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Graphitic-C$_3$N$_4$-hybridized Ag$_3$PO$_4$ tetrahedron with reactive {111} facets to enhance the visible-light photocatalytic activity

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Graphitic-C$_3$N$_4$-hybridized Ag$_3$PO$_4$ tetrahedron with reactive {111} facets was prepared though a facile solvent evaporation method and applied for the photocatalytic degradation of methyl blue (MB) in aqueous solution and removal of NO at the indoor air level under visible light irradiation (>400 nm). On top of the superior photocatalytic performance of highly reactive {111} facets of tetrahedral Ag$_3$PO$_4$, the hybridization with g-C$_3$N$_4$ was confirmed to further improve the photocatalytic activity, and the content of g-C$_3$N$_4$ had a great influence on the photocatalytic activity. The photocatalytic activity enhancement of g-C$_3$N$_4$/Ag$_3$PO$_4$ {111} hybrid photocatalysts could be ascribed to the efficient separation of electron-hole pairs through a $Z$-scheme system composed of Ag$_3$PO$_4$, Ag and g-C$_3$N$_4$, in which Ag particles acted as the charge separation center. Furthermore, $h^-$ and $O^-$ played the major roles in the photocatalysis process. This work suggested that the synthesized g-C$_3$N$_4$/Ag$_3$PO$_4$ {111} hybrid would be a promising visible light driven photocatalytic material for environmental remediation.

1 Introduction

The growing concerns about environmental pollution and energy crises have attracted extensive research on solar energy utilization. Semiconductor photocatalysis technology is believed to be a promising clean, low-cost, and environmentally friendly approach to cope with these crises [1,2]. Unfortunately, TiO$_2$ as the most widely employed semiconductor photocatalyst is only active under UV light irradiation (less than 5% of solar light). Therefore, the development of efficient visible light driven photocatalysts is a major challenge in this field. Recently, silver orthophosphate (Ag$_3$PO$_4$) has been reported as an active visible light driven photocatalyst for decolorization of organic pollutants and water photooxidation, and the photocatalytic performance of Ag$_3$PO$_4$ is significantly higher than that of currently known visible light photocatalysts, such as TiO$_2$, SnO$_2$, ZnO, CeO$_2$, Fe$_2$O$_3$, Bi$_2$WO$_6$, BiPO$_4$, BiOI, WO$_3$, oxidized graphene, graphene, carbon nanotubes, etc.) is one of the effective methods because they can enhance the photogenerated charges separation [9-20].

A novel metal-free photocatalyst, named graphitic carbon nitride (g-C$_3$N$_4$) with layered structure similar to graphene is recognized as a promising candidate for photodegradation of organic pollutants and photocatalytic hydrogen evolution under visible-light irradiation due to its remarkable structure, mechanical and electronic properties. The two-dimensional planar structure with $\pi$-conjugated system benefits the transport of charge carriers, and its high nitrogen content enable g-C$_3$N$_4$ to provide more active reaction sites. Therefore, g-C$_3$N$_4$ is widely used to couple with other semiconductor photocatalysts for enhancement of their photocatalytic activity, such as, TiO$_2$, SiO$_2$, ZnO, Al$_2$O$_3$, WO$_3$, BiVO$_4$, Ag$_2$CO$_3$, Ag$_3$VO$_4$, Bi$_2$MoO$_6$, In$_2$O$_3$ and so on [21-30]. Currently, a few studies have been focused on combining g-C$_3$N$_4$ with Ag$_3$PO$_4$. Zhang et al [31] used the ion-impregnating method to synthesis graphitic carbon nitride/silver phosphate (g-C$_3$N$_4$/Ag$_3$PO$_4$) bulk heterojunction, and it showed enhanced photocatalytic activity for decolorization of RhB. Santosh Kumar et al [32] developed a facile and reproducible template free in situ precipitation method for the synthesis of Ag$_3$PO$_4$ nanoparticles on the surface of a g-C$_3$N$_4$ photocatalyst at room temperature with improved photocatalytic performance. Katsumata et al [33] used a facile in situ precipitation method to prepare g-C$_3$N$_4$/Ag$_3$PO$_4$ which displayed the higher photocatalytic activity than pure g-C$_3$N$_4$ and Ag$_3$PO$_4$ for the decolorization of methyl orange (MO).

