Article

Highly Efficient Ag₃PO₄/g-C₃N₄ Z-Scheme Photocatalyst for Its Enhanced Photocatalytic Performance in Degradation of Rhodamine B and Phenol

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Abstract: Ag₃PO₄/g-C₃N₄ heterojunctions, with different g-C₃N₄ dosages, were synthesized using an in situ deposition method, and the photocatalytic performance of g-C₃N₄/Ag₃PO₄ heterojunctions was studied under simulated sunlight conditions. The results revealed that Ag₃PO₄/g-C₃N₄ exhibited excellent photocatalytic degradation activity for rhodamine B (Rh B) and phenol under the same light conditions. When the dosage of g-C₃N₄ was 30%, the degradation rate of Rh B at 9 min and phenol at 30 min was found to be 99.4% and 97.3%, respectively. After five cycles of the degradation experiment for Rh B, g-C₃N₄/Ag₃PO₄ still demonstrated stable photodegradation characteristics. The significant improvement in the photocatalytic activity and stability of g-C₃N₄/Ag₃PO₄ was attributed to the rapid charge separation between g-C₃N₄ and Ag₃PO₄ during the Z-scheme charge transfer and recombination process.

Keywords: Ag₃PO₄; g-C₃N₄; semiconductor photocatalyst; Z-scheme mechanism

1. Introduction

With the rapid development of industry, environmental pollution caused by industrial wastewater is becoming increasingly serious. Photocatalysis is an effective technology to degrade pollutants in water, which has been widely researched [1,2]. However, one-component semiconductor photocatalysts always face various defects, such as low visible-light availability and easy recombination of photogenerated charges. It has been proven that the construction of semiconductor heterostructures is an effective route to improve photocatalytic efficiency [3,4]. In recent years, an all-solid Z-scheme semiconductor composite photocatalyst has been applied in photocatalysis [5-9]. When Z-scheme photocatalysts are excited, h⁺ from the valence band (VB) at a higher energy level can combine with e− from the conduction band (CB) at a lower energy level, while e− with a stronger reducing ability in CB at a higher energy level and h⁺ with a stronger oxidation ability in lower VB at a lower energy level can participate in the reduction and oxidation processes during photocatalytic degradation, respectively. This method is conducive to obtain high charge separation efficiency and strong redox ability simultaneously, thus improving the photocatalytic efficiency [8,9].

In recent years, Z-scheme Ag₃PO₄-based photocatalysts with a high photocatalytic activity have been designed and applied in wastewater treatment and environmental control [10-13], including Ag₃PO₄/MoS₂ [14], Bi₂MoO₆/Ag₃PO₄ [15], Ag₃PO₄/Bi₂WO₆ [16], Ag₃PO₄/RGO/BiMoO₄ [17], Ag₃PO₄/Ag/WO₃-x [18], and Ag₃PO₄/Pd/LaPO₄ [19]. Lamellar g-C₃N₄ nanosheets possess high surface area, suitable band gap (2.7 eV), low cost, and good
thermal and chemical stability, which has attracted extensive attention in the field of photocatalysis [20–23]. When g-C\textsubscript{3}N\textsubscript{4} is combined with Ag\textsubscript{3}PO\textsubscript{4}, the resultant g-C\textsubscript{3}N\textsubscript{4}/Ag\textsubscript{3}PO\textsubscript{4} photocatalyst is expected to show significantly enhanced photocatalytic activity.

Among the many types of pollutants, dyes and dangerous compounds are two main pollutants in industrial wastewater. Rh B and phenol are the typical substances of the two pollutants, respectively. Rh B is very harmful to human health. It can cause redness of skin and viscera, mild congestion of cerebral vascular, rupture of myocardial fiber, and other symptoms. Phenol has a strong corrosive effect on skin and mucous membrane, inhibiting the central nervous system and damaging the function of liver and kidney, etc. In addition, phenol is more difficult to degrade than other pollutants in water. Thus, they were chosen as the degradation object in photocatalytic experiments.

In this paper, we synthesized the Ag\textsubscript{3}PO\textsubscript{4}/g-C\textsubscript{3}N\textsubscript{4} Z-scheme heterojunction photocatalyst using the in situ deposition method and evaluated the photocatalytic activity by the degradation experiment for Rh B and phenol. The influence of g-C\textsubscript{3}N\textsubscript{4} and Ag\textsubscript{3}PO\textsubscript{4} on photocatalytic activity was studied in detail and the probable photocatalytic mechanism of Ag\textsubscript{3}PO\textsubscript{4}/g-C\textsubscript{3}N\textsubscript{4} was proposed.

