Ag-Modified g-C$_3$N$_4$ Prepared by a One-Step Calcination Method for Enhanced Catalytic Efficiency and Stability

Runxue Liu, Wanliang Yang, Guwei He, Wei Zheng, Maokun Li, Wenliang Tao, and Mengkui Tian$^{*}$

ABSTRACT: Ag-decorated g-C$_3$N$_4$ (denoted as Ag/CN-x) was prepared by a one-step calcination method, and the influences of calcination time on structure, morphology, surface composition, photocatalytic performance, and catalytic reduction activity of the prepared Ag/CN-x samples were investigated. The tests showed that the Ag/CN-8 prepared through by calcination for 8 h exhibited the best photocatalytic degradation efficiency of methyl orange (98.7% within 2 h) and the best catalytic reduction property of 4-nitrophenol (100% within 70 s). Meanwhile, these Ag/CN-x samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET), X-ray photoelectron spectroscopy (XPS), UV–vis diffuse reflectance spectra (DRS), photoluminescence (PL), photocurrent response, and electrochemical impedance spectroscopy (EIS) Nyquist plots. It was found that the Ag/CN-8 prepared through calcination for 8 h had a higher specific surface area, higher dispersibility of silver nanoparticles (Ag NPs), the widest range of visible light response, and the lowest photogenerated electron–hole recombination rate. The results of the trapping experiments indicated that a superoxide radical plays a major role. Moreover, a possible mechanism of photocatalytic degradation in methyl orange and catalytic reduction 4-nitrophenol was proposed.

1. INTRODUCTION

With the development of industrial and agricultural areas, environmental pollution was becoming progressively worse. The dyes of organic pollutants were often discharged into wastewater. The color of dyes affects the transparency of water, aesthetics, and the solubility of gas in water, and a large number of dyes were carcinogenic in nature. In addition to dyes of organic pollutants, the release of nonbiodegradable aromatic pollutants in water showed an exponential increase. Among them, nitrophenol was a class of common pollutants in industrial and agricultural areas, which has carcinogenicity, high toxicity, and hard decomposition, and cause tremendous damage to human health. In summary, the issue of organic pollution in water needs to be solved urgently. Photocatalysis technology has been applied for environmental remediation owing to the advantage of transforming solar energy into chemical energy.

Graphite carbon nitride (g-C$_3$N$_4$), as an organic metal-free polymer photocatalyst, has attracted great interest due to its visible-light harvesting capacity with an appropriate band gap (2.7 eV). In addition, g-C$_3$N$_4$ also has the advantages of nontoxicity, low cost, easy synthesis, and good thermal/chemical stability. Therefore, g-C$_3$N$_4$ has a wide range of applications in the fields of degradation of organic pollution and hydrogen production under visible light. Unfortunately, the photocatalytic activity of g-C$_3$N$_4$ was unsatisfactory because of a low specific surface area, poor light absorption, and rapid recombination of photogenerated electron–hole pairs. The catalytic activity of g-C$_3$N$_4$ could be effectively improved by metal deposition, nonmetal doping, introduction of vacancy defects, morphology or the pore structure design, or coupling with other semiconductors.

Increasing the specific surface area of g-C$_3$N$_4$ could increase the number of active sites to improve the photocatalytic reaction activity. There had been many reports about improving the specific surface area of g-C$_3$N$_4$ with a hard template method, soft template method, and template free method. For instance, Obregon et al. fabricated mesoporous g-C$_3$N$_4$ by using SBA-15 as a hard template, and they found that the prepared mesoporous g-C$_3$N$_4$ showed a higher specific surface area than bulk g-C$_3$N$_4$, which could enhance the properties of hydrogen production. Yan et al. synthesized porous carbon nitride using a soft template, and the prepared CN-P123-x held higher specific surface areas. Wu et al. reported that the exfoliation of bulk g-C$_3$N$_4$ by post calcination showed excellent properties of hydrogen produc-
tion, which could be attributed to the enlarged BET surface area and negatively shifted CB potential.

Moreover, many methods had been used for solving the problems of poor light absorption and rapid recombination of photogenerated electron–hole pairs of g-C$_3$N$_4$ through metal/nonmetal doping, noble metal deposition, and combination with semiconductors. Among these methods, the deposition of noble metal has caused much attention owing to the surface plasmon resonance (SPR) effect.25 Compared with other precious metals, such as gold (Au), platinum (Pt), and ruthenium (Ru), silver nanoparticles (Ag NPs) have attracted much more attention because of the lower price.26 Massive literature studies had reported the application of Ag/g-C$_3$N$_4$ in the degradation of organic pollutants and water splitting. Wang et al.27 prepared Ag/g-C$_3$N$_4$ porous nanofiber photocatalysts with superior photocatalytic properties with a new metal–organic supramolecular hydrogel method. Ag-modified mesoporous g-C$_3$N$_4$ were synthesized by Bu et al.28 using a photoassisted reduction method. Fu et al.29 fabricated a Ag nanoparticle-decorated g-C$_3$N$_4$ sheet photocatalyst using a NaBH$_4$ reduction method. Then, the methods described above required multiple steps of synthesis. To the best of our knowledge, the catalytic ability of Ag/g-C$_3$N$_4$ was usually controlled by changing the AgNO$_3$ content in the precursor.30–32 Moreover, there have been few reports on the adjustment of the calcination time to change the specific surface area and the Ag content of Ag/CN.

