

Article

Engineering Phosphorus Doping Graphitic Carbon Nitride for Efficient Visible-Light Photocatalytic Hydrogen Production

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Abstract

Modulating the electronic structure and surface properties of graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) by chemically phosphorus doping is an effective strategy for improving its photocatalytic performance. However, in order to benefit from practical applications, the cost-effectiveness, efficiency, and optimization of the doping level need to be investigated further. Herein, we report a structural doping of P into $g\text{-C}_3\text{N}_4$ by in situ polymerization of the mixture of dicyandiamide (DCDA) and phosphorus pentoxide (P_2O_5). As an alternative to previous studies that used complex organic phosphorus precursors or post-treatment strategies, this work proposed a one-pot thermal polycondensation method that is low-cost, scalable, and enables controlled phosphorus substitutions at carbon sites of the $g\text{-C}_3\text{N}_4$ heptazine structure. Most of the structural features of $g\text{-C}_3\text{N}_4$ were well retained after doping, but the electronic structures and light harvesting capacity had been effectively altered, which provided not only a much better charge separation but also an improvement in photocatalytic activity toward H_2 evolution under irradiation of a simulated sunlight. The optimized sample with P-doping content of 9.35 at.% (0.5PGCN) exhibited an excellent photocatalytic performance toward H_2 evolution, which is over 5 times higher than that of bulk $g\text{-C}_3\text{N}_4$. This work demonstrates a facile one-step in situ route for producing high-yield photocatalysts using low-cost commercial precursors, offering practical starting materials for studies in solar cells, polymer batteries, and photocatalytic applications.

Keywords: water splitting; hydrogen evolution reaction; P-doped $g\text{-C}_3\text{N}_4$; P doping optimization; green hydrogen production

1. Introduction

Energy from the sun represents a renewable and sustainable source of power, which provides eternal energy for human existence. Graphene-like carbon nitride, a 2D material containing heptazine motifs, has attracted considerable interest in fields such as catalysis, photocatalysis, and optoelectronic applications owing to its remarkable thermal and chemical stability as well as its favorable photocatalytic activity [1]. A catalytic activation of benzene using $g\text{-C}_3\text{N}_4$ was reported by Goettmann et al. in 2006 [2]. Three years later, Wang and co-workers discovered that $g\text{-C}_3\text{N}_4$ is capable of photocatalytic hydrogen production upon visible light irradiation [3], marking a significant milestone in metal-free photocatalysts. Typically, bulk $g\text{-C}_3\text{N}_4$ is easily fabricated through thermal polycondensation of common N-rich starting materials such as melamine [4,5], cyanamide [6], dicyandiamide (DCDA) [7,8], urea [9–13], thiourea [14–16], 3-amino-1,2,4-triazole [17], and ammonium thiocyanate [18]. This approach, however, produces bulk $g\text{-C}_3\text{N}_4$ that has low dispersibility in reaction media and high recombination rates of photoinduced charge carriers, which are



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the bottlenecks of particle-based H₂ evolution. Nevertheless, thermal polycondensation remains the most widely adopted and scalable method for g-C₃N₄ synthesis, so it is important to overcome its inherent limitations by making rational modifications to the structure and electronic properties.

Among the various modification strategies, heteroatom doping onto g-C₃N₄ has proven particularly effective in improving charge separation and photocatalytic performance. Chemical doping is widely recognized as an efficient approach to tailor the electronic band structure and surface characteristics of photocatalysts, thereby promoting the separation efficiency of photoinduced electron/hole pairs. In particular, phosphorus doping in g-C₃N₄ tailors its electronic structure, charge transport, and surface reactivity simultaneously. With this multifaceted modulation, photocatalytic H₂ evolution rates are dramatically improved while chemical stability and scalability are maintained [19–22]. Zhou et al. reported P-doped g-C₃N₄ with enhanced charge separation, evidenced by PL quenching and photocurrent enhancement, resulting in photocatalytic H₂ evolution rate improvement. The P dopant introduced electron-rich and electron-deficient sites, which resulted in internal dipoles that might promote charge carrier separation. The P incorporation not only altered the g-C₃N₄ surface from positively to negatively charged, which enhanced the proton adsorption and H₂ evolution step, but also generated P⁺ centers that act as Lewis acid sites synergistic with -NH₂ groups Lewis base sites of g-C₃N₄, which enhanced photocatalytic kinetics reaction [20]. Fang et al. claimed an alternation of the electronic band structure caused by the P atoms substituting for C and N atoms in the heptazine framework, which creates P-N and P-C bonds, creating sub-bandgap states and extending light adsorption up to near-infrared regions. Moreover, the P-doped g-C₃N₄ promoted the nanostructures' porosity and layers exfoliation compared to bulk g-C₃N₄, which supported increasing the accessible active sites density and charge diffusion efficiency [21,22].

As summarized in the comprehensive Table S3, recent P-doped g-C₃N₄ photocatalysts typically exhibit H₂ evolution rates ranging from several hundred to thousands of $\mu\text{mol g}^{-1} \text{h}^{-1}$ under visible-light irradiation, depending strongly on the dopant source, phosphorus loading level, synthesis route, and light irradiation conditions. However, most reported studies employ a single phosphorus content or rely on phosphorus doping of bulk g-C₃N₄ using relatively complex phosphorus precursors. Although phosphorus doping has been widely demonstrated to enhance the photocatalytic activity of g-C₃N₄, the composition-dependent photocatalytic behavior and systematic optimization of the phosphorus doping level as a function of hydrogen evolution performance remain largely unexplored [23,24]. Herein, through a facile and mass-production technique of in situ polymerization of precursor mixtures, we controlled the phosphorus level to optimize the phosphorus doping on g-C₃N₄ for maximum photocatalytic activity toward the evolution of H₂. Photocatalytic H₂ evolution was evaluated under a simulated sunlight irradiation (Asashi MAX-350 Xenon light source), using triethanolamine (TEOA) as a sacrificial agent (10 vol%), Eosin Y as a photosensitizer, and platinum nanoparticles as a cocatalyst. The amount of produced H₂ was determined using an automated injection setup coupled to online gas chromatography operating with a thermal conductive detector (TCD) and a Carboxen 1000 column.

