**c**) and Au 4f high-resolution spectrum (**d**) for 3% Au/P-g-C₃N₄.

Samples	Binding Energy of P 2p	Binding Energy of Au 4f _{5/2} and 4f _{7/2}	Surface C/N Atomic Ratio	P cont. [wt.%]	Au cont. [wt.%]
P-g-C ₃ N ₄	133.7 eV	-	0.74	0.67	-
3% Au/P-g-C ₃ N ₄	133.8 eV	79.8 eV and 83.6 eV	0.74	0.66	2.96

The morphology and structure of 3% Au/P-g-C₃N₄ were analyzed by TEM. The 3% Au/P-g-C₃N₄ showed morphology of ultrathin nanosheets (Figure 3a). These nanosheets were soft and loose, which meant that g-C₃N₄ was exfoliated during the doping process. The nanosheets possessed a larger surface area and abundant reactive sites. Meanwhile, Au nanoparticles (black colored dots) were uniformly and adequately anchored on the surface of $P-g-C_3N_4$ nanosheets, which can be found in Figure 3b clearly. We could observe that a strong combination between Au and P-g- C_3N_4 , ensuring the electrons transfer between Au and P-g-C₃N₄ smoothly. This strong combination also enhanced plasmonic properties of the 3% Au/P-g-C₃N₄. Figure 3c shows the HRTEM image of single Au nanoparticle. The lattice spacing of 0.203 nm belonged to the (200) lattice planes of metallic Au [24]. The composition of 3% Au/P-g-C₃N₄ was analyzed by EDS. The EDS spectrum of 3% Au/P-g-C₃N₄ showed characteristic peaks of C, N, P and Au (Figure 3d). This data was also in accordance with XRD and XPS results. Meanwhile, mean particle size and particle size distribution of all Au loaded samples are shown in Table 2. TEM images for the whole series of catalysts are shown in Figure S1. The BET surface areas of samples were calculated used nitrogen adsorption-desorption isotherms of samples (Figure S2) [26]. The BET specific surface areas of $g-C_3N_4$, P- $g-C_3N_4$ and 3% Au/P- $g-C_3N_4$ were 63.2, 77.5 and 77.8 m²/g, respectively. The BET specific surface area of P-g-C₃N₄ was slightly larger than that of raw g-C₃N₄, which could have resulted from the P doped into the structures of g-C₃N₄, indicating that the interlayer stacking distance of P-g- C_3N_4 was increased. This meant that the process of doping was exfoliated (larger surface area). Moreover, the BET specific surface areas of P-g-C₃N₄ and 3% Au/P-g-C₃N₄ were uniform, this meant that the deposition process did not change BET surface area.



Figure 3. TEM image with low-magnification (**a**) of 3% Au/P-g-C₃N₄ and high-magnification (**b**) of 3% Au/P-g-C₃N₄. (**c**) Corresponding HRTEM image of a single Au nanoparticle and (**d**) EDS spectrum of 3% Au/P-g-C₃N₄.

Samples	Mean Particle Size	Particle Size Distribution
3% Au/g-C ₃ N ₄	24 nm	13–56 nm
1% Au/P-g-C ₃ N ₄	12 nm	8–33 nm
3% Au/P-g-C ₃ N ₄	22 nm	11–54 nm
5% Au/P-g-C ₃ N ₄	70 nm	20–130 nm

Table 2. Mean particle size and particle size distribution of all Au loaded samples.

UV-vis diffuse reflectance spectroscopy was used to investigate the optical absorption of the obtained samples. As shown in Figure 4, the band gap of g-C₃N₄ was 2.59 eV (inset), which exhibited an absorption edge located at 479 nm. Remarkably, the band gap of P-g-C₃N₄ was 2.47 eV, which exhibited a stronger absorption edge located at 502 nm. The reason for the absorption edge's red shift was that the P 3p state was located at the bottom of the conduction band in the g-C₃N₄ host, resulting in the decrease of band gap [27]. This means P-g-C₃N₄ have improved visible light utilization ability. Meanwhile, with the incorporation of Au, the SPR of Au nanoparticles resulted in an intense absorption on the interface between Au and P-g-C₃N₄, which promoted the separation rate of photogenerated charge [20]. In addition, some of hot electrons generated by the SPR of Au could directly inject into the conduction band of the P-g-C₃N₄ crossing the Schottky barrier, improving the light utilization abilities of Au/P-g-C₃N₄ nanocomposites [28]. Band gap, relative conduction band and valence band of all obtained samples are shown in Table 3.