In this study, a series of Ag/CN-x photocatalysts were successfully prepared by a one-step method at different calcination times. Furthermore, the effects of calcination time on the structure, morphology, surface composition, photocatalytic performance, and catalytic reduction activity of the prepared Ag/CN-x samples were investigated. Moreover, the possible photocatalytic mechanism for the degradation of MO was proposed. After five photocatalytic cycles of degradation, Ag/CN-8 still keeps excellent stability and photocatalytic activity. Therefore, Ag/CN-x can be used for catalytic reduction of 4-NP.

2. RESULTS AND DISCUSSION

2.1. Catalytic Properties. The photocatalytic activities of the as-prepared sample composites were assessed by the photodegradation of MO at room temperature under the irradiation of visible light ($\lambda > 420$ nm). As shown in Figure 1a, when MO had been under the irradiation of visible light for 2 h, the absorbance of MO solution changed slightly, which indicated that MO was quite stable under the illumination. For bulk g-C$_3$N$_4$, the CN-8 (33.5%) photodegradation efficiency of MO is higher than that of CN-1 (24.3%). With the increasing calcination time from 1 to 8 h,
the photocatalytic activity of Ag/CN-x obviously increased. While increasing calcination time to 10 h, the photocatalytic activity decreased. Among them, the Ag/CN-8 had the best degradation effect on MO, and the degradation efficiency had been 98.6% in 2 h. Moreover, the as-prepared Ag/CN-8 was employed for catalytic reduction of 4-NP, as shown in Figure S1. When a small amount (2 mg) of prepared catalysts was added to the solution containing 4-NP and NaBH4, the Ag/CN-8 composite could absolutely convert 4-NP to 4-AP in only a 70 s reaction time. In addition, Figure 1b shows the curves of CN and Ag/CN-x catalytic reduction of 4-NP within 70 s. By comparing the catalysts with different calcination times, the Ag/CN-8 with 8 h of calcination time had the best catalytic reduction property.

The photodegradation kinetics of MO by the Ag/CN-x photocatalysts was also studied. Figure S2a shows that the photodegradation process of MO obeyed the first-order kinetics model. According to Figure S2a, the kinetic constants of Ag/CN-x photocatalysts with different calcination times (1, 2, 4, 8, 6, and 10 h) were increased by 2.58, 4.52, 6.91, 23.21, 28.41, and 18.56 times, respectively, compared with CN-1. Meanwhile, during the catalytic reduction reaction, the concentration of NaBH4 was much higher than that of 4-NP. Thus, the reduction reaction kinetics of 4-NP could be described in the pseudo-first order. As shown in Figure S2b, the Ag/CN-8 exhibited the highest catalytic activity and the kinetic constant of Ag/CN-8 was 523 times that of CN-1.

In addition, the as-prepared Ag/CN-x in this study showed better photocatalytic activity for MO and catalytic reduction activity of 4-NP than other Ag-loaded g-C3N4 composites, as shown in Tables S1 and S2, respectively.

2.2. XRD Patterns. Figure 2a shows the XRD patterns of the as-papered samples. Similar to g-C3N4, there were two X-ray diffraction peaks at 13.1 and 27.5°, indicating that g-C3N4 and Ag/CN-x were typical graphite phase carbon nitride materials without other impurity phases. Among them, the strong diffraction peak centered at 27.63° was the typical interlayer stacking of the conjugated aromatic system,
corresponding to the (002) crystal plane of graphite phase carbon nitride; the diffraction peak centered at 13.1° was related to the (100) attributed to the in-plane structural packing motif of tri-s-triazine units. However, from Figure 2b, it was found that, with the increase of calcination time, the diffraction angle for the (002) peak of g-C₃N₄ gradually increased from 27.6° (CN-1) to 28.12° (Ag/CN-8), indicating that the decrease was in the layer distance, which favors for the
migration and separation of photogenerated carriers between layers, enhancing the photoreactivity.\(^{24}\) However, the interlayer spacing increased with the calcination time extended to 10 h, indicating that the calcination time was too long to be favorable for the activity of the sample. In addition, for the CN-1, the peak width became narrower after the incorporation of silver, indicating that it was beneficial to improve the relative crystallinity of the sample after the incorporation of silver. No obvious characteristic peaks of Ag were found in samples with calcination time from 1 (Ag/CN-1) to 8 h (Ag/CN-8), which may be due to the fact that the Ag was highly dispersed on the g-C\(_{3}\)N\(_{4}\) and the diffraction peaks of Ag NPs were too weak to be detected in the background.\(^{28}\) For Ag/CN-10, peaks at 2\(\theta\) of 38.1, 44.3, 64.5, and 77.5° were assigned to the (111), (200), (220), and (311) crystal planes of the face-centered cubic structure of Ag, respectively (JCPDS 04-0783).\(^{34}\)