2. Results and Discussion

2.1. Crystal Structure and Chemical Composition

The as-prepared photocatalysts were synthesized via a facile in situ polymerization of a mixture of the g-C₃N₄ and P precursors, which enables mass production. The mixture was thoroughly ground in a conventional oven to prevent water adsorption. The melting points of DCDA and P₂O₅ were, respectively, 209.5 °C and 340 °C, which ensured a com-

plete mixing during the polymerization reaction at 550 °C. The elemental composition of as-prepared samples was determined by EA, ICP-OES, and XPS. The EA and ICP-OES were used to analyze CHN-O and P content, respectively (Table 1). While the samples' surface compositions were investigated by XPS (Table S1). As shown in Table 1, the 0.25PGCN sample exhibited a clear compositional change after P doping. The atomic percentage of nitrogen remained almost unchanged, while the carbon content gradually decreased with the increase of phosphorus content. This result suggests that the incorporated phosphorus atoms substituted for carbon atoms within the heptazine framework. The amount of phosphorus introduced into the 0.25PGCN sample was approximately equal to the reduction of carbon compared with pristine GCN, showing a consistent substitution behavior. A similar trend was also observed in the surface elemental compositions obtained from XPS analysis (Table S1). As the P doping level increased in the PGCN samples, the atomic percentage of nitrogen slightly decreased, which could be attributed to the reduced polymerization efficiency during the condensation process. The carbon content also decreased with increasing phosphorus doping, while the combined concentration of carbon and phosphorus in the PGCN samples remained approximately equal to the carbon percentage in pristine GCN (average total of C and P = 31.30 at.% compared with 31.21 at.% of C in GCN). These results provide clear evidence that the introduced phosphorus heteroatoms substituted for carbon atoms in the g-C₃N₄ framework during the P-doping reaction.

Table 1. Elemental compositions of the photocatalysts analyzed by elemental analysis (C, H, N, O analyzer) and ICP-OES (for P).

Sample	N (at. %)	C (at. %)	H (at. %)	O (at. %)	P (at. %)
GCN	50.26	31.21	15.49	3.04	0
0.25PGCN	49.86	25.26	15.29	4.03	5.55
0.5PGCN	49.22	21.04	14.22	6.18	9.35
0.75PGCN	46.12	16.27	14.37	7.76	15.48
1PGCN	44.46	10.54	16.16	7.13	21.72

HRP-XRD analysis was carried out to examine the crystallographic features of the synthesized GCN and PGCN samples (Figure 1). The diffraction peaks observed at ca. 13.3° and ca. 27.4° correspond to the (100) and (002) planes of g-C₃N₄, respectively. Based on JCPDS 87-1526, these reflections are attributed to the in-plane arrangement of repeating heptazine units and the interlayer stacking of the conjugated aromatic layers [1]. With increasing P doping, the (100) peak becomes weaker and broader, which is caused by P doping disrupting the tri-s-triazine order in the heptazine motifs of g-C₃N₄. Moreover, compared to GCN, the PGCN sample exhibited a red shift in the plane (002) due to lattice expansion from the larger P atoms (atomic radius ca. 110 pm vs. C ca. 70 pm, N ca. 65 pm), which was assigned to the expansion of the interlayer spacing caused by P-doping on the crystal planes. The (002) peak exhibits a significant red-shift from pristine g-C₃N₄ to 0.25PGCN, with the red-shift decreasing up to the 0.75PGCN sample, and no further shift observed from 0.75PGCN to 1PGCN, indicating phosphorus doping that over 30 wt.% reached saturation for interlayer spacing expansion (Table 1). This change in the crystal structure of the graphitic carbon nitride system contributed to an imbalance in the Van der Waals force in the π - π aromatic system between layers, which resulted in an enhancement of the dispersibility of PGCN in the reaction media. A reduction in the (002) peak intensity was inversely proportional to the increasing mass ratio of P₂O₅ to DCDA, from 0.25:1 to 1:1 (Figure 1a), with minimal change observed from the 0.75PGCN to 1PGCN samples.

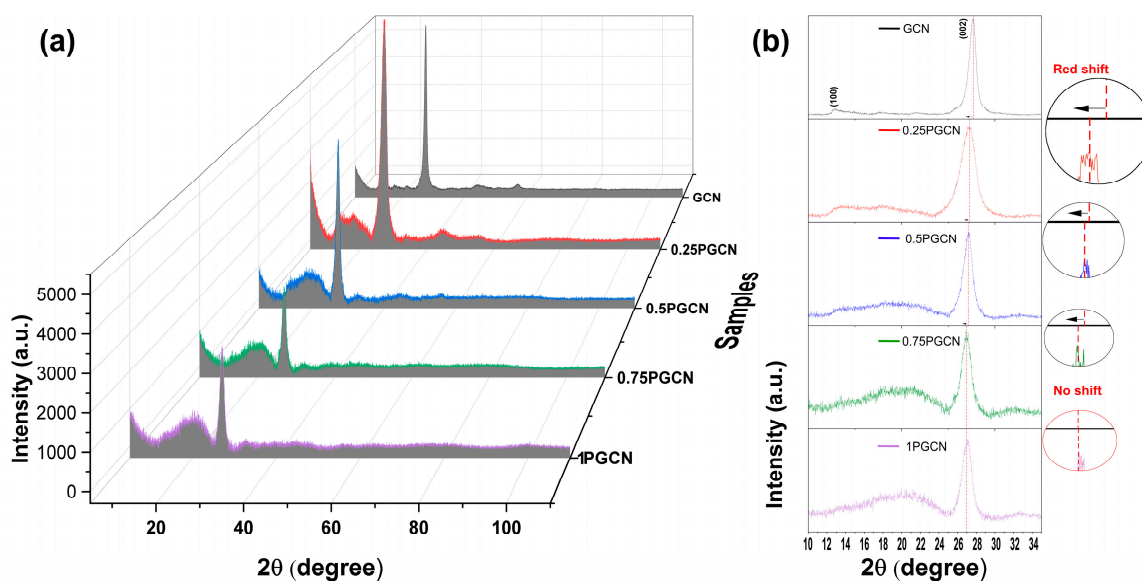


Figure 1. (a) XRD spectra of GCN and PGCN samples. (b) Highlight XRD spectra of the samples, which show red-shifts from GCN to 0.75PGCN and no further shifting from 0.75PGCN to 1PGCN sample.

