The study of visible-light photocatalytic degradation activity of Ag doped g-C₃N₄ obtained by heating process

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Abstract
In this paper, Ag nanoparticles (Ag NPs) were loaded on pure g-C₃N₄ (CN) via two different methods of direct heating and indirect heating to form g-C₃N₄/Ag-DX and g-C₃N₄/Ag-IDX photocatalysts, respectively. Using methylene blue as the degradation dye, the photocatalytic performance of g-C₃N₄/Ag-DX and g-C₃N₄/Ag-IDX was studied through visible light photocatalysis experiments. The results demonstrated that the photocatalytic performance of g-C₃N₄/Ag-DX and g-C₃N₄/Ag-IDX both increases with the increase in content of Ag nanoparticles. It is obvious that g-C₃N₄/Ag-ID8 has the optimal photocatalytic activity. Meanwhile, the g-C₃N₄/Ag-ID8 has excellent stability and can be reused in photocatalysis experiments.

1. Introduction

In the early 1890s, methylene blue (MB) was used to treat bacterial malaria and was successful. MB has been widely used in industrial dyeing, aquaculture, skincare and medical treatment. However, MB is widely accumulated in our aquatic environment due to the improper treatment of wastewater from industrial dyeing and aquaculture. The ionic compound formed by MB in the aqueous solution competes with the microbial enzyme system for hydrogen ions, which will inhibit the growth of bacteria and other microorganisms, thereby causing the microorganisms to lose their viability and posing a serious threat to the ecosystem [1, 2]. Although MB has outstanding applications in the medical field, if the dosage of MB is too high, it will cause some symptoms, such as Heinz body anemia, changing in red blood cell morphology and necrotizing swelling [3–5], and the residual MB will be passed into the aquatic environment through the patient excretion of urine or feces, thus causing water pollution and bringing great harm to human health. The application of semiconductor photocatalytic oxidation technology to degrade organic pollutants in water bodies is an efficient and energy-saving water pollution treatment technology. Under the action of light, this technology can convert organic pollutants in the water into environmentally friendly carbon dioxide and water at room temperature without secondary pollution, thereby solving the problem of environmental pollution. According to the above, it is very meaningful and important to develop a photocatalyst with excellent photocatalytic performance for environmental governance.

Graphite carbon nitride (g-C₃N₄) is a typical non-toxic, non-metallic and visible-light-driven semiconductor catalyst, which can be used in the photo degradation of organic matter, hydrogen production by photo decomposition of water, photocatalysis synthesis of organic matter and hydrocarbon fuel, etc. However, the pure g-C₃N₄ obtained by the conventional thermal polymerization method has the shortcomings of high recombination rate of electron–hole pairs and low utilization of visible light, which seriously affects its photocatalytic performance and stability. In order to overcome these problems, many methods have been adopted to optimize the performance of pure g-C₃N₄ [6, 7]. Among many improved methods, the strategy of doping precious metals into semiconductor photocatalysts has attracted a great deal of attention [8]. According to the reported studies, the modification of g-C₃N₄ surface with metal (Ag [9, 10], Au [11], Pd [12], Pt [13], Cu [14]) and metal oxide (TiO₂ [15–17], ZnO [18]) can effectively suppress the recombination of photogenerated...
electron-hole pairs, which can greatly improve the photocatalytic performance of g-C_3N_4. So far, a large number of researchers have reported that the doping of Ag nanoparticles on the surface of g-C_3N_4 can effectively enhance the photocatalytic performance of the catalyst [19, 20]. Most of the Ag-doped g-C_3N_4 photocatalysts were synthesized by the thermal exfoliation and photo-reduction method, and the experiment process is relatively complicated. This paper proposes two simpler methods to form g-C_3N_4/Ag photocatalyst.

In this paper, Ag was doped into pure g-C_3N_4 via direct heating and indirect heating, and forming g-C_3N_4/Ag-DX and g-C_3N_4/Ag-IDX photocatalysts, respectively. The structural characteristics of the g-C_3N_4/Ag photocatalysts were used to reduce the band gap energy of the catalyst, and improve separation rate of photogenerated electron-hole pairs, thereby enhancing performance of g-C_3N_4/Ag photocatalysts. In addition, the main reactive species of g-C_3N_4/Ag-ID8 composites in the photocatalytic degradation process were verified by free radical scavenging experiments.