2. Experimental Section

2.1. Sample Preparation

Preparation of g-C\textsubscript{3}N\textsubscript{4}: A typical calcination method was used to prepare g-C\textsubscript{3}N\textsubscript{4}. Briefly, 10 g urea powder was placed in an alumina crucible with a lid. The crucible was heated in air at a heating rate of 2 °C min\textsuperscript{-1} to 550 °C and, then held at this temperature for 2 h to obtain g-C\textsubscript{3}N\textsubscript{4}. Subsequently, the bulk g-C\textsubscript{3}N\textsubscript{4} was thermally exfoliated into g-C\textsubscript{3}N\textsubscript{4} nanosheets by calcination at 600 °C for 2 h in air. The light yellow product was collected and ground using an agate mortar for subsequent use.

Synthesis of Ag\textsubscript{3}PO\textsubscript{4}/g-C\textsubscript{3}N\textsubscript{4}: Fifty milligrams of g-C\textsubscript{3}N\textsubscript{4} nanosheets were dispersed in 80 mL of deionized water by ultrasonication. Silver ammonia solution (0.1 g L\textsuperscript{-1}) was dropped into the aqueous dispersion of g-C\textsubscript{3}N\textsubscript{4} nanosheets and, then magnetically stirred for 1 h to fully adsorb Ag(NH\textsubscript{3})\textsuperscript{2+} ions on the surface of g-C\textsubscript{3}N\textsubscript{4} nanosheets. Then, the KH\textsubscript{2}PO\textsubscript{4} solution (0.1 g L\textsuperscript{-1}) was dropped into the above mixture under magnetic agitation and the mixture continued to be stirred for 1 h. The final product was collected by centrifugation, washed with deionized water and ethanol thrice, and dried at 70 °C for 1 h. Finally, the product was collected and ground with an agate mortar for subsequent use.

According to the theoretical dosage of g-C\textsubscript{3}N\textsubscript{4}, the as-prepared samples were named Ag\textsubscript{3}PO\textsubscript{4}/g-C\textsubscript{3}N\textsubscript{4}-10 wt\%, Ag\textsubscript{3}PO\textsubscript{4}/g-C\textsubscript{3}N\textsubscript{4}-20 wt\%, Ag\textsubscript{3}PO\textsubscript{4}/g-C\textsubscript{3}N\textsubscript{4}-30 wt\%, and Ag\textsubscript{3}PO\textsubscript{4}/g-C\textsubscript{3}N\textsubscript{4}-40 wt\%. The actual dosage of g-C\textsubscript{3}N\textsubscript{4} detected by EDS were 9.2 wt\%, 16.3 wt\%, 27.7 wt\%, and 41.8 wt\%, respectively. In addition, the simple physical mixture of Ag\textsubscript{3}PO\textsubscript{4} and 30 wt\% g-C\textsubscript{3}N\textsubscript{4} was named the Ag\textsubscript{3}PO\textsubscript{4}/g-C\textsubscript{3}N\textsubscript{4}-30% mixture.

2.2. Sample Characterization

The crystal structure was analyzed by a Bruker D8 X-ray diffractometer (XRD, Bruker, Germany), equipped with a Cu K\textsubscript{α} irradiation light source (\(\lambda = 0.154 \text{ nm}\)). The microstructure was observed using a Tecnai G2 F20 transmission electron microscopy (TEM, FEI, Hillsboro, OR, USA). Room-temperature transient photoluminescence (PL) spectra were recorded using an FLS1000 spectrometer (Edinburgh Instruments, UK). UV-Vis diffuse reflectance spectra (UV-Vis, Hitachi, Tokyo, Japan) were measured by using a UH4150 UV-Vis near-infrared spectrophotometer. The photocurrent response was measured using a CHI 760E electrochemical workstation (Chenhua, Shanghai, China).