The elemental composition and chemical bonding states at the sample surfaces were analyzed using X-ray photoelectron spectroscopy (XPS). Figure 2a presents the XPS survey spectra of the as-prepared samples, which reveal their surface chemical states and electronic structures. As the phosphorus content increased, the C 1s peak intensity decreased, while the P 2s and P 2p peak intensities increased. This trend suggests that phosphorus atoms likely substitute carbon within the heptazine units to form P-N coordination structures, as indicated by the P 2s and P 2p peaks at 190.8 eV and 133.6 eV, respectively [25]. Figure 2b–d shows the XPS core-level spectra for P 2p, C 1s, and N 1s. For all PGCN samples (Figure 2b), a peak appears at approximately 133.6 eV, corresponding to P-N bonds, whereas P-C bonding would be expected at ca. 2 eV lower binding energy [26,27]. The intensity of the P 2p peak shows an enhancement by increasing the P amount. Moreover, deconvolution P 2p XPS spectra displayed two peaks with binding energies of ca. 133.2 and 134.1 eV, which were assigned to the typical P-N and P=N species (Figure S1) [19]. The introduction of P-N and P=N bonds in the g-C₃N₄ framework indicated heteroatom doping, as the P atoms replaced the corner C atoms and the bay C atoms, respectively. This result is consistent with the FTIR results presented hereafter. As shown in the deconvoluted C 1s XPS spectra (Figure 2c), characteristic carbon peaks appear at 284.80, 288.14, and 289.63 eV, assigned to graphitic C-C bonds, sp²-hybridized N₂-C=N structures, and oxygen-containing C-O functionalities, respectively [4,5]. It is clearly evident that, with an increase in P content in the structure, the (C_{sp²}/graphitic C) ratio decreases. This confirms that P substitutes at the carbon position in the heptazine units, in agreement with the P-N coordination observed in the P core-level spectra [26–28]. Whilst when the P content increases in the 0.75PGCN sample, this ratio shows a sharp decrease in C_{sp²} and a clear increase in graphitic C. This may be a sign of partial destruction of the heptazine units, which could negatively affect the photocatalytic properties. Furthermore, we calculated the peak area percentage of the N₂-C=N bond in the heptazine units of the as-prepared photocatalysts (Table S2) [29], which decreased gradually with increasing P-doping levels and reached a saturation level at the 0.75PGCN sample. These results verified the loss of C atoms in the C-N framework of the g-C₃N₄ by P atom substitutions during the thermal polymerization reaction, which is consistent with the EA results. The peak positioned near 289.63 eV reflects the incorporation of C-OH and C-NH₂ groups generated during thermal

polymerization under atmospheric conditions. The nitrogen distribution in the samples was evaluated using N 1s core-level XPS spectra (Figure 2d). The energy contribution at 398.5 eV corresponds to nitrogen coordinated to two carbons in heptazine units. The peak centered at 399.9 eV reflects overlapping signals from tertiary bridging nitrogen ($-N<$) and amino groups ($-NH_x$), which is characteristic of tri-s-triazine units in $g-C_3N_4$. Additionally, a faint signal at ca. 293 eV in C 1s and 404.1 eV in N 1s is attributed to π -electron delocalization within the heterocyclic framework.

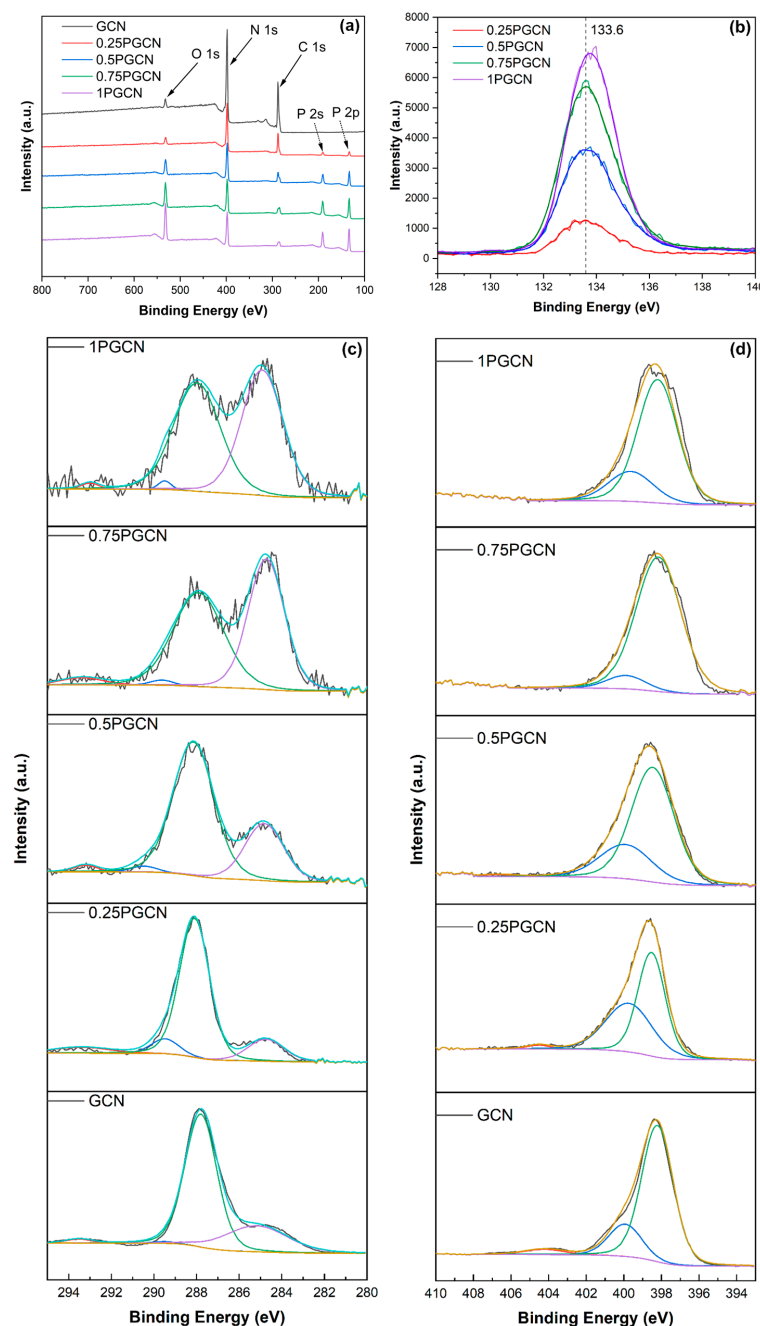


Figure 2. XPS spectra of as-prepared samples. (a) Survey spectra, and deconvolution of (b) P 2p spectra, (c) C 1s spectra, and (d) N 1s spectra.