2. Materials and experiments

2.1. Materials

Silver nitrate (AgNO_3 ≥99.8%), Melamine (C_3H_6N_6 ≥99.0%), Ethanol (C_2H_5OH ≥99.7%), Ammonium oxalate ((NH_4)_2C_2O_4), Tert-butyl alcohol and P-benzoquinone, were obtained from Sinopharm Chemical Reagent Co. Ltd, China. All the reagents used in this research are analytical grade without any further purification.

2.2. Synthesis of bulk g-C_3N_4 photocatalyst

Bulk g-C_3N_4 photocatalyst was synthesized by conventional thermal polymerization method. Putting 10 g of melamine in a muffle furnace, and heating it at 550 °C (2.5 °C min^{-1}) for 4 h. After natural cooling, approximately 10 g of the yellow product obtained was collected and ground into powder. The yellow powder products were designated as g-C_3N_4.

2.3. Synthesis of g-C_3N_4/Ag composite photocatalyst

The deposition of silver nanoparticles in g-C_3N_4 was carried out via two methods without light irradiation, namely direct heating and indirect heating. Direct heating: 1 g of melamine and a certain amount of silver nitrate were dispersed in 50 ml deionized water by ultrasonication for 30 min, the mixture was heated in a water bath until white crystals were precipitated, and dried at 60 °C in air overnight. Then, the white product was put in the muffle furnace at 550 °C for 4 h in air atmosphere (2.5 °C min^{-1}). The resulting mixture was yellow product and ground into powder. The yellow powder products were designated as g-C_3N_4/Ag-DX (CN/Ag-DX), where X stands for the mass of silver nitrate and was 0.002 g, 0.004 g, 0.008 g, 0.016 g, respectively.

Indirect heating: 0.5 g of bulk g-C_3N_4 were dispersed in 20 ml deionized water by ultrasonication for 30 min, then a certain amount of silver nitrate add to the dispersion, the suspension was magnetically stirred for 1 h, and dried at 60 °C in air overnight. The following steps are the same as the steps of direct heating. The yellow powder products were designated as g-C_3N_4/Ag-IDX (CN/Ag-IDX), where X refers to the mass of silver nitrate and was 0.002 g, 0.004 g, 0.008 g, 0.016 g, respectively.

2.4. Photocatalytic experiment

MB was chosen as the model pigment for photocatalytic degradation experiments under the visible light irradiation. In a typical photocatalytic activity test, firstly, 0.06 g of catalyst was added into a 60 ml MB solution (20 mg l⁻¹), and the obtained mixture was stirred for 1 h in the darkness to reach an adsorption-desorption equilibrium state between MB molecule and catalyst. Then the mixture of an adsorption-desorption equilibrium state was placed under the irradiation of a 300 W xenon lamp to conduct photocatalytic test. During the irradiation, an amount of 2 ml of reaction suspension was extracted from the reactor at 30 min intervals, after centrifugation, the supernatant was absorbed. Then, the supernatant was diluted ten times with deionized water, and the relative concentration of MB solution was tested via a UV–vis spectrophotometer. Finally, the ultraviolet spectral data were analyzed.