### 2.3. SEM and EDS Analysis

Figure 3 shows the SEM images of pure CN-1 and Ag/CN-8 composites as well as EDS of a prepared Ag/CN-8 sample. It could be seen from Figure 3a that the Ag/CN-1 showed a compact Tremella-like structure, and when the calcination time was increased to 8 h, it could be seen that the sample was more fluffy (Figure 3b), similar to the accumulation of some thin sheets of 5–10 nm in thickness, which may reflect that bulk g-C\(_{3}\)N\(_{4}\) was oxidized and exfoliated due to the thermal corrosion over a long period of time. The mass ratio of Ag after normalization was 11.17% by EDS analysis, and elemental mapping of Ag/CN-8 revealed that the sample mainly contained three elements (C, N, and Ag), which may be a strong evidence that Ag NPs were successfully prepared onto the g-C\(_{3}\)N\(_{4}\) by a simple one-step calcination method.

### 2.4. TEM

The morphology information of the Ag/CN-8 catalyst and size distribution of Ag NPs are shown in Figure 4. As it could be seen, Figure 4a,b shows that g-C\(_{3}\)N\(_{4}\) presented an irregular layered structure and Ag NPs were anchored almost evenly on g-C\(_{3}\)N\(_{4}\). Figure 4c shows the size distribution of Ag NPs in Ag/CN-8 by counting the diameters of 387 black spots from TEM images. It could be seen from Figure 4c that the diameter range of Ag NPs was mainly 5–20 nm. The larger particle size of Ag NPs may be explained by the aggregation of Ag NPs during the sample preparation by a one-step calcination method. However, this was not the main factor affecting the catalytic ability of composites.

### 2.5. XPS Analysis

The XPS spectra were adopted to investigate surface elements and chemical composition of Ag/CN-8 and CN-1 (Figure 5). As shown in Figure 5a, there were the peaks of Ag, C, N, and O of the samples. Furthermore, a small amount of O elements shown in the survey spectrum may be due to the surface absorption and oxidation.\(^{35}\)

In Figure 5b, the high-resolution spectra of C 1s could be fitted into three peaks at about 283.2, 284.7, and 288.2 eV in Ag/CN-8, which were assigned to the aromatic carbon atom, the C–C coordination, and the N=C–N coordination, respectively.\(^{36–39}\) Figure 5c shows that the N 1s spectra could also be separated into two peaks centered at 398.7 and 400.3 eV in Ag/CN-8, which were ascribed to C–N=C, N≡C–(C)\(_{3}\), and N–H, respectively.\(^{40–42}\) Compared with CN-1, the C 1s and N 1s peak of Ag/CN-8 shifted to a higher binding energy, which could be assigned to the interaction between Ag and g-C\(_{3}\)N\(_{4}\).\(^{43}\)

The Ag 3d spectra in Figure 5d showed that the two peaks were centered at about 374.1 and 368.1 eV, belonging to the metallic Ag 3d\(_{5}/2\) and Ag 3d\(_{3}/2\) binding energy, respectively,\(^{29,44}\) corresponding to the literature values for metallic Ag\(^{0}\) species. The results were in accordance with the XRD analysis of Ag/CN and confirm the presence of metallic Ag in the nanocomposites. In addition, the valence band spectra of the Ag/CN-8 catalysts were characterized, as shown in Figure S3.

### 2.6. BET Results

The specific surface area of the sample was studied by a N\(_{2}\) adsorption–desorption isotherm, which was the key to the photocatalytic activity of the photocatalyst. As shown in Figure 6, the CN-1 Ag/CN-8 and Ag/CN-10 showed a type IV isotherm with an H\(_{3}\) hysteresis loop, implying the presence of mesopores. As shown in Figure 6, Ag/CN-8 and Ag/CN-10 exhibited increased specific surface areas (31.48 and 15.3 m\(^{2}\)/g\(^{−1}\), respectively) compared to bulk CN-1 (11.9 m\(^{2}\)/g\(^{−1}\)). The increase of a specific surface area was due to the oxidation and exfoliation of g-C\(_{3}\)N\(_{4}\) caused by long-time calcination, and the larger specific surface area meant that the production had more active sites, which was beneficial to adsorption in the photocatalytic reaction to enhance the photocatalytic properties.