Furthermore, the synthesis of crystals with highly reactive facets has sparked cosmic research interest because crystals usually exhibit fascinating surface-dependent properties. For Ag$_3$PO$_4$, evidenced by both theoretical and experimental studies, the {111} facets of Ag$_3$PO$_4$ are the most reactive facets among the {111}, {110} and {100} facets due to their highest surface energy [34]. The order of the average surface energies of Ag$_3$PO$_4$ reported in the literature is 1.65 J m$^{-2}$ for {111} > 1.31 J m$^{-2}$ for {110} > 1.10 J m$^{-2}$ for {100} [35]. In consideration of this, we proposed that combining two strategies (exposed facets control and hybridization) to improve photocatalysis efficiency of Ag$_3$PO$_4$ together. Therefore, g-C$_3$N$_4$ hybridized Ag$_3$PO$_4$ with reactive {111} facets photocatalyst is expected to...
display excellent photocatalytic performance under visible light irradiation. To the best of our knowledge, g-C3N4/Ag3PO4 \{111\} hybrid has not been reported in literatures so far. Furthermore, no one has ever reported the use of g-C3N4/Ag3PO4 photocatalyst for the photocatalytic degradation of gaseous nitrogen monoxide (NO) thus far. Therefore, another significance of our work is that the newly developed photocatalyst is for the first time applied to photocatalytic NO removal, which would expand the research and application of g-C3N4/Ag3PO4 materials.

In this paper, we developed a novel photocatalyst, g-C3N4/Ag3PO4 \{111\} hybrid, via a solvent evaporation process. The photocatalytic performance was evaluated by photodegradation of methylene blue (MB) in aqueous solution and removal of NO at the indoor air level under visible light irradiation (>400 nm). The effect of the ratio of g-C3N4 and Ag3PO4 on photocatalytic activity was also investigated. In addition, the enhancement mechanism of the photocatalytic activity of g-C3N4/Ag3PO4 \{111\} was also discussed.

2 Experimental

2.1 Preparation of few-layer g-C3N4

The few-layer g-C3N4 was prepared by polymerization and chemical exfoliation method. Typically, melamine (C3H6N3) was put into a crucible, and then heated at 600 °C for 3 h. After the product cooled to room temperature, the resultant yellow powder was then collected and ground into a powder. Subsequently, as-prepared powder was treated with acetic acid (HAc) for chemical exfoliation. Finally, the sample of acid treatment was dispersed into ethanol, and then executed with ultrasonic-processing continuously for about 4 hours. The initial formed suspension was then centrifuged to remove the residual unexfoliated g-C3N4 and the centrifugal liquid was obtained for further use.

2.2 Preparation of g-C3N4/Ag3PO4 \{111\} hybrid

Tetrahedral Ag3PO4 microcrystals (TE Ag3PO4) with exposed \{111\} facets were hybridized with g-C3N4 through a simple two-step route. In a typical process, 0.17 g silver nitrate (AgNO3) ethanol solution was slowly dropped into 0.1 M phosphoric acid (H3PO4) ethanol solution [35]. After stirring at 60 °C for 1 h, the obtained yellow precipitate was washed with ethanol several times, and the TE Ag3PO4 powders were obtained. Subsequently, the Ag3PO4 powders were added into a certain amount of g-C3N4 dispersion. The mixture was sonicated for 30 min to completely disperse Ag3PO4 crystals and then stirred until the ethanol was volatilized completely [36]. The obtained samples were referred to as xCA with x representing the weight ratios of g-C3N4 and Ag3PO4, and x varied from 2% to 20%. For comparison, the "Blank" was fabricated by mechanically blending of g-C3N4 and Ag3PO4 (wG-C3N4/wAg3PO4=10%). Meanwhile, irregular Ag3PO4 crystals (IR Ag3PO4) were synthesized by direct precipitation method as follows: diisodium hydrogen phosphate (Na2HPO4) solution was added drop by drop to the AgNO3 solution under stirring. After stirring for 1 h, the above suspension experienced centrifugation, washing and drying.

2.3 Characterization

X-ray diffraction (XRD) patterns of the samples were identified using a Shimadzu XRD-6000 powder diffractometer (Cu Kα radiation). The morphology observations were observed on a JSM-6390A scanning electron microscope (SEM) equipped with energy-dispersive X-ray (EDS) and a Tecnai G2F20S-TWIN transmission electron microscope (TEM). Besides, the Fourier transform infrared spectra (FTIR) of the products were recorded using PerkinElmer Frontier. UV-Vis absorption spectra were recorded using a Shimadzu UV-3600 UV/Vis/NIR spectrophotometer with BaSO4 as a reference. X-ray photoelectron spectroscopy (XPS) was obtained with a Kratos AXIS NOVA spectrometer. The surface areas of samples were measured using the Brunauer-Emmett-Teller ( BET) method by N2 adsorption Quantachrome NOVA 2000e, and photoluminescence (PL) measurements were carried out on a Hitachi F-7000 florescence spectrophotometer.