2.3. Photocatalytic Activity Test

The photocatalytic activity was evaluated by the pollutant degradation experiments at room temperature. A Polfilet xenon lamp (300 W) with a 320-nm filter was used as the light source. The spectra of the xenon lamp are shown in Figure S1 and detailed experimental devices are shown in Figure S2. The reaction solution consisted of 50 mL
of rhodamine B (Rh B, 5 mg·L\(^{-1}\)) or 50 mL of phenol (10 mg·L\(^{-1}\)), and the photocatalyst was 0.03 g Ag\(_3\)PO\(_4\), g-C\(_3\)N\(_4\), or Ag\(_3\)PO\(_4\)/g-C\(_3\)N\(_4\). The photocatalyst was weighed and added to the reaction solution, and the reaction solution was continuously stirred in the dark for 30 min to achieve an adsorption–desorption balance between the photocatalytic material and pollutant. Subsequently, the solution was irradiated by a full-wavelength Xenon lamp, and the absorbance of the supernatant was measured at certain intervals. In the cyclic experiments, the photocatalyst was separated from the reaction system after each degradation experiment, washed with ethanol and deionized water, and re-dispersed in the newly-prepared reaction solution to repeat the degradation experiment.

### 3. Results and Discussion

#### 3.1. Structural Analysis and Microstructure

Figure 1 shows the XRD patterns of Ag\(_3\)PO\(_4\), g-C\(_3\)N\(_4\), and Ag\(_3\)PO\(_4\)/g-C\(_3\)N\(_4\)-30 wt%. As shown in Figure 1, a strong peak appeared in the diffraction pattern of g-C\(_3\)N\(_4\) at 20 = 26.5°, corresponding to the (002) planes of g-C\(_3\)N\(_4\) (JCPDS card no. 87-1526), which is the characteristic interlayer stacking peak of g-C\(_3\)N\(_4\) [24]. The Ag\(_3\)PO\(_4\) and Ag\(_3\)PO\(_4\)/g-C\(_3\)N\(_4\)-30 wt% exhibited similar XRD patterns and all strong diffraction peaks corresponded to the cubic Ag\(_3\)PO\(_4\) phase (JCPDS card no. 06-0505). The inset provided the refined XRD patterns of Ag\(_3\)PO\(_4\) and Ag\(_3\)PO\(_4\)/g-C\(_3\)N\(_4\)-30 wt%. Compared with Ag\(_3\)PO\(_4\), the XRD pattern of Ag\(_3\)PO\(_4\)/g-C\(_3\)N\(_4\) showed the characteristic peaks of g-C\(_3\)N\(_4\); however, the peak intensities were far weaker than that of Ag\(_3\)PO\(_4\). This may be attributed to the inferior crystallinity and lower content of well-exfoliated g-C\(_3\)N\(_4\).

![XRD patterns of as-prepared Ag\(_3\)PO\(_4\), g-C\(_3\)N\(_4\), and Ag\(_3\)PO\(_4\)/g-C\(_3\)N\(_4\).](image)

Figure 2 shows TEM images of Ag\(_3\)PO\(_4\), g-C\(_3\)N\(_4\), and Ag\(_3\)PO\(_4\)/g-C\(_3\)N\(_4\) photocatalysts. Figure 2a illustrates that Ag\(_3\)PO\(_4\) consisted of approximately cubic particles with a size of 200–300 nm. As shown in Figure 2b, g-C\(_3\)N\(_4\) presented thin wrinkled nanosheets. After thermal exfoliation, the specific surface area of g-C\(_3\)N\(_4\) increased significantly, due to morphological changes. Figure 2c shows that the small-sized Ag\(_3\)PO\(_4\) particles were attached to the surface of g-C\(_3\)N\(_4\), forming a stable composite.
3.2. Optical Properties

Figure 3 shows the UV-vis diffuse reflectance spectra of Ag₃PO₄, g-C₃N₄, and Ag₃PO₄/g-C₃N₄-30 wt% photocatalysts. As shown in Figure 3a, the absorption cutoff edges of Ag₃PO₄ and g-C₃N₄ were located at about 460 and 530 nm, respectively. Compared with Ag₃PO₄, the absorption edge of Ag₃PO₄/g-C₃N₄-30 wt% was basically unchanged. Based on the UV-vis absorption data, the bandgap width of the photocatalysts was calculated and results are shown in Figure 3b. The calculated bandgap width of g-C₃N₄ was about 2.78 eV, whereas the bandgap of Ag₃PO₄ and Ag₃PO₄/g-C₃N₄-30wt% decreased to 2.45 eV.