3. Results and discussion

To confirm the successful synthesis of g-C_3N_4/Ag composite photocatalyst, a series of characterization were carried out. Firstly, the crystal structure evolution of all the samples was indicated by x-ray diffraction spectroscopy (XRD), and the results are shown in figure 1. Two characteristic wide peaks were found in all the prepared samples at 13.1° (100) and 27.4° (002), which correspond to the s-triazine structural units of the planar structure and the layer stacking of conjugated aromatic systems of g-C_3N_4, respectively [21, 22]. The diffraction
peaks intensity at 13.1° (100) of all g-C3N4/Ag samples slightly decreased with the increase of Ag concentration, which may be attributed to the highly dispersed Ag nanoparticles on the surface, and the inter-layer structure of g-C3N4 not only reduced the mass ratio of g-C3N4 in CN/Ag composites but also decreased the exposed surface area of g-C3N4. Meanwhile, the diffraction peak intensity at 27.4° (002) of CN/Ag-IDX samples slightly weakened with the increase of Ag concentration, indicating that the massive g-C3N4 in CN/Ag-IDX composites was exfoliated by the thermal exfoliation procedure. However, as the increase of silver concentration, the diffraction peak intensity (002) of CN/Ag-DX is stronger than that of CN, and first increases and then decreases, this may be attributed to the insufficient heat treatment time of the CN/Ag-DX composites, resulting the g-C3N4 in the CN/Ag-DX composites is not completely exfoliated by the thermal exfoliation procedure, and the different Ag content of each CN/Ag-DX composites resulted in the different peeling degree of g-C3N4. Figure 1(b) revealed the fitted curves of the (002) peak of all the samples, and we can clearly see the position shift of peak. Obviously, the position of (002) peak shifted slightly toward bigger value of 2θ angle, which indicates that the inter-planar spacing of the (002) crystal plane in CN has decreased. The above observation results prove that the doping of Ag nanoparticles affects the crystal structure of g-C3N4. It is worth noting that we cannot observe the characteristic peaks of metallic Ag in all the CN/Ag photocatalysts, this may be ascribed to the low amounts and high dispersion of metallic Ag on the surface and inter-layer structure of CN/Ag.

The morphology of the pure CN and CN/Ag samples were studied by TEM. Figure 2(a) clearly revealed that the g-C3N4 photocatalyst forms a wrinkled two-dimensional structure by stacking flake-like, which is consistent with the previously reported results. Figures 2(b), (c) both showed that some Ag nanoparticles were attached to the surface and inter-layer structure of g-C3N4. Since the proportion of Ag in g-C3N4/Ag composites is too small, the adhesion of Ag nanoparticles in the figure is not obvious. However, the morphology of g-C3N4 in CN/Ag-D8 and CN/Ag-ID8 composite photocatalysts were still the stacking flake-like structures. In short, the Ag nanoparticles did not destroy the stacking flake-like structures of g-C3N4, and Ag nanoparticles were successfully distributed in g-C3N4 with relatively uniform distribution, without negatively random agglomeration.

For further verify that Ag nanoparticles were successfully doped in g-C3N4, EDS elemental analysis has been used to characterize the prepared CN/Ag-ID8 as shown in figure 3. Figure 3(a) was the scanning area of the electron microscope image of the CN/Ag-ID8 composites. Figures 3(b), (c) depicted the sample contains C and N elements, and the stoichiometric ratio of C and N distributed in the CN/Ag-ID8 composites is about 3:4, indicating that g-C3N4 was successfully prepared. Although the content of Ag nanoparticles is very low, it can be noticed that the Ag elements in figure 2(d) were uniformly distributed in the CN/Ag-ID8 composite photocatalyst without agglomeration. In summary, Ag nanoparticles were successfully distributed in g-C3N4, which is consistent with the above characterization results.
Since the x-ray photoelectron spectroscopy (XPS) can clarify the surface chemical compositions and chemical valence states of different elements on the surface of the materials, we carried out XPS to further prove the deposition of Ag nanoparticles in catalysts. The XPS survey spectra in figure 4(a) revealed that the pure g-C₃N₄ only contained the C, N, and O elements, the element O may originated from adventitious oxygen species in air. Compared with pure g-C₃N₄, the CN/Ag-D8 and the CN/Ag-ID8 photocatalysts samples were both showed the typical peaks of C 1s, N 1s, O 1s and extremely weaken peaks Ag 3d, which was mainly because the content of metallic Ag in them was too low. Inset of figure 4(a) displays the magnified area of peaks Ag 3d, which indicate that the success of the deposition of Ag nanoparticles in the prepared catalysts. No other impurity peaks were found, which proved the high purity of prepared catalysts. The high resolution XPS spectra of the figure 4(b) showed that no characteristic diffraction peaks featured to the metallic Ag particles were observed in the pure g-C₃N₄, while two peaks were located at around 368 and 374 eV in the CN/Ag-D8 and CN/Ag-ID8 composites, representing Ag 3d₅/₂ and Ag 3d₃/₂, respectively. The spectrum of Ag 3d₅/₂ is further split into two peaks at 367.7 and 368.2 eV, meantime, the spectrum of Ag 3d₃/₂ is further split into two peaks at 373.7 and
374.3 eV, too. The peaks at 368.2 and 374.3 eV correspond to the metallic Ag° species [23], which significantly demonstrates the presence of Ag NPs in the CN/Ag composites. In figure 4(c), XPS spectra of the C1s peak for the prepared catalysts are shown into three peaks centered at 284.8, 286.2 and 288.3 eV, which are ascribed to the C–C bonds of adventitious carbon species, C–NH2, and the sp2-hybridized (N–C=N), respectively [24, 25]. Comparatively, the intensity of C1s peaks of CN/Ag-ID8 is stronger than that of CN/Ag-D8. Figure 4(d) showed the XPS spectra of the N1s peaks for samples, where four secondary peaks with binding energy are 398.4, 400.1, 401.2 and 404 eV, which correspond to the sp2-hybridized nitrogen (C–N=C) from the triazine rings, the tertiary nitrogen (N–(C)3), the N atoms bonded with H(C–H), and the charging effects in the heterocycles, respectively [26, 27].