2.4 Photocatalytic degradation of MB

The as-obtained samples were evaluated by degradation of MB in aqueous solution under visible light irradiation. In a typical process, 40 mg photocatalysts were added into 50 mL MB solution (10 mg/L). Prior to irradiation, the suspensions were magnetically stirred in dark for 30 min to ensure the adsorption-desorption equilibrium of MB on the surface of the photocatalysts. 300 W xenon lamp (Microsolar 300) with a 400 nm cut off filter was used as visible light source, which was positioned on the top of the reaction cell. The above suspensions with air blown were photoirradiated under continuous stirring throughout the test at room temperature. At regular intervals, 2 mL suspensions were sampled and centrifuged, the upper clear liquid was evaluated according to the absorbance at recording the maximum absorption band (664 nm for MB) using a Shimadzu UV-3600 UV/Vis/NIR spectrophotometer.

2.5 Photocatalytic removal of NO

The photocatalytic experiments for NO removal were performed at ambient temperature in a continuous flow reactor [37] (Fig. S1, Supporting Information). For each experiment, 0.1g catalyst powders were set in the center of the reactor by a dish with a diameter of 6.5 cm. The reactant gas mixture (the concentration of NO was 600 ppb) was fed into the reactor with a total flow rate of 400 mL/min, and the residence time of mixture gas in the reaction vessel was about 57 s. After the adsorption-desorption equilibrium was achieved, the 300 W xenon lamp (Microsolar 300) with a 400 nm cut off filter was turned on. The concentration of NO was continuously measured by an electrochemical NO analyzer (Shenzhen Jishunan Technology Co., Ltd., JS9A-NO). The NO conversion (η) was calculated as: \( \eta(\%) = (1 - C/C_0) \times 100\% \), where C is the outlet concentration of NO after reaction for time t, and C0 represents the inlet concentration after achieving the adsorption-desorption equilibrium.

2.6 Active species trapping experiment

For the trapping of photogenerated active species during photocatalytic reactivity, hydroxyl radicals (•OH), superoxide radical (O2•−) and holes (h+) were investigated using isopropanol (IPA, a quencher of •OH), p-benzoquinone (BQ, a quencher of O2•−) and triethanolamine (TEOA, a quencher of h+) respectively [38]. The process of active species trapping experiment was similar to the MB
photodegradation experiment. Before adding the photocatalyst, scavengers were introduced into the MB solution respectively.

3 Results and discussion

3.1 Characterization of the samples

X-ray diffraction (XRD) patterns of g-C3N4, Ag3PO4 and 10CA are shown in Fig. 1. For g-C3N4 sample, the two peaks at 13.1° and 27.4° correspond to the (100) and (002) planes of the tetragonal phase g-C3N4 (JCPDS 87-1526), respectively. All diffraction peaks of the Ag3PO4 sample can be well indexed to the cubic-phase Ag3PO4 (JCPDS 06-0505). The diffraction pattern of Ag3PO4 shows peaks at 21.1, 30.0, 33.6, 36.8, 42.7, 48.1, 52.9, 55.3, 57.5, 61.9, 66.1, 70.1, 72.1 and 74.1, which correspond to planes (110), (200), (210), (211), (220), (310), (222), (320), (321), (400), (330), (420), (421) and (332), respectively. There are no peaks of impurities, and the strong and sharp peaks indicate the high crystallinity of the Ag3PO4 sample. The XRD pattern of the 10CA is similar to that of the bare Ag3PO4, and the characteristic peaks of g-C3N4 are not observed due to the exfoliation of g-C3N4 [25].