FT-IR was carried out to further examine the structural characteristics of the synthesized samples and to identify the chemical functionalities present in the photocatalysts. Figure 3 shows the typical FT-IR patterns of as-prepared samples. A band ca. 808 cm^{-1} was linked to the vibration of the heptazine motif, while the broad feature between 900

and 1700 cm^{-1} (typical peaks at ca. 1238 cm^{-1} , 1318 cm^{-1} , 1409 cm^{-1} , and 1573 cm^{-1}) was assigned to the stretching modes of C-N rings and aromatic C-C bonds. The wide bands at $3000\text{--}3500\text{ cm}^{-1}$ were attributed to N-H and the stretching mode of epoxide and hydroxyl groups [1]. Although the preserved characteristic peaks in the FT-IR spectra suggest that P incorporation does not alter the overall structural framework of $\text{g-C}_3\text{N}_4$, the band at 808 cm^{-1} shifts to higher wavenumbers as the P content increases (Figure 3b). This blue shift reflects stronger vibrational modes, likely caused by changes in the electron cloud distribution of the C-N and C=N bonds induced by P doping. Furthermore, two new P-related absorption peaks appear at approximately 940 cm^{-1} and 2360 cm^{-1} in the PGCN samples, which were assigned to the P-N bond motion [30]. This feature confirms the successful incorporation of phosphorus into the $\text{g-C}_3\text{N}_4$ framework, and those results were consistent with the above XRD results.

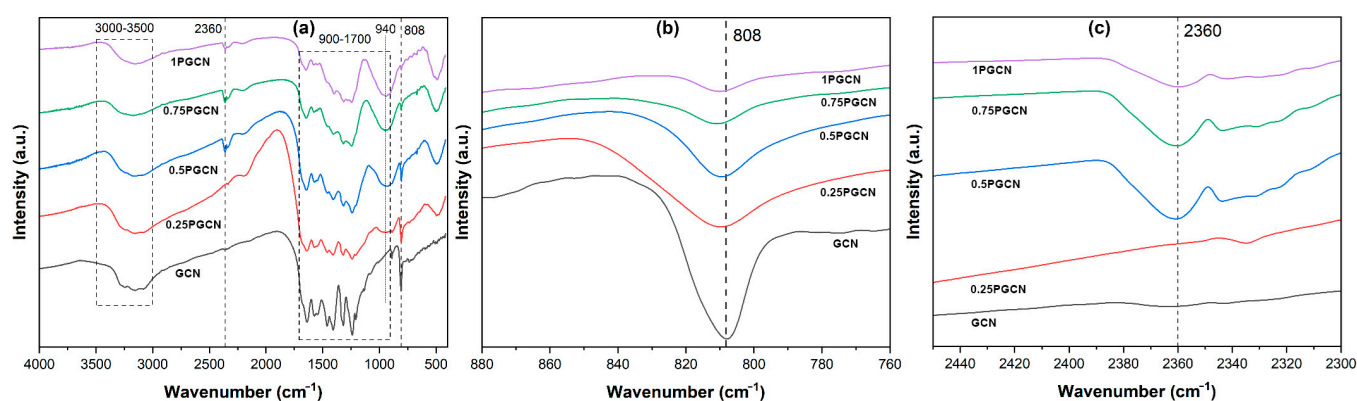


Figure 3. (a) FT-IR spectra of as-prepared photocatalysts. (b) The enlarged spectra at 808 cm^{-1} . (c) The enlarged spectra at 2360 cm^{-1} .

The surface features of the synthesized samples were examined using LSCM and FE-SEM. As shown in Figure 4a, the LSCM image ($20\times$ magnification) reveals the inherent surface texture of GCN. FE-SEM provided further insight into the dried sample morphology. The GCN displays a layered, plate-like structure with a relatively smooth surface, indicating multilayer stacking formed during the thermal polymerization step (Figure 4b). This graphite-like arrangement offers limited accessible active sites because of its low surface area and hydrophobic nature, making it less favorable for water adsorption during the reaction. The surface morphology of PGCN samples exhibits increased roughness, accompanied by disrupted layer-by-layer stacking (Figure 4c–f). The reduction in lateral layer dimensions primarily results from P_2O_5 interfering with the polymerization of DCDA during synthesis, hindering the formation of extended tri-s-triazine networks.

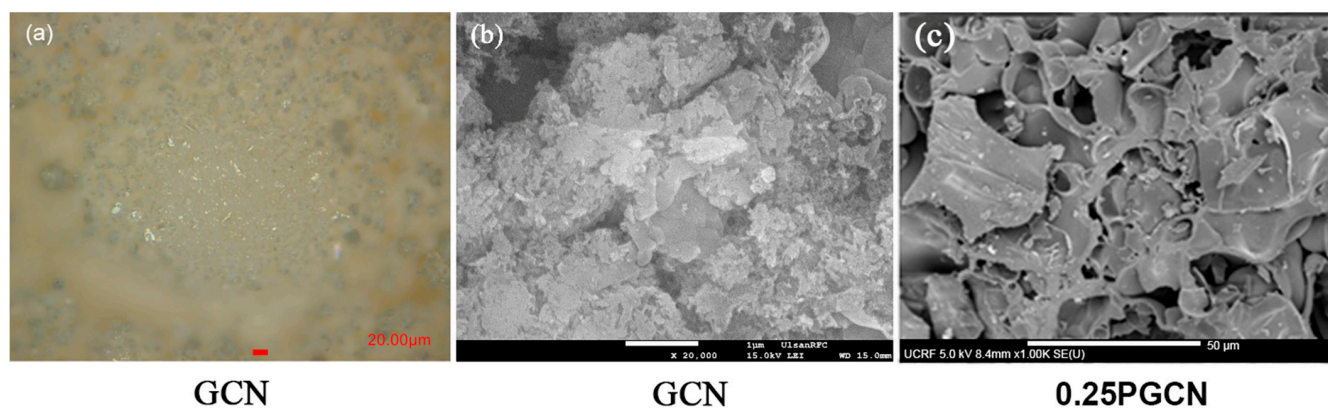


Figure 4. Cont.