### 2.7. UV–vis Analysis

As shown in Figure 7a, the obvious absorption edge of CN-1 was at about 460 nm. At the same calcination time, the obtained Ag/CN-1 composite photocatalyst had an obvious red shift compared with CN-1, which could be attributed to the surface plasmon resonance effect of Ag nanoparticles. This enhanced light absorption facilitated the yield of more electron–hole pairs, resulting in higher photocatalytic activity. In turn, enhanced absorption provided strong evidence that silver NPs are present in g-C\(_{3}\)N\(_{4}\). It was found that the absorption ranges of visible light of Ag/CN-8 and Ag/CN-10 were significantly increased to 580 and 742 nm, respectively, which indicated that increasing the calcination time could improve the light absorption in the visible region of the sample.\(^{31}\) In addition, as shown in Figure 7b, the band gaps of CN-1, Ag/CN-1, Ag/CN-8, and Ag/CN-10 were estimated by UV–vis DRS according to the following equation of the Tauc plot (eq \(\text{1}\))\(^{35}\)

\[
(\alpha h\nu)^{1/2} = A(\nu - E_{g}) \tag{1}
\]

Among them, \(\alpha\), \(h\), \(\nu\), \(A\), and \(E_{g}\) were the absorbance coefficient, Planck’s constant, light frequency, and constant and band gap energy, respectively. It was determined that the band
gaps of Ag/CN-1, Ag/CN-8, and Ag/CN-10 were 2.69, 2.57, and 1.75 eV, respectively, which were narrower than pure CN-1 (2.72 eV).

2.8. PL Analysis. Photoluminescence (PL) analysis was helpful to reveal the efficiency of carrier transfer and separation and to study the lifetime of charge carriers. Figure 8 shows the PL emission spectra of CN-1, Ag/CN-1, and Ag/CN-8 photocatalysts. As it can be seen, CN-1 had a strong emission peak centered at around 460 nm, indicating that the photoexcited carriers recombined rapidly. The emission intensity of Ag/CN-1 decreased slightly, indicating that the recombination of photogenerated electron–hole pairs was effectively suppressed after combining Ag NPs and the g-C₃N₄. However, the Ag/CN-8 had the lowest emission intensity, which indicated that the increasing calcination time had great potential to increase the separation efficiency of photogenerated carriers.

2.9. Photocurrent and EIS Analysis. The transient photocurrent response and EIS of CN-1 and Ag/CN-8 were tested to confirm the separation and transfer abilities of photogenerated charge carriers. The transient photocurrent of CN-1 and Ag/CN-1 was under a 300 W Xe lamp with a bias voltage at 0.6 V in sodium sulfate solution (0.1 M). As shown in Figure 9a, the photocurrent of the Ag/CN-8 sample was higher than CN-1, which indicated that the Ag/CN-8 had better photogenerated electron–hole pairs of separation efficiency. In addition, all samples showed repeatedly photocurrent responses after five on–off cycles under intermittent illumination at an interval of 40 s, implying that all samples had good photoelectrochemical stability.

Figure 9b shows the EIS Nyquist curve. As it could be seen, the arc radius of Ag/CN-8 was smaller than CN-1. This result was well fitted with PL and photocurrent analysis, indicating that Ag/CN-8 had better transfer efficiency of photogenerated charge carriers, and it was conducive to enhance the photocatalytic property.

Figure 7. (a) UV–vis DRS and (b) band gap of CN-1, Ag/CN-1, Ag/CN-8, and Ag/CN-10.

Figure 8. PL spectra of pure CN-1, Ag/CN-1, and Ag/CN-8.

PL emission spectra of CN-1, Ag/CN-1, and Ag/CN-8 photocatalysts. As it can be seen, CN-1 had a strong emission peak centered at around 460 nm, indicating that the photoexcited carriers recombined rapidly. The emission intensity of Ag/CN-1 decreased slightly, indicating that the recombination of photogenerated electron–hole pairs was effectively suppressed after combining Ag NPs and the g-C₃N₄. However, the Ag/CN-8 had the lowest emission intensity, which indicated that the increasing calcination time had great potential to increase the separation efficiency of photogenerated carriers.

Figure 9. (a) Transient photocurrent responses. (b) EIS of CN-1 and Ag/CN-8.
2.10. Catalytic Mechanism. To investigate the mechanism of photocatalytic degradation of MO by Ag/CN-8, the capture experiment of active substances was performed using IPA, BQ, EDTA-2Na, and argon as trapping agents for ·OH, ·O$_2^-$, h', and dissolved oxygen, respectively. As shown in Figure 10, the photodegradation efficiency of Ag/CN-8 decreased obviously when BQ and argon were added to the solution, indicating that ·O$_2^-$ was the main active substance. Although the photodegradation efficiency of IPA was inhibited, the effect was not as strong as that of BQ and argon, which indicated that ·OH was not the main active substance. In conclusion, ·O$_2^-$ was the main active substance.