In order to study the effect of the noble metal Ag-doped g-C3N4 on the capture and transfer of photogenerated carriers, the photoluminescence experiments were carried out at room temperature. Figure 5(a) shows the PL spectra of pure g-C3N4 and CN/Ag-D, and figure 5(b) shows the PL spectra of pure g-C3N4 and CN/Ag-ID. It can be clearly observed that the curves of the PL spectra of all prepared samples are similar. Compared with pure g-C3N4, the emission peak intensity of CN/Ag-D and CN/Ag-ID both gradually decreased with the increase of the content of Ag nanoparticles. However, the emission peak intensity of CN/Ag-ID16 and CN/Ag-ID16 is stronger than that of CN/Ag-D8 and CN/Ag-ID8, respectively. This may be due to the fact that the content of Ag nanoparticles in CN/Ag-D16 and CN/Ag-ID16 is higher than that in CN/Ag-D8 and CN/Ag-ID8, respectively. It is reported that the weaker intensity of the PL spectral peak, the faster speed of interface electron transfer, the higher separation rate of photogenerated electron-hole pairs [28–30]. According to the above-mentioned experimental data analysis, Ag nanoparticles were successfully doped on g-C3N4 and acted as traps for photogenerated electrons, photogenerated electrons from the conduction band of g-C3N4 can be quickly transferred to the Ag species via the interfaces, which enhanced the ability to capture photogenerated carriers, increased the transfer speed of charge, improved the separation efficiency rates. It is worth noting that the CN/Ag-ID8 sample shows the lowest PL intensity as shown in figure 5(c), we speculate that the CN/Ag-ID8 composite photocatalyst may have the strongest charge transfer and separation efficiency. It will be further proved in the later photocatalytic degradation experiments of MB.

The optical performances of all the prepared samples were investigated by using UV–Visible (DRS). It can be apparently seen that pure g-C3N4 exhibits an absorption edge at around 460 nm in figure 6, while the absorption edges of all CN/Ag-DX and CN/Ag-IDX composite photocatalysts in the visible light range are significantly red-shifted. This trend suggests that CN/Ag-DX and CN/Ag-IDX composite photocatalysts can effectively use visible light and generate more electron-hole pairs under visible light irradiation, thereby increasing the separation rate of electron-hole pairs. This may be attributed to the surface plasmon resonance (SPR) effect generated by the noble metal Ag particles under visible light irradiation. Converting from the UV–visible diffuse reflectance spectroscopy of all the samples, we can deduce band gap energy (Eg), which is an important parameter to characterize the light absorption performance. Eg can be calculated using the semiconductor forbidden band derivation formula (Tauc equation) [31].
Where the $\alpha$, $h$, $\nu$, $n$, $A$ and $E_g$ represents the absorption coefficient, the Planck constant ($4.136 \times 10^{-15}$ eV·s), the light frequency ($3.0 \times 10^8$ m·s$^{-1}$), the indirect gap semiconductor ($n = 1/2$), the proportionality constant ($A = 1$) and the energy band gap, respectively [32]. As shown in the inset of figure 6(a), it can be found that the band gap of CN is 2.74 eV. The band gap of CN/Ag-D decreased with the content of Ag nanoparticles increase, the band gap of CN/Ag-D8 was 2.67 eV. As shown in the inset of figure 6(b), the band gap of CN/Ag-ID decreased with the content of Ag nanoparticles increase, too. It is worth noting that the CN/Ag-ID8 photocatalyst shows a smaller band gap value, 2.63 eV. Therefore, the doping of Ag nanoparticles not only enhanced the light absorption intensity of the CN/Ag in the range of 460 to 600 nm, but also narrowed the band gap energy.