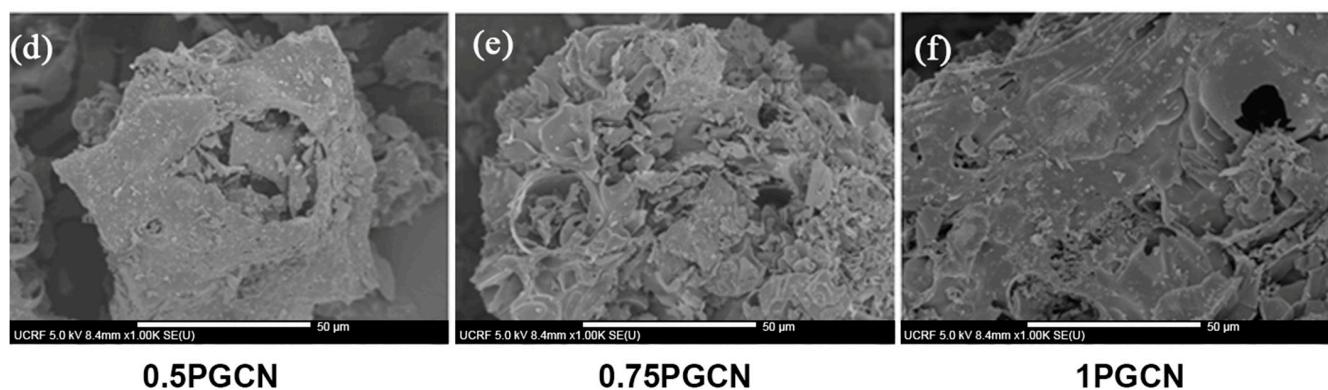


Figure 4. (a) LSCM image of GCN, and FE-SEM images of (b) GCN, (c) 0.25PGCN, (d) 0.5PGCN, (e) 0.75PGCN, and (f) 1PGCN samples.

2.2. Optical Bandgap and Charge Carrier Separation and Transfer

The optical properties of the as-prepared samples were studied using Ultraviolet-Visible Diffuse Reflectance Spectroscopy (UV-DRS). As shown in Figure 5a, the data were converted to absorption, and the two absorption peaks, approximately at 250–350 nm and 350–450 nm, are attributed to electronic transitions within the conjugated networks [27,28,31]. This confirms that the π -conjugated system of GCN is maintained after P-doping. P-doping in the bulk structure of GCN did not shift the intrinsic band-edge positions but increased absorption in the visible range (Figure 5a). This was also confirmed by the bandgap calculation, which showed an energy gap of around 2.7 eV for GCN and all P-doped samples (Figure 5b–f) [32]. In addition to estimating the bandgap energies, the plots also suggested the appearance of extra electronic transitions within the bandgap of the doped samples at around 1.8 eV, commonly referred to as mid-gap states (Figure 5b–f). These trap states allowed excitation by lower-energy photons, extending the light absorption range into the visible region [26], which was also observed in the UV-Vis results of the samples dispersed in reaction media (Figure S2).

P in the GCN structure substitutes for carbon in the heptazine units. P will take part in the conduction band (C formed conduction band) and create new energy states under the conduction band. Some of these new energy states act as recombination centers, while others increase the density of electrons in the band gap. The photoluminescence (PL) emission spectroscopy was utilized to illustrate the net effect of the energy states on the electronic structure of P-doped samples (Figure 6a) [33]. All PGCN samples displayed quenched PL signals compared with pristine GCN, reflecting improved charge carrier separation and a reduction in charge recombination. These findings demonstrate that the P-induced mid-gap states facilitate more effective charge separation and transfer. In the heptazine framework, phosphorus bonds with three neighboring nitrogen atoms and contributes its lone pair to the π -system, which enhances overall π -electron delocalization [26].

Therefore, it can cause higher charge density and more electron transfer within the tris-s-triazine units. Moreover, there is an optimum amount for P-doping. At first, increasing phosphorus decreases the recombination rate, as shown for samples 0.25PGCN and 0.5PGCN, but further increases in samples 0.75PGCN and 1PGCN, the recombination rate starts to increase. Therefore, the 0.5PGCN sample exhibits optimal charge-carrier separation and transfer among the doped samples. Additionally, time-resolved PL spectroscopy was used to study the kinetics of photoexcited charge carriers in GCN and doped samples. The decay spectra of GCN and PGCN samples are shown in Figure 6b. The prolonged average lifetime of 4.19 ns in the 0.5PGCN sample relative to that of 3.26 ns in the GCN sample clearly demonstrates the suppressed recombination rate of generated charge carriers and

facilitated charge carriers' dynamics. Moreover, the transport of charge carriers within the samples plays a decisive role in directing them toward the active sites where the reactions occur. To assess this charge-transport behavior, EIS measurements were performed. The Nyquist plots show that 0.5PGCN displays the smallest semicircle (Figure 6c), indicating its superior ability to reduce the charge-transfer resistance between the catalyst surface and the reactant species.