Using the band gap value (2.57 eV) and VB potential (1.87 eV) of Ag/CN-8, the conduction band (CB) potential can be calculated from the following equation

$$E_{CB} = E_{VB} - E_g$$

Thus, the estimated $E_{CB}$ value of Ag/CN-8 was $-0.7$ eV. According to the demonstration of the above results and the related literature reports, the mechanism of the enhanced photocatalytic activity of Ag/CN-8 is proposed in Scheme 2.

First, under the irradiation of visible light, both g-C$_3$N$_4$ and metallic Ag absorbed visible light to generate photogenerated electron–hole pairs, and then, photogenerated electrons in the VB of the g-C$_3$N$_4$ could be transferred into the CB. Due to the SPR effect of metallic Ag, the generation rate of e$_{CB}^-$ and h$_{VB}^+$ of g-C$_3$N$_4$ was increased. Second, the electrons on CB of the g-C$_3$N$_4$ were transferred to the surface of Ag nanoparticles rapidly, and these accumulated electrons in the Ag nanoparticles could reduce O$_2$ to yield ·O$_2^-$ ($-0.046$ V vs NHE) radicals, which produced additional hydroxyl radicals (·OH). However, the energy potential of h$_{VB}^+$ of g-C$_3$N$_4$ (+1.87 eV) was not sufficiently positive to react with OH$^-$ to generate ·OH radicals (+1.99 V vs NHE). Finally, the ·O$_2^-$ and ·OH photodegraded MO into H$_2$O and CO$_2$. Throughout the above analysis, the overall electron transfer and degradation reactions and charge carrier transfers were described as follows:

$$g$·C$_3$N$_4$ + h$_v$ → g$·C$_3$N$_4$(e$^-$ + h$^+$)  

(3)

$$g$·C$_3$N$_4$(e$^-$) → Ag(e$^-$)  

(4)

$$O_2 + e^- → ·O_2^-$$  

(5)

$$·O_2^- + 2H^+ → 2$·OH$$  

(6)

In addition, in the presence of the NaBH$_4$ and Ag/g-C$_3$N$_4$ catalyst, the possible mechanism of reducing 4-NP to 4-Ap is shown in Figure S4.

2.11. Stability of Ag/CN-8. In addition to excellent photocatalytic properties, good stability and repeatability were also required for the catalyst. Figure 11a shows that Ag/CN-8 had stable photodegradation activity during 600 min under five cycles of reaction. Furthermore, after the fifth cycle experiment, the degradation rate of MO solution could still maintain at 92%. As shown in Figure 11b, the catalyst also had good 4-NP reduction properties in five cycles. After five cycles, the reduction rate reached 95.23% in 70 s.

3. CONCLUSIONS

In conclusion, a one-step calcination method was developed to prepare Ag/CN-x composite photocatalysts with different Ag contents by controlling the calcination time. Due to effect of SPR, the visible photocatalytic property and photoinduced
electron–hole pair separation efficiency of Ag/CN-x were significantly higher than those of CN-1. Among a series of photocatalysts, Ag/CN-8 had the highest degradation efficiency of MO under visible light irradiation. According to the capture experiment, the main active substance was a super oxygen free radical. Meanwhile, Ag/CN-8 had the highest activity for catalytic reduction of 4-NP in the presence of NaBH₄. In addition, Ag/CN-8 had strong cycle stability in the cycle experiment. In five cycles, the degradation of MO and the reduction efficiency of 4-NP were 92 and 95.12%, respectively. All results showed that the catalytic property of the as-prepared catalysts was affected by changing the calcination time, and Ag/CN-x was a promising photocatalyst for the treatment of organic waste in natural sunlight.

4. EXPERIMENTAL SECTION

4.1. Chemicals. All chemicals were of reagent grade and used without further purification. Dicyandiamide (C₆H₄N₄), silver nitrate (AgNO₃), ethanol (C₂H₆O), methyl orange (MO), 4-nitrophenol (C₆H₄NO₂), sodium borohydride (NaBH₄), and deionized water were used for preparing all aqueous solutions.

4.2. Synthesis of the Ag/CN-x Catalyst. The Ag/CN-x catalyst was prepared with a one-step calcination method (Scheme 1). First, 1 g of dicyandiamide was added into alcohol and sonicated until it had been dissolved. Subsequently, 1 mL of silver ammonia solution (0.4 mmol/mL) was dropped into the above solution and it had been ultrasonically treated for 6 h at room temperature. After that, rotary evaporation was used for removing the excess solvent, and then, the solution had been dried under vacuum at 60 °C for 12 h. The obtained grayish white precipitate was placed into the crucible with a cover and heated to 550 °C at a ramping rate of 5 °C/min, and then, it had been continuously heated to 550 °C and calcinated for different times (1, 2, 4, 8, 6, and 10 h). After being cooled to room temperature, a series of Ag/CN-x was successfully obtained and designated as Ag/CN-1, Ag/CN-2, Ag/CN-4, Ag/CN-6, Ag/CN-8, and Ag/CN-10, respectively. At the same time, under the same external conditions, the CN-1 and CN-8 were prepared through calcination for 1 and 8 h, respectively.