![Figure 3. (a) UV-vis diffuse reflectance spectra, (b) estimated bandgap of Ag₃PO₄, g-C₃N₄, and Ag₃PO₄/g-C₃N₄-30 wt%.

By testing the photoelectrochemical properties of Ag₃PO₄, g-C₃N₄, and Ag₃PO₄/g-C₃N₄-30 wt% photocatalysts, the separation and transfer efficiency of photogenerated electron-hole pairs were studied and results are shown in Figure 4. Figure 4a presents the photoluminescence (PL) spectra of the as-synthesized photocatalysts. The PL emission peak of g-C₃N₄ was located at 460 nm, showing the highest PL intensity and indicating that the photogenerated charge of g-C₃N₄ exhibited high recombination efficiency. The PL emission peak of Ag₃PO₄ was located at 460 nm, showing a far lower PL intensity than g-C₃N₄. When Ag₃PO₄ was combined with g-C₃N₄, the location of the PL emission peak of Ag₃PO₄/g-C₃N₄-30 wt% was basically the same as Ag₃PO₄, but the PL peak intensity of Ag₃PO₄/g-C₃N₄-30 wt% was significantly lower than Ag₃PO₄. Among Ag₃PO₄, g-C₃N₄, and Ag₃PO₄/g-C₃N₄-30 wt%, Ag₃PO₄/g-C₃N₄ exhibited the lowest PL peak intensity, which corresponded to the lowest recombination efficiency for photogenerated charges. As can be observed in Figure 4b, all photocatalyst electrodes exhibited rapid response when irradiated by a Xenon lamp (full wavelength). The Ag₃PO₄/g-C₃N₄-30 wt% showed the highest photocurrent response of about 16.35 μA-cm⁻², which was 2.79 times higher...
than Ag$_3$PO$_4$ (5.87 $\mu$A·cm$^{-2}$) and 21.8 times higher than g-C$_3$N$_4$ (0.75 $\mu$A·cm$^{-2}$). These results indicate that the combination of Ag$_3$PO$_4$ and g-C$_3$N$_4$ reduced the recombination efficiency of photogenerated electrons and holes, and accelerated the charges transfer, which is beneficial for photocatalysis.

![Figure 4](image)

**Figure 4.** (a) Photoluminescence spectra and (b) transient photocurrent response curves of Ag$_3$PO$_4$, g-C$_3$N$_4$, and Ag$_3$PO$_4$/g-C$_3$N$_4$-30 wt%.

3.3. Photocatalytic Activity

Furthermore, using Rh B and phenol as target pollutants, we simulated the photocatalytic reaction under sunlight irradiation using Xenon lamp (full wavelength) irradiation, and evaluated the photocatalytic activity, as shown in Figure 5. Figure 5a shows the photocatalytic activity of Ag$_3$PO$_4$/g-C$_3$N$_4$ with different amounts of g-C$_3$N$_4$. After irradiation by the Xenon lamp for 9 min, the photocatalytic degradation rate of RhB by Ag$_3$PO$_4$, g-C$_3$N$_4$, Ag$_3$PO$_4$/g-C$_3$N$_4$-10 wt%, Ag$_3$PO$_4$/g-C$_3$N$_4$-20 wt%, Ag$_3$PO$_4$/g-C$_3$N$_4$-30 wt%, and Ag$_3$PO$_4$/g-C$_3$N$_4$-40 wt% was found to be 71.1%, 22.2%, 79.8%, 95.5%, 99.4%, and 89.9%, respectively. With the increase of g-C$_3$N$_4$ content, the photocatalytic activity of Ag$_3$PO$_4$/g-C$_3$N$_4$ initially increased, followed by a decrease. The optimal photocatalytic activity was achieved for Ag$_3$PO$_4$/g-C$_3$N$_4$-30 wt%. The first-order kinetic model [25,26] was used to calculate the corresponding reaction rate constants ($k$), and the results are shown in Figure 5c. The observed reaction rate constant of Ag$_3$PO$_4$, g-C$_3$N$_4$, Ag$_3$PO$_4$/g-C$_3$N$_4$-10 wt%, Ag$_3$PO$_4$/g-C$_3$N$_4$-20 wt%, Ag$_3$PO$_4$/g-C$_3$N$_4$-30 wt%, and Ag$_3$PO$_4$/g-C$_3$N$_4$-40 wt% was found to be 0.1033, 0.0209, 0.1333, 0.2591, 0.4227, and 0.1911 min$^{-1}$, respectively. The $k$ value of Ag$_3$PO$_4$/g-C$_3$N$_4$-30 wt% (0.4227 min$^{-1}$) was the highest, which was 20.24 times higher than Ag$_3$PO$_4$ and g-C$_3$N$_4$, respectively.
Figure 5. (a,b) Photocatalytic curves, (c,d) rate constants in the degradation of Rh B and phenol, with different g-C3N4 content.