The surface morphologies of g-C3N4, Ag3PO4 and g-C3N4/Ag3PO4 {111} are shown in Fig. 2. As shown in Fig. 2a, the synthesized TE Ag3PO4 samples are tetrahedral particles with the particle size of 0.4~2.1 µm and average size of 0.74 µm, and the tetrahedron is enclosed completely by four perfect equilateral triangles, which consists of {111} facets. IR Ag3PO4 are near-spherical particles with the particle size of 0.3~1 µm (Fig. 2b). Fig. 2c and Fig. 2e show the SEM and TEM images of pure g-C3N4, and the gauze-like and sheet-like morphology can be clearly observed, indicating that g-C3N4 nanosheets with few-layer structure can be prepared by a simple chemical exfoliation process. In the g-C3N4/Ag3PO4 {111} hybrid (Fig. 2d and Fig. 2f), g-C3N4 is overlaid on the surface of Ag3PO4 particles or scattered around Ag3PO4 particles. During ultrasonication and ethanol evaporation process, the g-C3N4 assembled on the surface of Ag3PO4 or gathered around Ag3PO4 to achieve a minimum surface energy [39,40]. Comparing with the pure Ag3PO4, the g-C3N4 not only prevents the agglomeration of Ag3PO4 particles, but also forms heterojunction with Ag3PO4 in the composite. The morphology studies revealed that g-C3N4 could serve as a support to bound Ag3PO4 particles in the hybrid system, which leads to the formation of interfacial contact between g-C3N4 and Ag3PO4 and to a favorable photogenerated charge transfer at the interface when using as hybrid photocatalyst. The energy-dispersive X-ray spectrometry (EDS) analysis of 10CA hybrid is shown in Fig. S3, and C, N, O, P and Ag as major elements are detected from sample, further suggesting the existence of C3N4 and Ag3PO4.

The FT-IR spectra of g-C3N4, Ag3PO4 and g-C3N4/Ag3PO4 hybrids are shown in Fig. 3. For the pristine g-C3N4, it reveals a typical molecular structure of graphitic carbon nitride. The peaks at 1634, 1574, 1460, 1405, 1317 and 1238 cm\(^{-1}\) are attributed to the stretching modes of C-N heterocycles, and the peak at 807 cm\(^{-1}\) is the characteristic breathing mode of triazine units [41]. The broad band at 3000-3400 cm\(^{-1}\) is due to uncondensed terminal amino groups (\(\equiv\)NH or \(\equiv\)NH) at the defect sites of the aromatic ring [42]. For pure Ag3PO4, the observed strong peaks at 548 and 951 cm\(^{-1}\) may be attributed to the characteristic peaks of PO\(^{3-}\). In addition, all characteristic peaks corresponding to g-C3N4 and
Ag$_3$PO$_4$ appear in g-C$_3$N$_4$/Ag$_3$PO$_4$ hybrids, and the relative intensity of the peaks of g-C$_3$N$_4$ increases with the increase of g-C$_3$N$_4$ contents in composites.

The UV-Vis absorption spectra of the samples were investigated and shown in Fig. 4. Pure g-C$_3$N$_4$ can absorb visible light with wavelengths shorter than 440 nm, whereas pure Ag$_3$PO$_4$ has a broader absorption in the visible region with an absorption edge at about 530 nm. The g-C$_3$N$_4$/Ag$_3$PO$_4$ hybrids exhibit the two absorption edges at both 440 and 530 nm, suggesting that these samples contain both g-C$_3$N$_4$ and Ag$_3$PO$_4$ semiconductors.

According to the plot of (F(R)hv)$^{1/2}$ vs hv, the band gaps ($E_g$) of Ag$_3$PO$_4$ and g-C$_3$N$_4$ were estimated to be 2.51 and 3.08 eV, respectively (Fig. S3, Supporting Information). The band structure of g-C$_3$N$_4$/Ag$_3$PO$_4$ hybrids, and the relative intensity of the peaks of g-C$_3$N$_4$ increases with the increase of g-C$_3$N$_4$ contents in composites.

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\[ E_{VB} - E_{CB} = \chi \]

where $E_{VB}$ and $E_{CB}$ are the energy of free electrons on the hydrogen scale and the energy; $E_c$ is the energy of free electrons on the hydrogen scale (about 4.5 eV vs NHE); $E_g$ is the band gap energy of the semiconductor. Thus, the calculated values of the CB and VB potentials of Ag$_3$PO$_4$ and g-C$_3$N$_4$ are listed in Table 1.