4.3. Characterization. The X-ray diffraction patterns (XRD) of the synthesized samples were measured by a BRUKER D8 ADVANCE at a scanning rate of 2°/min. The morphology and distribution of particle sizes were obtained with transmission electron microscopy (TEM) by a JEOL JEM 2100FP. Scanning electron microscopy (SEM) with a Hitachi S-4700 electron microscope was used for examining the elemental mapping and energy-dispersive spectrum.

X-ray photoelectron spectroscopy (XPS) was measured using a Thermo ESCALAB 250XI. The analysis of Brunauer–Emmett–Teller (BET) N₂ adsorption was characterized by an ASAP-2020 surface analyzer.

The photoluminescence (PL) spectra were obtained by a Hitachi F-4600 spectrometer with an excitation wavelength of 325 nm. UV–vis diffuse reflectance spectra (UV–vis DRS) were measured by an Agilent Cary 5000. The photocurrent response and electrochemical impedance spectroscopy (EIS) were carried out on an electrochemical system (CHI-760E, CHI Shanghai) using a conventional three-electrode cell.

4.4. Photocatalytic Performance. The photocatalytic property of the as-prepared nanocomposite (25 mg) was investigated by a photodegrading MO (10 mg/L, 100 mL) under the visible light (a 300 W xenon lamp with a 420 nm filter to cut-off the UV irradiation) at room temperature. The mixtures had been magnetically stirred for 30 min in the dark to reach the adsorption–desorption equilibrium, and the lamp was then turned on. Every 20 min, 3 mL of the reaction solution was taken out and filtered through a 0.45 mm membrane filter and then analyzed on a UV–vis spectrometer to detect the residual concentration of MO in the solution.

In addition, to detect the generated active species in the photocatalysts, 1,4-benzoquinone (BQ) (1 mM), disodium ethylenediaminetetraacetate (Na₂EDTA) (1 mM), isopropyl alcohol (IPA) (1 mM), and introducing argon into the reaction solution were used as a superoxide radical (·O₂⁻), photogenerated holes (h⁺), hydroxyl radical (·OH), and dissolved oxygen scavengers, respectively, with all similar other conditions.

4.5. Catalytic Reduction of 4-NP. The obtained nanocomposite (2 mg) was evaluated through the catalytic reduction of 4-nitrophenol by excessive NaBH₄. Typically, 100 mL of 4-NP (15 mg/L) was added and mixed with 5 mL of freshly prepared ice-cold aqueous NaBH₄ solution (0.5 M), and then, a deep yellow solution was formed. The reaction was unable to proceed when in the absence of either the catalyst or reductant. The reaction solution (3 mL) was taken out every 10 s from the reactor and then analyzed by a UV–vis spectrometer.

Figure 11. (a) Five times cycled use of the photocatalyst to degrade MO under visible light. (b) Five times recycling of the photocatalyst for catalytic reduction in 4-NP solution.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02161.

Time evolution of UV–vis absorbance spectra for reduction of 4-NP with Ag/CN-8 as the catalyst, kinetic fit for MO degradation and 4-NP reduction for all of the nanocomposites, XPS spectra of the valence band of Ag/CN-8, the proposed mechanism of catalytic hydrogenation of p-NP over Ag/CN-8 in the presence of NaBH4, XRD patterns of the as-prepared Ag/CN-8 composite before and after five cycles, and comparison of as-prepared samples with other Ag-loaded g-C$_3$N$_4$ composites for MO degradation and 4-NP reduction (PDF).

AUTHOR INFORMATION

Corresponding Author
Mengkui Tian — College of Chemistry and Chemical Engineering, Guizhou University, Guizhou 550025, China; orcid.org/0000-0001-3576-8353; Email: tianmk78@126.com

Authors
Runxue Liu — College of Chemistry and Chemical Engineering, Guizhou University, Guizhou 550025, China
Wanliang Yang — College of Chemistry and Chemical Engineering, Guizhou University, Guizhou 550025, China; orcid.org/0000-0002-2823-3282
Guiwei He — International Research Center for Renewable Energy, State Key Laboratory of Multiphase Flow in Power Engineering, Xi’an Jiaotong University, Shaanxi 710049, China
Wei Zheng — College of Chemistry and Chemical Engineering, Guizhou University, Guizhou 550025, China
Maokun Li — College of Chemistry and Chemical Engineering, Guizhou University, Guizhou 550025, China
Wenliang Tao — College of Chemistry and Chemical Engineering, Guizhou University, Guizhou 550025, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c02161

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This work was supported by Natural Science Foundation of China (no. 21663009), the Excellent Youth Fund of Guizhou Province [2017]5605, the Platform and Talent Program from Guizhou Province [2017]5788, the Joint Project of Science and Technology Department of Guizhou Province (LH[2014] 7621), the Science and Technology Project of Guizhou Province (2019[2835]), and the National Key Research and Development project (2018YFC1801706-1).