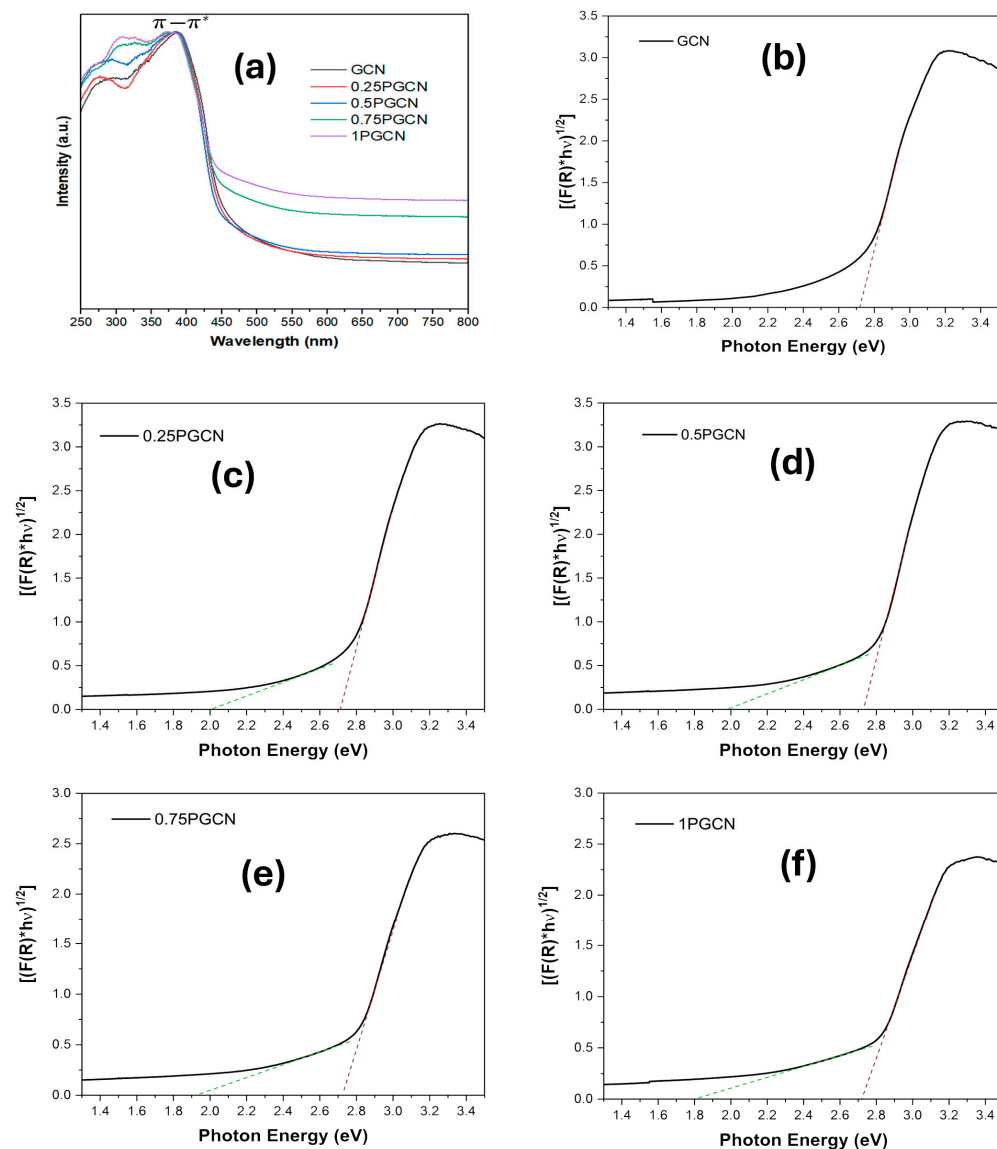


Figure 5. (a) UV-Vis Diffuse Reflectance spectra. Corresponding Tauc plot for band gap determination of (b) GCN, (c) 0.25PGCN, (d) 0.5PGCN, (e) 0.75PGCN, (f) 1PGCN.

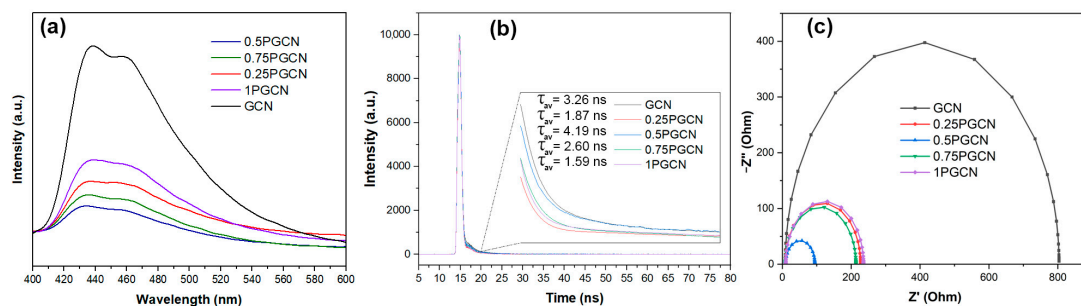


Figure 6. (a) PL emission spectra, (b) Time-resolved PL decay spectra, and (c) EIS Nyquist plots of GCN and PGCN samples.

2.3. Photocatalytic Performance and Mechanism

Photocatalytic hydrogen production was evaluated under simulated sunlight, employing 3 wt.% Pt-loaded photocatalysts, 10 vol% TEOA as the sacrificial agent, and Eosin Y as the photosensitizer (mass ratio 1:1 to catalyst). As shown in Figure 7, the average H_2 evolution rate was 656.35, 1748.81, 3396.59, 1940.67, and 1861.27 $\mu\text{mol h}^{-1} \text{g}^{-1}$ for GCN, 0.25PGCN, 0.5PGCN, 0.75PGCN, and 1PGCN, respectively (Figure 7b). Figure 7a shows the enhanced hydrogen evolution over time of the as-prepared photocatalysts. Particularly, the 0.5PGCN sample performed the highest H_2 evolution yield among all the PCGN samples, which is over 5 times higher than that of the GCN sample. Moreover, as shown in Table S3, the optimized PCGN sample in this work exhibited a photocatalytic H_2 evolution rate comparable to previously reported P-doped $g\text{-C}_3\text{N}_4$ photocatalysts under visible-light irradiation. This performance is achieved via a simple in situ polymerization approach using inexpensive precursors and controlled phosphorus content, highlighting the advantage of composition-dependent optimization while maintaining synthetic simplicity and scalability. The synergistic effects of phosphorus doping and heterostructure formation, which result in enhanced charge separation and transfer, improved light-harvesting capability, and increased dispersibility in the reaction medium, account for the significant improvement in photocatalytic performance.

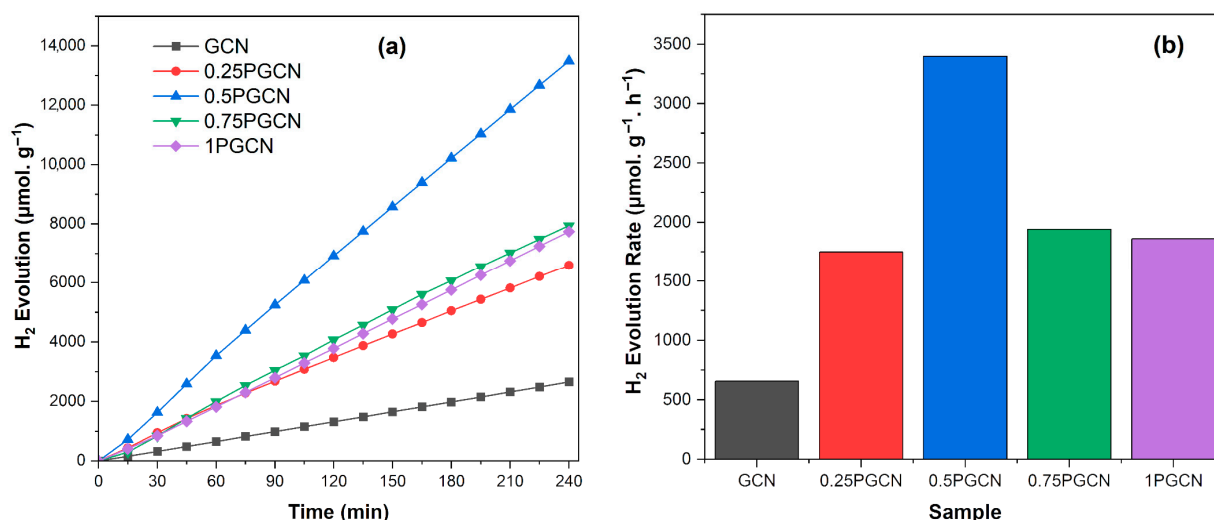


Figure 7. (a) Amount of H_2 produced vs. reaction time of GCN and PGCN samples. (b) Averaged H_2 evolution rate of the corresponding photocatalysts.