The elemental composition and chemical status of 10CA were further characterized by X-ray photoelectron spectroscopy (XPS), as shown in Fig. 5. It is found that the two C 1s peaks are located at 284.6 and 288.1 eV, respectively (Fig. 5a). The former is ascribed to the contaminated carbons, whereas the latter one is assigned to sp$^2$-bonded carbon (N$\equiv$C$\equiv$N) [38]. The N 1s peaks can be deconvoluted into three fitted peaks at binding energies of 398.1 (N1), 399.6 (N2) and 403.9 eV (N3) (Fig. 5b), respectively. The dominant N1 is commonly attributed to sp$^2$-bonding N atoms involved in triazine rings, while the N2 is assigned to bridging N atoms in N-C or N bonded with H atoms. The very weak N3 can be assigned to sp$^2$-bonded carbon (N$\equiv$C$\equiv$N) [38]. The N 1s peaks can be deconvoluted into three fitted peaks at binding energies of 398.1 (N1), 399.6 (N2) and 403.9 eV (N3) (Fig. 5b), respectively. The dominant N1 is commonly attributed to sp$^2$-bonding N atoms involved in triazine rings, while the N2 is assigned to bridging N atoms in N-C or N bonded with H atoms. The very weak N3 can be assigned to the charging effects or positive charge localization in heterocycles and the cyano-group [44]. As shown in Fig. 5c, the peaks of Ag 3d5/2 and Ag 3d3/2 are located at 368 and 374 eV, respectively. These two bands could be further deconvoluted into two peaks. The strong peaks at 367.8 and 373.8 eV are assigned to Ag$^+$ of Ag$_3$PO$_4$, while the weak peaks at 369.2 and 375.3 eV belongs to the metallic Ag species [45], which originates in the formed metallic Ag during the hybrid preparation. Because g-C$_3$N$_4$ has the electron-rich structure, and [111] facets of Ag$_3$PO$_4$ only contain Ag$^+$ cations proved by the surface atomic configurations studies [46], g-C$_3$N$_4$...
can easily provide electrons to Ag⁺ on the surface of Ag₃PO₄ to form Ag⁺ particles which contact with both Ag₃PO₄ and g-C₃N₄ in the hybrid catalyst. For the O 1s (Fig. 5d), the peak at 530.6 eV is assigned to the crystal lattice oxygen, while the peak at 532.1 eV is related to adsorbed oxygen [45], which favours the degradation of organic pollutants in water and gaseous pollutants in the gas phase. The spectrum of P 2p is shown in Fig. 5c, and a broad peak in the range of 130 to 136 eV appears to be attributable to the P element in PO₄³⁻ [47].

3.2 Photocatalytic degradation of MB

Photocatalytic tests of samples were evaluated by degradation of MB under visible light irradiation (λ > 400 nm), and the results are shown in Fig. 6. Fig. 6a shows the remaining MB in solution after adsorption equilibrium and the MB degradation (C/C₀) with the irradiation time over the catalysts. After adsorption equilibrium, 65%, 94% and 90% of MB remains in the solution with the g-C₃N₄, Ag₃PO₄ and 10CA photocatalysts, respectively, and the adsorptive ability of g-C₃N₄/Ag₃PO₄ hybrids increases with the increasing contents of g-C₃N₄ in composites. It is obvious that g-C₃N₄ has superior adsorptive ability because aromatic molecules such as MB could be adsorbed on the g-C₃N₄ surface with offset face to face orientation via π-π conjugation until an adsorption-desorption equilibrium is reached. By modification with g-C₃N₄, the adsorptivity of Ag₃PO₄ to MB is enhanced, which is beneficial to the photodecomposition of MB. MB self-photolysis without catalyst under visible light irradiation is not observable, which indicates that MB self-photolysis is negligible in the process of photocatalysis. It can be found that the photocatalytic activity of 10CA is the highest among all samples under visible light irradiation: about 99% of MB is photocatalytically degraded after 14 minutes irradiation. A pseudo-first-order kinetic model was employed to fit the degradation data by using the equation [12]: In (C/C₀) = kt, where k is the apparent reaction rate constant (min⁻¹), and C and C₀ are the adsorption equilibrium concentration and MB concentration at reaction time t. The results are illustrated in Fig. 6b. It can be clearly seen that the TE Ag₃PO₄ (0.2093 min⁻¹) shows better photocatalytic activities than that of IR Ag₃PO₄ (0.0808 min⁻¹), and the k of TE Ag₃PO₄ is about 2.59 times higher than that of IR Ag₃PO₄ due to the higher surface energy and more active sites of {111} facets. Meanwhile, except for 20CA, the photocatalytic activities of g-C₃N₄/Ag₃PO₄ hybrids are higher than that of bare Ag₃PO₄, greatly depending on the g-C₃N₄ content. The photodegradation rates first increase and then decrease with rising g-C₃N₄ content, and 10CA displays the highest degradation rate. The k of 10CA is 0.3214 min⁻¹, which is 1.54 and 8.10 times as high as that of pure Ag₃PO₄ (0.2093 min⁻¹) and pure g-C₃N₄ (0.0397 min⁻¹). In addition, the “Blend” (Wg-C₃N₄/WAg₃PO₄=10%) is labeled as for reference to explain the difference in physical mixture and hybrid from solvent evaporation process. The “Blend” exhibits similar adsorptivity to the hybrid, while it shows related lower photocatalytic performance than 10CA, even lower than pure Ag₃PO₄. These results clearly demonstrate that the remarkable enhancement of photoactivity is only achieved when hybridized with g-C₃N₄ by the solvent evaporation process and the interfacial interaction between these two components in the hybrid makes the photocatalytic reaction more efficient than that in physical mixture. Moreover, Fig S6a shows photocatalytic degradation of MB over