REFERENCES
(1) Ismail, M.; Khan, M. I.; Khan, S. B.; Khan, M. A.; Akhtar, K.; Asiri, A. M. Green synthesis of plant supported Cu-Ag and Cu-Ni bimetallic nanoparticles in the reduction of nitrophenols and organic dyes for water treatment. J. Mol. Liq. 2018, 260, 78–91.
(2) Ratna, P. B. S. Pollution due to synthetic dyes toxicity & carcinogenicity studies and remediation. Int. J. Environ. Sci. 2012, 940.
(3) Ma, M.; Yang, Y.; Li, W.; Feng, R.; Li, Z.; Lyu, P.; Ma, Y. Gold nanoparticles supported by amino groups on the surface of magnetite microspheres for the catalytic reduction of 4-nitrophenol. J. Mater. Sci. 2019, 54, 323–334.
(4) Hu, P.; Long, M. Cobalt-catalyzed sulfate radical-based advanced oxidation: A review on heterogeneous catalysts and applications. Appl. Catal., B 2016, 181, 103–117.
(5) Li, Q. Q.; Loganath, A.; Chong, Y. S.; Tan, J.; Obbard, J. P. Persistent organic pollutants and adverse health effects in humans. J. Toxicol. Environ. Health Part A 2006, 69, 1987–2005.
(6) Goyal, A.; Bansal, S.; Singhal, S. Facile reduction of nitrophenols: Comparative catalytic efficiency of MFe$_2$O$_4$ (M = Ni, Cu, Zn) nano ferrites. Int. J. Hydrogen Energy 2014, 39, 4985–4998.
(7) Yu, B.; Liu, Y.; Jiang, G.; Liu, D.; Yu, W.; Chen, H.; Li, L.; Huang, Q. Preparation of electrospun Ag/g-C3N4loaded composite carbon nanofibers for catalytic applications. Mater. Res Express 2017, 4, 015603.
(8) Ji, M.; Xia, J.; Di, J.; Liu, Y.; Chen, R.; Chen, Z.; Yin, S.; Li, H. Graphene-like boron nitride induced accelerated charge transfer for boosting the photocatalytic activity of Bi$_2$O$_3$ towards bisphenol A removal. Chem. Eng. J. 2018, 331, 355–363.
(9) Wang, X.; Maeda, K.; Chen, X.; Takanabe, K.; Domen, K.; Hou, Y.; Fu, X.; Antonietti, M. Polymer semiconductors for artificial photosynthesis: Hydrogen evolution by mesoporous graphitic carbon nitride with visible light. J. Appl. Chem. Sci. 2009, 131, 1680–1681.
(10) Wu, X.; Gao, D.; Yu, H.; Yu, J. High-yield lactic acid-mediated route for a g-C$_3$N$_4$nanosheet photocatalyst with enhanced H$_2$ evolution performance. Nanoscale 2019, 11, 9608–9616.
(11) Wu, X.; Ma, H.; Zhong, W.; Fan, J.; Yu, H. Porous crystalline g-C$_3$N$_4$: Bifunctional NaHCO$_3$ template-mediated synthesis and improved photocatalytic H$_2$-evolution rate. Appl. Catal., B 2020, 271, 118899.
(12) Zhang, C.; Liu, J.; Huang, X.; Chen, D.; Xu, S. Multistage Polymerization Design for g-C$_3$N$_4$ Nanosheets with Enhanced Photocatalytic Activity by Modifying the Polymerization Process of Melamine. ACS Omega 2019, 4, 17148–17159.
(13) Karimi-Nazarabad, M.; Goharshadi, E. K. Highly efficient photocatalytic and photoelectrocatalytic activity of solar light driven WO$_4$/g-C$_3$N$_4$ nanocomposite. Sol. Energy Mater. Sol. Cells 2017, 484–493.
(14) He, Y.; Cai, J.; Zhang, L.; Wang, X.; Lin, H.; Teng, B.; Zhao, L.; Weng, W.; Wang, H.; Fan, M. Comparing Two New Composite Photocatalysts, t-LaVO$_4$/g-C$_3$N$_4$ and m-LaVO$_4$/g-C$_3$N$_4$, for Their Structures and Performances. Ind. Eng. Chem. Res. 2014, 53, 5905–5915.
(15) Cheng, N.; Tian, J.; Liu, Q.; Ge, C.; Qusti, A. H.; Asiri, A. M.; Al-Youbi, A. O.; Sun, X. Au-nanoparticle-loaded graphitic carbon nitride nanosheets: green photocatalytic synthesis and application toward the degradation of organic pollutants. ACS Appl. Mater. Interfaces 2013, 5, 6815–6819.
(16) Liu, G.; Niu, P.; Sun, C.; Smith, S. C.; Chen, Z.; Lu, G. Q.; M.; Cheng, H.-M. Unique Electronic Structure Induced High Photo-reactivity of Sulfur-Doped Graphitic C3N4. J. Appl. Chem. Sci. 2010, 11, 1642.
(17) Zhang, Y.; Antonietti, M. Photocurrent Generation by Polymeric Carbon Nitride Solids: An Initial Step towards a Novel Photovoltaic System. Chem. –Asian J. 2010, 5, 1307–1311.
(18) Niu, P.; Liu, G.; Cheng, H.-M. Nitrogen Vacancy-Promoted Photocatalytic Activity of Graphitic Carbon Nitride. J. Phys. Chem. C 2012, 116, 11013–11018.
(19) Li, X.; Ward, A. J.; Masters, A. F.; Maschmeyer, T. Solar hydrogen from an aqueous, noble-metal-free hybrid system in a continuous-flow sampling reaction system. Chemistry 2014, 20, 7345–7350.
(20) Wóźnica, M.; Chaoui, N.; Taabache, S.; Blechert, S. THF: An Efficient Electron Donor in Continuous Flow Radical Cyclization Photocatalyzed by Graphitic Carbon Nitride. Chem-Eur J 2014, 20, 14624–14628.
Visible Light Photocatalytic Degradation of Organic Dyes. ACS Omega 2019, 4, 17301–17316.