Figure 4. UV-visible absorption spectra of $g-C_3N_4$, P- $g-C_3N_4$, 3% Au/ $g-C_3N_4$ and different Au/P- $g-C_3N_4$ samples. Corresponding band gap calculation (inset).

Table 3. Band gap (Eg), relative conduction band (E_{CB}) and valence band (E_{VB}) of all obtained samples.

Samples	Eg (eV)	E _{CB}	E _{VB}
g-C ₃ N ₄	2.59	-1.07	1.52
P-g-C ₃ N ₄	2.47	-1.01	1.46
3% Au/g-C ₃ N ₄	2.58	-1.07	1.51
1% Au/P-g-C ₃ N ₄	2.45	-1.00	1.45
3% Au/P-g-C ₃ N ₄	2.47	-1.01	1.46
5% Au/P-g-C ₃ N ₄	2.46	-1.01	1.45

The photocatalytic activities for H₂ generation of prepared $g-C_3N_4$, P- $g-C_3N_4$, 3% Au/ $g-C_3N_4$ and different Au/P- $g-C_3N_4$ composites were assessed in methanol aqueous solution under visible light

irradiation. As shown in Figure 5a, the P-g- C_3N_4 showed higher photocatalytic activity than g- C_3N_4 . The reason was the narrow band gap and large surface area of P doped g-C₃N₄. The narrow band gap and large surface area meant abundant reactive sites and improved visible light utilization ability. When g-C₃N₄ was coupled with Au nanoparticles, 3% Au/g-C₃N₄ showed enhanced photocatalytic activities compared with $g-C_3N_4$. The reason was the SPR effect of Au, which brought an advanced separation rate of photogenerated charge. The 3% Au/P-g-C₃N₄ sample exhibited the strongest photocatalytic activity for H_2 generation and the H_2 generation rate was 8.4 times compared with the pristine g-C₃N₄ under visible light irradiation. The improvement of photocatalytic activity of 3% Au/P-g-C₃N₄ could be ascribed to the above-mentioned reasons. These reasons could be summed up as synergic effect between gold induced surface plasmon resonance and the modified structural and electronic properties of the g-C₃N₄ induced by the phosphorus dopant. Furthermore, from the practical applications of 3% Au/P-g-C₃N₄, the photocatalytic stability of 3% Au/P-g-C₃N₄ sample was evaluated under the same conditions. The 3% Au/P-g-C₃N₄ exhibited a good catalytic stability (Figure 5b), keeping a similar level of activity after four cycles. Therefore, $Au/P-g-C_3N_4$ had a potential practical application value. Reacted 3% Au/P-g-C₃N₄ was analyzed using XRD, XPS and TEM. The results are presented in Figures S3 and S4. By comparison, distinct XRD diffraction peaks of fresh 3% Au/P-g-C₃N₄ and used 3% Au/P-g-C₃N₄ were almost changeless, implying that the chemical structure of 3% Au/P-g-C₃N₄ was maintained. As shown in Figure S4a, the P 2p signal was attributed to the P-N species, indicating P replaced C. The Au 4f signal means Au⁰ species were dispersed on the surface of P-g-C₃N₄. As shown in Figure S4b, the morphology and mean particle size of 3% Au/P-g-C₃N₄ was not changed after the reaction. The P and Au contents of the fresh catalyst determined by ICP were 0.62 and 2.86 wt.%. The P and Au contents of the used catalyst determined by ICP were 0.61 and 2.84 wt.%. These results all implied that the chemical structure of 3% Au/P-g-C₃N₄ was maintained with minimal leaching of P and Au.



Figure 5. Photocatalytic activities for (**a**) H_2 generation rates for prepared photocatalysts under visible light illumination. (**b**) Circling runs of 3% Au/P-g-C₃N₄ composite for H_2 generation rates under visible light irradiation.