The photocatalytic activities of all the prepared samples were measured by the degradation of MB solution under Xenon lamp irradiation at room temperature, and the results are shown in figure 7. The degradation rate of MB solution was quantified indirectly through the concentration ratio $C_t/C_0$, where the $C_t$ and $C_0$ represents the concentration of MB solution at the reaction time ($t$) and the initial concentration of MB solution, respectively. Before running the photoreaction, the mixed solution of all the prepared samples and MB were separately stirred in the darkness for 1 h to reach an adsorption-desorption equilibrium state between MB
molecules and as-prepared catalysts. As shown in figures 7(a), (b), when there is no catalyst in the MB solution, the concentration ratio $C_t/C_0$ is always 1, indicating that the MB solution cannot be degraded under the condition of no catalyst. Under the dark conditions, the concentration ratio $C_t/C_0$ is always remained, indicating that MB solution can hardly be degraded under dark conditions. Under the irradiation in visible light, as the content of Ag nanoparticles in the catalyst increase (0, 0.002 g, 0.004 g, 0.008 g), the concentration ratio $C_t/C_0$ corresponding to CN/Ag-DX and CN/Ag-ID8 decreases gradually. However, when the content of Ag nanoparticles increases to 0.016 g, the concentration ratio $C_t/C_0$ corresponding to CN/Ag-D16 and CN/Ag-ID16 decreases further, indicating that MB solution can hardly be degraded under dark conditions. Under the irradiation in visible light, electron-hole pairs are formed when visible light irradiated on the surface of g-C3N4. Compared with the sample Ag-D obtained by direct heat treatment of melamine and AgNO3, CN/Ag-ID8 is the best, a pseudo-first-order reaction model is applied to describe the experimental data [34]. The kinetic equation can be expressed as follow:

$$\ln\left(\frac{C_0}{C_t}\right) = kt$$

Where the $k$ and $t$ represents the first-order rate constant and the photoreaction time, respectively. As far as we know, the larger the $k$, the better the photocatalytic performance. As shown in figures 7(c), (d), it was clearly found that the $k$ of MB degradation over CN/Ag-DX and CN/Ag-ID8 photocatalysts both higher than the pure g-C3N4 sample, and the $k$ of MB degradation over CN/Ag-DX and CN/Ag-ID8 photocatalysts both increases with the increase of the content of silver nanoparticles. However, the $k$ of MB degradation over CN/Ag-D16 and CN/Ag-ID16 are both lower than the $k$ of MB degradation over CN/Ag-D8 and CN/Ag-ID8, respectively. Obviously, the $k$ of MB degradation over CN/Ag-ID8 is the highest, 0.0125. It was further confirmed that the photocatalytic activity of CN/Ag-ID8 is the best.

Figure 7(e) shows the change of MB concentration with time in the UV–vis absorption spectrum of CN/Ag-ID8 photocatalyst. It can be found that the absorption peak of CN/Ag-ID8 at 664 nm shifted slightly, and the intensity gradually decreased with the extension of the illumination time. The process of the absorption peak shifting from 664 nm to 650 nm is the process of the gradual degradation of the MB molecular skeleton. During this process, the MB molecules are gradually decolorized and degraded by the adsorption and catalysis of the CN/Ag-ID8 photocatalyst.