Fig. 6 (a) Photocatalytic degradation curves of MB over samples under the visible-light irradiation (> 400 nm); (b) the kinetic constants of photocatalysts; (c) UV-Visible spectra of MB at different visible irradiation times in the presence of 10CA.

Fig. 7 (a) Plots of the removal ratio of NO vs irradiation time on different photocatalysts under visible light (> 400 nm); (b) reaction rate constant (min⁻¹) in the presence of the as-prepared photocatalysts under visible light (> 400 nm).
g-$\text{C}_3\text{N}_4$/Ag$_3$PO$_4$(IR), BiVO$_4$ and P25 under the visible light irradiation (> 400 nm). g-$\text{C}_3\text{N}_4$/Ag$_3$PO$_4$(111) showed obvious higher photocatalytic performance than that of g-$\text{C}_3\text{N}_4$/Ag$_3$PO$_4$(IR) and dramatically higher than that of BiVO$_4$ and P25, indicating the photocatalytic performance in the single material (TE Ag$_3$PO$_4$) is still maintained in the heterojunction and the high efficiency of C$_3$N$_4$/Ag$_3$PO$_4$(111) for photocatalytic degradation of MB.

3.3 Photocatalytic removal of NO

NO in low concentration ppb levels are representative of indoor and outdoor air pollutants. The as-prepared samples were employed in the photocatalytic removal of NO from air to investigate their potential capability for gas-phase pollutant degradation. Fig. 7 shows the photodegrading NO ability of samples. It is found that the photolysis of NO without light or without photocatalyst under visible light irradiation is negligible, indicating removal NO is a photocatalytic process. It is obvious from Fig. 7a that the rapid increase in NO conversion with irradiation time is observed over all the photocatalysts, and then approach a steady state. For pure g-$\text{C}_3\text{N}_4$, IR Ag$_3$PO$_4$ and TE Ag$_3$PO$_4$ samples, 20.9%, 15.0% and 32.4% removal of NO is obtained at continuous system. In the case of Ag$_3$PO$_4$ hybridized with g-$\text{C}_3\text{N}_4$, the removal ratios of NO increase. The g-$\text{C}_3\text{N}_4$/Ag$_3$PO$_4$ {111} removal ability of NO improves with the increase of g-$\text{C}_3\text{N}_4$ content, and then decrease with the further added. The optimal rate of g-$\text{C}_3\text{N}_4$ and Ag$_3$PO$_4$ is 10%, whose removal ratio of NO is 49.3%. The removal ratio of NO of "Blend" is 28.9%, which is much lower than that of the 10CA heterojunction, implying that the heterojunction formed between Ag$_3$PO$_4$ and g-$\text{C}_3\text{N}_4$ plays a major role in improving the photocatalytic activity. In order to produce a further comparison among the tested samples, first order rate constants were calculated from the experimental data relative to the first 1 min of irradiation [48,49]. The data are displayed in Fig. 7b. It can be clearly seen that the $k$ of TE Ag$_3$PO$_4$ (0.3675 min$^{-1}$) is about 2.71 times higher than that of IR Ag$_3$PO$_4$ (0.1357 min$^{-1}$), the $k$ of 10CA (0.633 min$^{-1}$) is nearly 1.72 and 2.91 times higher than that of pure TE Ag$_3$PO$_4$ and g-$\text{C}_3\text{N}_4$ (0.2173 min$^{-1}$), respectively. Furthermore, the performance of photocatalytical removal of NO over g-$\text{C}_3\text{N}_4$/Ag$_3$PO$_4$(IR), BiVO$_4$ and P25 under the visible light irradiation (> 400 nm) are shown in Fig 6Sb. Fig S6b shows g-$\text{C}_3\text{N}_4$/Ag$_3$PO$_4$(111) has obvious higher photocatalytic performance than that of g-$\text{C}_3\text{N}_4$/Ag$_3$PO$_4$(IR), BiVO$_4$ and P25.