In order to further verify the superior photocatalytic activity of Ag3PO4/g-C3N4, the photocatalytic degradation experiment for phenol was also carried out and the results are shown in Figure 5b. Under Xenon lamp irradiation for 30 min, the degradation rate of phenol by Ag3PO4, g-C3N4, Ag3PO4/g-C3N4-10 wt%, Ag3PO4/g-C3N4-20 wt%, Ag3PO4/g-C3N4-30 wt%, and Ag3PO4/g-C3N4-40 wt% was found to be 43.0%, 15.8%, 63.9%, 90.9%, 99.6%, and 77.5%, respectively. Figure 5d shows that the Ag3PO4/g-C3N4-30 wt% exhibits the highest rate constant \( k \) (0.0540 min\(^{-1}\)), which was ≈5.35 and 20.00 times higher than Ag3PO4 (0.01009 min\(^{-1}\)) and g-C3N4 (0.0027 min\(^{-1}\)), respectively. Hence, Ag3PO4/g-C3N4 showed obvious advantages for the degradation of pollutants.

Figure 6 presents the cyclic stability of Rh B degradation by Ag3PO4, g-C3N4, and Ag3PO4/g-C3N4-30 wt% photocatalysts. Under Xenon lamp irradiation, the loss rate of Rh B degradation by Ag3PO4, g-C3N4, and Ag3PO4/g-C3N4-30 wt% during the fifth cycle, compared with the initial degradation, was 32.5%, 11.5%, and 7.3%, respectively. The presence of g-C3N4 significantly reduced the loss rate for Rh B and phenol degradation. Hence, Ag3PO4/g-C3N4 showed excellent photocatalytic stability.
substance during the photocatalytic process by g-C_3N_4 because the potential of O_2 is 2.7 eV with the VB potential of ~2.9 eV and CB potential of ~0.45 eV [29]. The bandgap of g-C_3N_4 is 1.3 eV [27,28]. The potential of O_2^- is ~1.3 eV, which can reduce the molecular oxygen O_2 to O^2- because the potential of O_2^- is ~0.44 eV vs. NHE. Therefore, O^2- was the main active substance during the photocatalytic process by g-C_3N_4. The bandgap of Ag_3PO_4 was 2.45 eV with a VB potential of ~2.9 eV and CB potential of ~0.45 eV [29].

3.5. Energy Band Structure and Photocatalytic Mechanism

Figure 8 presents the Z-scheme charge transfer pathway of the Ag_3PO_4/g-C_3N_4 composite photocatalyst for the degradation of organic pollutants. The bandgap of g-C_3N_4 was 2.7 eV with the VB potential of ~1.4 eV and CB potential of ~1.3 eV [27,28].

3.4. Photocatalysis Species

In order to identify the active species during the photocatalytic process, free radical capture experiments were carried out using Rh B as a target pollutant. EDTA-2Na, p-benzoquinone (BZQ), and tert-butanol were introduced during the photocatalytic process as h^+, ·O_2^-, and OH^- inhibitors, respectively, and the results are shown in Figure 7. The introduction of tert-butanol during the photocatalytic process of Ag_3PO_4/g-C_3N_4-30 wt% rendered no influence on the photodegradation efficiency of Rh B, whereas EDTA-2Na and BZQ both significantly reduced the degradation efficiency of Rh B with a degradation rate of 4.4% and 12.4%, respectively. These results indicate that h^+ and O^2- are the main active species in Ag_3PO_4/g-C_3N_4-30 wt%.

Figure 6. Recycling runs results of Ag_3PO_4, g-C_3N_4, and Ag_3PO_4/g-C_3N_4-30 wt% in degradation of Rh B.