Figure 8 presents a proposed mechanism for the photocatalytic generation of H_2 . Under illumination from a solar simulator operating at 0.43 Sun, PCGN absorbs photons with energies meeting or exceeding its intrinsic bandgap, thereby promoting electron excitation from the valence band to the conduction band and generating holes. Concurrently, EY interacts with TEOA upon photoexcitation to yield EY^- , which shuttles electrons into the conduction band of $g\text{-C}_3\text{N}_4$. These electrons are then delivered to Pt cocatalyst particles, where the reduction of H^+ / H_2O takes place, forming H_2 . At the same time, the corresponding holes are quenched by oxidation of TEOA (Figure 8a) [1,34,35]. Because phosphorus possesses more valence electrons than carbon, substituting a C atom with a P atom within the $g\text{-C}_3\text{N}_4$ framework (Figure 8b) introduces additional electrons that can delocalize over the π -conjugated triazine units, forming positively charged P^+ centers (Figure 8b). These P^+ sites facilitate more efficient separation of photoexcited charge carriers. In addition, incorporating P into the basal plane of $g\text{-C}_3\text{N}_4$ generates mid-gap electronic

states (Figure 8a), enabling PGCN to be activated by lower-energy photons and enhancing visible-light absorption, consistent with the UV-DRS results.

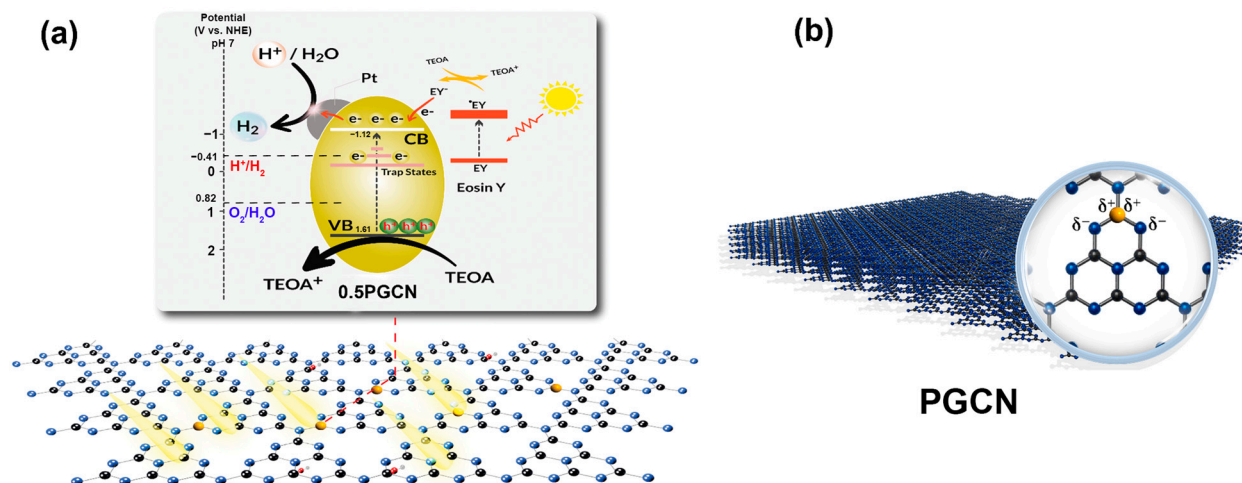


Figure 8. (a) Schematic illustration of the photocatalytic mechanism for 0.5PGCN sample under simulated sunlight irradiation, and (b) illustrated PGCN's structure.

3. Materials and Methods

3.1. Materials

Dicyandiamide (DCDA) and phosphorus pentoxide (P_2O_5) were used as a graphitic carbon nitride precursor and phosphorus source, respectively. DCDA, P_2O_5 , chloroplatinic acid solution (H_2PtCl_6 , 8 wt.% in H_2O), and triethanolamine (TEOA) were purchased from Sigma-Aldrich (Burlington, MA, USA). Eosin Y and ethyl alcohol were purchased from Samchun Chemicals (Seoul, Republic of Korea). High-grade argon (99.999%) was obtained from MS Gas Corporation (Busan, Republic of Korea). All chemical reagents were of analytical grade and were used as received without any further purification.

3.2. Synthesis Method of P-Doped $g-C_3N_4$ and Bulk $g-C_3N_4$

Typically, 60 g of P_2O_5 and 60 g of DCDA (mass ratio of 1:1) were well ground, placed in a U-form crucible and covered by aluminum foil, and then annealed at 550 °C for 5 h in a muffle furnace at a rate of 5 °C min⁻¹, followed by cooling naturally. The as-prepared sample was washed with DI water and ethyl alcohol by centrifugation at 10,000 rpm for 30 min, and the separated catalyst was vacuum dried at 70 °C for 24 h for further characterization. The sample was denoted as 1PGCN. Different mass ratio P_2O_5 :DCDA of 0.25:1, 0.5:1, 0.75:1 were also synthesized and named as 0.25PGCN, 0.5PGCN, 0.75PGCN, respectively. PGCN was the designation given to the P-doped $g-C_3N_4$ samples. The bulk graphitic carbon nitride, called GCN, was synthesized in a similar manner without using the phosphorus precursor. Briefly, 60 g of DCDA was placed in a U-shaped crucible, covered with aluminum foil, and calcined at 550 °C for 5 h at a heating rate of 5 °C min⁻¹, followed by natural cooling. The obtained product was washed with deionized water and ethanol and then dried at 70 °C for 24 h.

3.3. Photocatalytic Activity Toward Hydrogen Evolution

The photocatalytic H_2 production under simulated sunlight irradiation was measured to gauge the photocatalytic performance, employing TEOA as the sacrificial agent (10 vol%), Eosin Y as a photosensitizer (mass ratio 1:1 relative to the photocatalyst), and platinum as a cocatalyst. A calculated amount of platinum (3 wt.%) was decorated on the surface of the photocatalysts by photoreduction in aqueous solution with chloroplatinic acid as the

Pt precursor. Here, the suspension was vigorously stirred by a magnetic bar in the quartz reactor, and argon gas was used for purging the reactor at a flow rate of 25 sccm for 2 h, followed by applied simulated sunlight irradiation for 2 h. The products were washed with DI water by centrifugation at 10,000 rpm for 15 min, and the separated catalysts were dried at 70 °C for 24 h for further characterization.