The reusability and stability of the as-synthesized photocatalyst was studied by the circulating runs, and they were performed five times on 10% g-$\text{C}_3\text{N}_4$/Ag$_3$PO$_4$(111) and pure Ag$_3$PO$_4$ samples. The corresponding results are shown in Fig. 8. As exhibited in Fig. 8a, the photocatalytic performance of pure Ag$_3$PO$_4$ shows a significant reduction during the repeated photocatalytic reactions, but the photocatalytic activity of the 10CA shows just a little loss after five cycling runs of photodegradation of MB. Fig. 7(b) shows after 5 successive NO degradation, the photocatalytic activities of the 10CA is evidently more stable than that of pure Ag$_3$PO$_4$. There are two possible reasons to explain the enhanced stabilities of g-$\text{C}_3\text{N}_4$/Ag$_3$PO$_4$ hybrid photocatalysts compared with pure Ag$_3$PO$_4$ crystals. First, C$_3$N$_4$ coated on the surface of Ag$_3$PO$_4$ or scattered around Ag$_3$PO$_4$ can inhibit the dissolution of Ag$_3$PO$_4$ in aqueous solution, which will enhance its structural stability. Second, the photocatalytic performance deteriorates quickly due to the photo-corrosion of pure Ag$_3$PO$_4$ particles by the rich excited electrons on the surface of Ag$_3$PO$_4$. However, the rich excited electrons on the surface of Ag$_3$PO$_4$ in the g-$\text{C}_3\text{N}_4$/Ag$_3$PO$_4$ hybrids are transferred by the special structure of the g-$\text{C}_3\text{N}_4$/Ag$_3$PO$_4$ hybrids resulting in preventing Ag$_3$PO$_4$ from photo-corrosion.

3.4 Photocatalytic mechanism

It is well known that the high surface area and high separation efficiency of photogenerated electrons and holes are beneficial for the photocatalytic activity. Fig. S5 shows the nitrogen adsorption-desorption isotherms of pure Ag$_3$PO$_4$ and 10CA. The specific surface area of pure Ag$_3$PO$_4$ is 4.1 m$^2$/g. After coupling Ag$_3$PO$_4$ particles with g-$\text{C}_3\text{N}_4$, the specific surface area increases to 11.2 m$^2$/g. Meanwhile, PL spectrum analysis was carried out to investigate the separation efficiency of photogenerated electrons.

![Fig. 8. Cycling runs for the photocatalytic activity over pure Ag$_3$PO$_4$ and 10CA under visible light irradiation: (a) photocatalytic degradation of MB; photocatalytic removal of NO.](image)

![Fig. 9. Photoluminescence spectra of g-$\text{C}_3\text{N}_4$, Blend, 10CA and Ag$_3$PO$_4$ samples excited by 270 nm.](image)
and holes in photocatalysts. Fig. 9 shows the PL spectra of the pure g-C₃N₄, pure Ag₃PO₄, Blend and 10CA. Pure g-C₃N₄ exhibits a strong emission with an emission peak at about 441 nm, which was similar to the literatures [41]. Compared with g-C₃N₄, the PL intensities of pure Ag₃PO₄ and 10CA are much weaker, reflecting their slow recombination rates of photogenerated electron-hole pairs. Although the PL intensity of 10CA is slightly higher than that of pure Ag₃PO₄, it is much weaker than that of the "Blend", which suggests heterojunction between Ag₃PO₄ and g-C₃N₄ is effectively formed during the solvent evaporation process and it benefits to the separation of electron-hole pairs. The PL results are in accordance with the photocatalytic activity of the catalysts.

In order to deduce the migration path of the photogenerated electrons and holes in the composites, the active species trapping experiments were conducted. When bare Ag₃PO₄ is used as photocatalyst, the photodegradation of MB is significantly suppressed by the introduction of TEOA (a quencher of h⁺), indicating that holes are the main reactive oxidative species involved in the photocatalysis, which is consistent with reports that the oxidation mechanism of Ag₃PO₄ proceeds through direct h⁺ attack to target organic compounds. In contrast, the adding of BQ (a quencher of O₂•⁻) or IPA (a quencher of •OH) in the solution has no obvious effect on the photocatalytic activity of Ag₃PO₄ (Fig. 10), implying that O₂•⁻ and •OH radicals have no contribution to the degradation process. The photocatalytic behavior of g-C₃N₄/Ag₃PO₄ is similar to that of bare Ag₃PO₄ when TEOA or IPA is introduced into the photoreaction. However, the adding of BQ results in an unneglectable deactivation, indicating that besides holes, O₂•⁻ radicals are also involved in the photocatalytic process. For pure g-C₃N₄, it can be found that the photodegradation rates decrease in the order: BQ (O₂•⁻) < TEOA (h⁺) < IPA (•OH). It can be concluded that photogenerated holes (h⁺) are the most main active species and O₂•⁻ radicals are the second main active species in the photocatalytic process. Considering the CB and VB potentials of Ag₃PO₄ and g-C₃N₄, the photoexcited electrons on the CB of g-C₃N₄ in g-C₃N₄/Ag₃PO₄ composites could flow directly to the CB of Ag₃PO₄ and accumulate on the CB of Ag₃PO₄, but it results in the dominant reactive species of h⁺, which is inconsistent with the experimental result. Therefore, photoexcited electrons on the CB of g-C₃N₄ do not flow directly into CB of Ag₃PO₄ but enrich on the CB of g-C₃N₄ through other mechanism (thereby retaining sufficient capacity to reduce O₂ species to O₂•⁻).