Figure 7. Photocatalytic activities of Ag_3PO_4/g-C_3N_4-30 wt% for the degradation of Rh B in the presence of different scavengers.
The generated electrons (e\textsuperscript{−}) in the CB of Ag\textsubscript{3}PO\textsubscript{4} are insufficient to reduce O\textsubscript{2} into O\textsuperscript{2−}. Therefore, holes (h\textsuperscript{+}) play a major role during the photocatalytic degradation of organic matter by Ag\textsubscript{3}PO\textsubscript{4}.

Based on the energy band analysis, it can be inferred that the photogenerated e\textsuperscript{−} in the CB of Ag\textsubscript{3}PO\textsubscript{4} can combine with h\textsuperscript{+} in the VB of g-C\textsubscript{3}N\textsubscript{4} due to the formation of a heterojunction interface between Ag\textsubscript{3}PO\textsubscript{4} particles and g-C\textsubscript{3}N\textsubscript{4} nanosheets, resulting in the accumulation of e\textsuperscript{−} in the CB of g-C\textsubscript{3}N\textsubscript{4} and h\textsuperscript{+} in VB of Ag\textsubscript{3}PO\textsubscript{4}. The h\textsuperscript{+} in the VB of Ag\textsubscript{3}PO\textsubscript{4} can directly react with pollutants, whereas the electrons in CB of g-C\textsubscript{3}N\textsubscript{4} can reduce O\textsubscript{2} into O\textsuperscript{2−}, which reacts with pollutants. The Z-scheme charge transfer mechanism promotes the separation of electron-hole pairs, slows down the photocorrosion of Ag\textsuperscript{+}, and improves photocatalyst activity and stability.

4. Conclusions

In summary, the Z-scheme heterojunction Ag\textsubscript{3}PO\textsubscript{4}/g-C\textsubscript{3}N\textsubscript{4} photocatalyst was synthesized using an in situ deposition method and exhibited excellent photocatalytic degradation activity for Rh B and phenol under Xenon lamp irradiation. The observed rate constant (k) for the degradation of Rh B by Ag\textsubscript{3}PO\textsubscript{4}/g-C\textsubscript{3}N\textsubscript{4} was found to be 0.4227 min\textsuperscript{−1}, which was 4.09 and 20.24 times higher than pure Ag\textsubscript{3}PO\textsubscript{4} and g-C\textsubscript{3}N\textsubscript{4}, respectively. Moreover, the k value for the degradation of phenol by Ag\textsubscript{3}PO\textsubscript{4}/g-C\textsubscript{3}N\textsubscript{4} was 0.0540 min\textsuperscript{−1}, which was 5.35 and 20.00 times higher than pure Ag\textsubscript{3}PO\textsubscript{4} and g-C\textsubscript{3}N\textsubscript{4}, respectively. Overall, the formation of the Z-scheme heterojunction hindered the recombination of photogenerated electrons and holes, and accelerated the electron transfer, thus improving the activity and stability of photocatalysts.

Supplementary Materials: Figure S1: The spectra of xenon lamp, Figure S2: The picture of experimental setup.
Author Contributions: Validation, M.Z., J.J., C.Q.; investigation, Z.Z.; resources, Y.S.; data curation, H.D.; writing—original draft preparation, M.Z.; writing—review and editing, E.L.; supervision, Y.C.L.; project administration, Y.C.L.; All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Fund of China, grant number 51772099 and 51872091; the Scientific and Technological Research Projects of Colleges and Universities in Hebei Province, grant number QN2019049; the Postdoctoral Program of Hebei Province, grant number B2020003015; the Doctoral Initiation Fund, grant number BS2017025.

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to the ongoing follow-up studies.

Acknowledgments: The authors would like to thank Xiangguang Meng of North China University of Science and Technology for helpful discussions on topics related to this work. This work was supported by the National Natural Science Fund of China (Grant No. 51772099, 51872091), it is also supported by the Scientific and Technological Research Projects of Colleges and Universities in Hebei Province (QN2019049), the Doctoral Initiation Fund (BS2017025), and Innovation and Entrepreneurship Training Program for College Students of North China University of Science and Technology.

Conflicts of Interest: The authors declare no conflict of interest. The authors had no any personal circumstances or interest that may be perceived as inappropriately influencing the representation or interpretation of reported research results. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

Sample Availability: Samples of the Ag$_3$PO$_4$/g-C$_3$N$_4$ photocatalyst are available from the authors. However, it may be necessary to pay properly for the synthesis and mailing of samples.

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