(40) Le, S.; Jiang, T.; Li, Y.; Zhao, Q.; Li, Y.; Fang, W.; Gong, M. Highly efficient visible-light-driven mesoporous graphitic carbon nitride/ZnO nanocomposite photocatalysts. Appl. Catal., B 2017, 200, 601–610.

(41) Qian, J.; Huo, J.; Zhang, P.; Zeng, J.; Wang, T.; Zeng, H. Improving the photocatalytic hydrogen production of Ag/g-C3N4 nanocomposites by dye-sensitization under visible light irradiation. Nanoscale 2016, 8, 2249–2259.

(42) Yang, Y.; Guo, Y.; Liu, F.; Yuan, X.; Guo, Y.; Zhang, S.; Guo, W.; Huo, M. Preparation and enhanced visible-light photocatalytic activity of silver deposited graphitic carbon nitride plasmonic photocatalyst. Appl. Catal., B 2013, 142-143, 828–837.

(43) Liang, S.; Zhang, D.; Pu, X.; Yao, X.; Han, R.; Yin, J.; Ren, X. A novel Ag2O/g-C3N4 p-n heterojunction photocatalysts with enhanced visible and near-infrared light activity. Sep. Purif. Technol. 2019, 210, 786–797.

(44) Ge, L.; Han, C.; Liu, J.; Li, Y. Enhanced visible light photocatalytic activity of novel polymeric g-C3N4 loaded with Ag nanoparticles. Appl. Catal., A 2011, 409-410, 215–222.

(45) Wang, T.; Quan, W.; Jiang, D.; Chen, L.; Li, D.; Meng, S.; Chen, M. Synthesis of redox-mediatior-free direct Z-scheme AgI/WO3 nanocomposite photocatalysts for the degradation of tetracycline with enhanced photocatalytic activity. Chem. Eng. J. 2016, 300, 280–290.

(46) Yang, Z.-M.; Huang, G.-F.; Huang, W.-Q.; Wei, J.-M.; Yan, X.-G.; Liu, Y.-Y.; Jiao, C.; Wan, Z.; Pan, A. Novel Ag2PO4/ CeO2 composite with high efficiency and stability for photocatalytic applications. J. Mater. Chem. A 2014, 2, 1750–1756.

(47) He, Q.; Zhou, F.; Zhan, S.; Yang, Y.; Liu, Y.; Tian, Y.; Huang, N. Enhancement of photocatalytic and photoelectrocatalytic activity of Ag modified Mpg-C3N4 composites. Appl. Surf. Sci. 2017, 391, 423–431.

(48) Zhou, Z.; Tang, X.; Ma, C.; Song, M.; Gao, N.; Wang, Y.; Huo, P.; Lu, Z.; Yan, Y. Fabrication of conductive and high-dispersed Ppy@Ag/g-C3N4 composite photocatalysts for removing various pollutants in water. Appl. Surf. Sci. 2016, 387, 366–374.

(49) Li, Z.; Jin, C.; Wang, M.; Kang, J.; Wu, Z.; Yang, D.; Zhu, T. Novel rugby-like g-C3N4/BiVO4 core/shell Z-scheme composites prepared via low-temperature hydrothermal method for enhanced photocatalytic performance. Sep. Purif. Technol. 2020, 232, 115937.