The separation efficiency of the photogenerated charge was revealed by photoluminescence analysis. Figure 6 shows the spectra of all prepared samples excited by 365 nm. The PL intensity of nanocomposites had a significant decrease compared with the raw $g-C_3N_4$ and $P-g-C_3N_4$. The weaker the PL peak's intensity appeared, meant the lower the recombination rate of the photogenerated charge possessed [29].

For the purpose of further confirmation of the efficiency of the carrier separation and transfer, the transient photocurrent response data was collected by an electrochemical workstation. The photocurrent was measured under $\lambda \ge 420$ nm. The photoexcited electrons contributed to the photocurrent generation in our experiment. As shown in Figure 7, the g-C₃N₄ exhibited poor photocurrent density. The reason was limited visible light utilization and the high recombination rate of charge. The 3% Au/P-g-C₃N₄ sample had the strongest photocurrent density, the photocurrent

density attained as high as 15 μ A/cm². The excellent photocurrent density could be attributed to the enhanced light utilization ability and high efficiency of carrier separation and transfer, which resulted from the SPR effect of Au and P doping. The on-off cycles of photocurrent were quick-response and reversible, which meant the current was truly photogenerated [30].



Figure 6. PL spectra of g-C₃N₄, P-g-C₃N₄, 3% Au/g-C₃N₄ and different Au/P-g-C₃N₄ composites.



Figure 7. Transient photocurrent density of obtained samples.

Based on the above discussion, the mechanical illustration of 3% Au/P-g-C₃N₄ in the photocatalytic reaction is shown in Figure 8. Firstly, 3% Au/P-g-C₃N₄ had enhanced light utilization, which resulted from the P doping narrowing the band gap of g-C₃N₄ and an intense absorption in the region of

450–700 nm induced by SPR of Au nanoparticles. Secondly, an intense near-electric field induced by this SPR improved the efficiency of carrier separation. Meanwhile, when Au nanoparticles combined with P-g-C₃N₄, due to the difference of the work function, the free electrons would transfer from P-g-C₃N₄ to Au. The Fermi levels and the band position would change at interface. Finally, a Schottky barrier formed to hinder the electron transfer from gold to P-g-C₃N₄. Under light illumination, P-g-C₃N₄ could be excited to generate holes and electrons, the excited electrons from the CB of P-g-C₃N₄ transferred to the Au, resulting in a high efficiency of carrier separation and transfer [31]. Then the electrons would react with H⁺ for the generation of H₂ and the holes would be consumed by sacrificial agents. Hence, the 3% Au/P-g-C₃N₄ photocatalyst showed excellent photocatalytic activities.



Figure 8. The mechanical illustration of enhanced photocatalytic activity for 3% Au/P-g-C₃N₄ sample.

3. Materials and Methods

3.1. Synthesis of g- C_3N_4 and P-g- C_3N_4

The $g-C_3N_4$ was prepared by polymerization of urea, 7 g urea was thermally treated in a tube furnace at 550 °C for 4 h with a heating rate of 10 °C min⁻¹. When the ceramic container was cooled to room temperature, the yellow-colored product ($g-C_3N_4$) was collected and ground into powder.

The P doped $g-C_3N_4$ was prepared by copolymerization of the precursor according to the literature [1]. In a typical process, 7 g urea and 0.1 g NH₄H₂PO₄ were ground together in an agate mortar and then thermally treated in a tube furnace at 550 °C for 4 h with a heating rate of 10 °C min⁻¹. When the ceramic container was cooled to room temperature, the yellow-colored product (P-g-C₃N₄) was collected and ground into powder.

3.2. Synthesis of Composites

In a typical preparation of 3% Au/P-g-C₃N₄, 150 mg of P-g-C₃N₄ was dispersed in water with mild sonication (10 min). A 3 mL sample of isopropanol and 7.8 mL HAuCl₄ were added to the above suspension then with sonication (2 h, dark). The resulting mixture was stirred under UV light illumination (1.5 h) with continuous nitrogen sparging. Then the mixture was washed thoroughly with distilled water and finally dried in a vacuum oven at 50 °C. The nominal Au contents were 1, 3, and 5 wt.% for the Au/P-g-C₃N₄ composites using different amounts of HAuCl₄. Au/g-C₃N₄ was synthesized under the same conditions using the crude g-C₃N₄ synthesized as above.