The photocatalytic performance toward H₂ evolution was evaluated in a quartz reactor (300 mL) under simulated sunlight irradiation (the MAX-350's mirror solar module), which is able to shape the xenon spectrum similar to the sun spectrum in the wavelength range from 350 nm to 1100 nm. The incident light intensity directed onto the reaction solution was measured as 43.2 mW cm^{−2}. The produced H₂ was evaluated via an automated injection system coupled to online gas chromatography equipped with a TCD and a Carboxen 1000 column (Sigma-Aldrich, Burlington, MA, USA).

3.4. Characterizations

Analyzing the elemental compositions of samples was performed with a Flash 2000 elemental analyzer (Thermo Scientific, Waltham, MA, USA), and the concentration of P atoms was directly measured by ICP-OES (Agilent Technologies, Agilent 5110, Santa Clara, CA, USA). Fourier-transform infrared spectroscopy (FT-IR; Nicolet 380, Thermo Scientific, Waltham, MA, USA) was employed to identify the functional groups present in the synthesized photocatalysts. Field-emission scanning electron microscopy (FE-SEM; JSM-600F, JEOL, Tokyo, Japan) was used to examine the microstructure and morphology of the dried samples. The optical images of the resulting catalysts were captured using an Olympus laser scanning confocal microscope (LSCM, Olympus Corporation, Tokyo, Japan). The crystal structures of the prepared samples were examined using high-resolution powder X-ray diffraction (HRP-XRD; Rigaku D/MAZX 2500 V/PC, Tokyo, Japan) equipped with a Cu K α radiation source ($\lambda = 1.5415 \text{ \AA}$) and operated at a scanning speed of 2° (2 θ) per minute. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, Waltham, MA, USA) was employed to analyze the elemental composition, chemical states, and electronic states of the samples. UV-vis absorption spectra (Specord 210 Plus, Analytik Jena, Jena, Germany) together with UV-vis diffuse reflectance spectroscopy measurements (UV-Vis-NIR (%R), Cary 5000, Agilent, Santa Clara, CA) were recorded to study the optical properties of the photocatalysts. Photoluminescence measurements were performed at room temperature using a 473 nm diode laser on a Cary Eclipse fluorescence spectrophotometer (Agilent Technologies, Santa Clara, CA, USA). Time-resolved PL spectra were obtained with a FS5 spectrofluorometer (Edinburgh Instruments Ltd., Livingston, UK) under 400 nm laser excitation.

3.5. Electrochemical Measurement

Electrochemical impedance spectroscopy (EIS) was conducted using a VSP electrochemical workstation (BioLogic Science Instruments, Seyssinet-Pariset, France) in a standard three-electrode configuration under simulated sunlight at room temperature. The EIS tests were performed at open-circuit conditions after a 10 min stabilization period, using a frequency range of 100 kHz to 0.1 Hz and an amplitude of 10 mV at a DC potential of +0.8 VSCE. A spray-coating method was used to prepare the working electrode. Following typical preparation steps, 0.5 mg of the catalyst powder was ultrasonically dispersed in ethanol for 30 min, after which the suspension was spray-coated onto an FTO substrate (1 cm² spray area, other area was covered by black tape) placed on a 90 °C hotplate. A 1 M KOH solution (10 mL) served as the electrolyte. The reference electrode was a RE-61AP (Hg/HgO) electrode, and a platinum wire was used as the counter electrode. The SVC-3 voltammetry cell and electrodes were supplied by ALS Co., Ltd. (Tokyo, Japan).

4. Conclusions

Engineering phosphorus doping into the g-C₃N₄ framework was achieved through a facile in situ polymerization of commercially available, low-cost P₂O₅ and DCDA as the phosphorus and bulk g-C₃N₄ precursors, respectively, carried out at 550 °C in air. The P doping level was optimized at 9.35 at.%, which preserved the structural features of g-C₃N₄, as confirmed by HRP-XRD, FT-IR, and XPS. At this doping level, significant electronic modifications were introduced, leading to improved photoinduced charge separation and transfer, along with enhanced visible-light absorption, as demonstrated by UV-DRS, PL, TR-PL, and EIS results. Based on a systematic optimization of phosphorus content, it was possible to establish a clear relationship between structure, electronic properties, and performance for P-doped g-C₃N₄, which provides composition-dependent performance for photocatalytic H₂ evolution. In the PGCN lattice, phosphorus atoms replace the carbon sites of the heptazine units, forming P-N coordination bonds. Furthermore, the identification of distinct P-doping sites in the corner and bay carbon positions of the heptazine motifs by the transparent FT-IR vibrational features and P 2p core-level deconvoluted peaks provides new spectroscopic criteria for tracking P-doping configurations in g-C₃N₄. Although incorporating P into the framework reduced the conduction band minimum and the valence band maximum pairs of g-C₃N₄ photocatalyst, the doping simultaneously improves photocatalytic behavior, creating a seesaw-type relationship. Thus, optimizing the P content to the point where these effects balance yielded the highest photocatalytic performance. The 0.5PGCN sample achieved a hydrogen evolution rate as high as 3396.59 μmol h^{−1} g^{−1}, demonstrating its strong potential as a bulk material for future photocatalysis research.

Supplementary Materials: The following Supporting Information is available at <https://www.mdpi.com/article/10.3390/catal16010088/s1>; Table S1. Elemental compositions of the surface samples analyzed by XPS; Table S2. Peak area percentage of N2-C=N bond in the heptazine units of the as-prepared samples; Figure S1. Deconvoluted P 2p XPS spectra of PGCN samples; Figure S2. (a) UV-DRS spectra of as-prepared dried samples, (b) corresponding Tauc plot for band gap determination. (c,d) UV-Vis spectra of the photo-catalysts in the reaction media and enlarged spectra of 0.5PGCN, 0.75PGCN, 1PGCN samples; Figure S3. Ultraviolet photoelectron spectroscopy (UPS) spectrum of 0.5PGCN sample; Table S3. Comparison of photocatalytic H₂ evolution performance of reported g-C₃N₄-based heteroatom-doped composites. Refs. [36–49] are cited in Supplementary Materials.

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