Based on the above results, a possible mechanism for photocatalytic degradation MB and removal NO on g-C₃N₄/Ag₃PO₄ hybrid photocatalyst was proposed in Fig. 11. It can be ascribed to the efficient separation of photogenerated electrons and holes through the Z-scheme system composed of Ag₃PO₄, Ag and g-C₃N₄. A similar Z-scheme mechanism for Ag@AgBr@g-C₃N₄ composite photocatalysts has been reported by other researchers [50]. Under visible light irradiation, both Ag₃PO₄ and g-C₃N₄ are excited to generate photogenerated electrons (e⁻) and holes (h⁺), respectively. Because metallic Ag⁰ formed on the surface of Ag₃PO₄ can act as a charge transmission bridge, the e⁻ of Ag₃PO₄ can easily flow into metal Ag and then continually transfer to the VB of g-C₃N₄, making charge separation more efficient. Therefore, the Z-scheme mechanism is established, which keeps e⁻ on the CB of g-C₃N₄ high reduction capability and h⁺ on VB of Ag₃PO₄ strong oxidation capability. Because E_cb (g-C₃N₄, -1.32 eV) is more negative than the standard reduction potential of O₂/O₂•⁻ (E⁰ (O₂/O₂•⁻) = +0.13 eV), the e⁻ of g-C₃N₄ can further react with dissolved O₂ to form O₂•⁻ radicals, which can further oxidize pollutants. Considering that the CB potential of Ag₃PO₄ (0.21 eV) is higher than the potential of O₂/O₂•⁻, the electrons in the CB of pure Ag₃PO₄ can not reduce dissolved O₂ to O₂•⁻ through one-electron reduction. Clearly, the electron can enrich on the CB of g-C₃N₄ only when the electron and holes in g-C₃N₄/Ag₃PO₄ migrate by the Z-scheme mechanism. Meanwhile, the potential of the E_vb of Ag₃PO₄ (2.72 eV) is near E⁰ (•OH, H₂O/H₂O₂) = 2.72 eV, so the holes stayed on the VB of Ag₃PO₄ can not react with H₂O to form •OH radicals, which would photocatalytic oxidize pollutants directly [32]. By this manner, the photoexcited electron-holes in...
the composite are separated efficiently, thereby leading to the excellent photocatalytic activity.

### 4 Conclusions

In summary, the reactive \{111\} facets of tetrahedral Ag₃PO₄ microcrystals were hybridized with g-C₃N₄ in the facile solvent evaporation process. The photocatalytic experiments indicated that the as-prepared g-C₃N₄/Ag₃PO₄ exhibited significantly enhanced photocatalytic activity than that of pure g-C₃N₄ and Ag₃PO₄ samples toward photocatalytic degradation of methyl blue (MB) in aqueous solution and removal of NO at the indoor air level under visible light irradiation (> 400 nm), and 10CA had the highest activity. The photocatalytic activity enhancement of g-C₃N₄/Ag₃PO₄ hybrid photocatalysts could be ascribed to the combined effect of reactive \{111\} facets and the efficient separation of electron-hole pairs through a Z-scheme system composed of Ag₃PO₄, Ag and g-C₃N₄, in which Ag particles act as the charge separation center. Furthermore, \(\text{e}^−\) and \(\text{O}_2^−\) played the major role in photocatalysis process. This work suggests that the synthesized g-C₃N₄/Ag₃PO₄ \{111\} hybrid is a promising visible light driven photocatalytic material for the photocatalytic removal of NO in the gas phase as well as the environmental purification of organic pollutants in aqueous solution.

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