3.3. Characterizations

The crystal structure of the samples was tested by X ray powder diffraction (XRD), the parameters of XRD were graphite monochromator, $\lambda = 1.54184$ Å, room temperature, Bruker D2 PHASER X ray diffractometer. The valence states and chemical composition of samples was tested by X-ray photoelectron spectroscopy (XPS), the parameters of XPS were a monochromated Al Kα irradiation, PHI-5702, Physical Electronics. High-resolution transmission electron microscopy and transmission electron microscopy (HRTEM, TEM, Tecnai F30, 300 kV operated voltage) were used to observe the morphologies of the samples. The specific surface area (BET) of the sample was measured by a Micromeritics ASAP 2000 system. Perkin Elmer 950 spectrometer (DRS) and Photoluminescence emission spectra (PL, FLS-920T, 450 W xenon arc lamp) were used to test the optics and electronic properties. The type of electrochemical workstation was a CS 310, Wuhan Corrtest Instrument Co. Ltd. Reference electrodes (an Ag/AgCl electrode and a platinum foil electrode) with working electrodes were immersed in 0.1 M Na₂SO₄ aqueous solution (300 W Xe lamp irradiation) for the photoelectrochemical properties tested. All photoelectrochemical measurements were carried out at a constant electrode potential of 0 V to the reference electrode. In a typical preparation of the electrode, 15 mg 3% Au/P-g-C₃N₄, 40 μL terpilenol, 10 μL alcohol and 10 μL Nafion aq.(5 wt.%) were ground together, then the composite was coated on FTO (effective area is cm²) as a working electrode.

3.4. Evaluation of Photocatalytic Activity

An automatic gas circulation system (CEL-SPH2N-D9) was used for H_2 generation experiments. Methanol was employed as the sacrificial agent. In a typical process, 50 mg of sample was dispersed in a mixed solution (40 mL H_2O and 10 mL methanol). After sonication, the reaction unit and gas circulation system were thoroughly degassed for 0.5 h with a stationary temperature at 6 °C using a cooling device. Then the mixed solution was irradiated under a 300 W Xe lamp. Visible light (420–780 nm) was obtained using a UV-IR-CUT filter. Finally, an on-line gas chromatograph (GC-7920) equipped with a thermal conductivity detector (TCD) was employed for data acquisition, which used carrier gas (N₂) and 5Å molecular sieve column.

4. Conclusions

In summary, Au/P-g-C₃N₄ photocatalysts were prepared by facile thermal copolymerization and in situ photodeposition methods. The P element was doped into the structure of g-C₃N₄ marginally and the monodispersed Au nanoparticles were adequately anchored on the surface of P-g-C₃N₄. The obtained Au/P-g-C₃N₄ photocatalysts had the enhanced visible light utilization, improved photogenerated electron-hole pairs separation efficiency as well as abundant reactive sites, which were derived from the synergic effect between Au caused by the surface plasmon resonance effect and the dopant phosphorus-induced structural and electronic properties changing. Hence, Au/P-g-C₃N₄ photocatalysts show arresting photocatalytic activity under visible light illumination. This work could provide a promising approach to develop high-efficiency photocatalysts applied to H₂ generation. **Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4344/10/6/701/s1, Figure S1: TEM images of $g-C_3N_4$ (a), $P-g-C_3N_4$ (b), 3% Au/ $g-C_3N_4$ (c), 1% Au/ $P-g-C_3N_4$ (d), 3% Au/ $P-g-C_3N_4$ (e) and 5% Au/ $P-g-C_3N_4$ (f), Figure S2: N₂ adsorption-desorption isotherms of $g-C_3N_4$, $P-g-C_3N_4$ and 3% Au/ $P-g-C_3N_4$, Figure S3: XRD patterns of fresh and used 3% Au/ $P-g-C_3N_4$, Figure S4: XPS spectrum and TEM photograph of used 3% Au/ $P-g-C_3N_4$.

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