The stability of photocatalyst is very important in practical applications. The stability of the CN/Ag-ID8 photocatalyst was further evaluated by reusing the CN/Ag-ID8 photocatalyst after the visible-light degradation of MB solution, as shown in figure 8. It can be clearly seen that the MB degradation rate of CN/Ag-ID8 is close to 100%. Moreover, the degradation rate of CN/Ag-ID8 to MB is still more than 90% after four successive experiments of MB photocatalytic degradation. This result fully demonstrates the stability of CN/Ag-ID8 photocatalyst was not reduced significantly, confirming that the CN/Ag-ID8 can be recycled during the photocatalysis.

We collected the sample (g-C3N4/Ag-ID8) after the photocatalytic reaction and characterized them with XRD. Compared with the sample (g-C3N4/Ag-ID8) before the photocatalytic reaction, as shown in figure 9. We found that the characteristic peak has no change, which indicated that the composite catalyst is stable during the reaction.

Based on the above findings, it is easy to conclude that the photocatalytic activity of CN/Ag-ID8 is stronger than that of CN/Ag-DX. This result may be attributed to the fact that CN/Ag-ID is formed by indirect heat treatment of g-C3N4 and AgNO3, while CN/Ag-D is formed by direct heat treatment of melamine and AgNO3. The specific surface area of CN/Ag-ID obtained by indirect heat way is larger than that of CN/Ag-D obtained by direct heat way, and the binding capacity for Ag nanoparticles is also stronger, the formed defect energy level by CN/Ag-ID8 makes the band gap narrower, which is conducive to the adsorption and degradation of the reactant by the catalyst. Therefore, the CN/Ag-ID formed by indirect heat treatment has more excellent photophysical properties.

Figure 10 shows a proposed photocatalytic mechanism of g-C3N4/Ag composites under visible light irradiation. Electron-hole pairs are formed when visible light irradiated on the surface of g-C3N4/Ag composites, owing to the photon energy absorbed by the g-C3N4/Ag composites is greater than its own band gap energy ($E_g = 2.63$ eV), the photogenerated electrons in the valence band (VB) can jump into the conduction band (CB), and leaving photogenerated holes on the VB. The holes ($h^+$) in the VB react with OH on the surface to generate hydroxyl radicals species (-OH). Some electrons in the CB react with O2 to generate superoxide.
radicals (·O₂⁻). Because of the energy difference between the CB bottom level of g-C₃N₄ and the Fermi level of Ag nanoparticles, Ag can act as an electron sink, therefore, the remaining electrons in CB are captured by Ag and react with O₂ in H₂O to generate ·O₂⁻, thereby improving the separation efficiency of photo-generated electron-hole pairs [35]. The main reactive species h⁺, ·OH and ·O₂⁻ react with MB, and finally form pollution-free CO₂ and H₂O. Ag has no the performance of photocatalytic degradation, but g-C₃N₄ and Ag in the g-C₃N₄/Ag composite form a Schottky barrier [36], which improves the separation efficiency of charges and the speed of interface electron transfer, thereby increasing photocatalytic degradation performance of g-C₃N₄/Ag composite.

In order to verify the main reactive species of g-C₃N₄/Ag-ID8 composites in the visible light degradation reaction system, free radical scavenging experiments were carried out. Ammonium oxalate, Tert-butyl alcohol and P-benzoquinone are used as scavengers for holes (h⁺), hydroxyl radicals (·OH) and superoxide radicals (·O₂⁻), respectively. As shown in figure 11, the concentration ratio Cₜ/C₀ of MB degraded by g-C₃N₄/Ag-ID8 is the highest with the presence of Ammonium oxalate. This is due to the inability to generate ·OH after adding Ammonium oxalate to the degradation mixture, (2 h⁺ + 2H₂O = 2·OH + H⁺), which indicates that h⁺ has the strongest photocatalytic effect on the sample g-C₃N₄/Ag-ID8. Except for the blank experiment, the concentration ratio Cₜ/C₀ of MB degraded by g-C₃N₄/Ag-ID8 is the lowest with the presence of p-benzoquinone, indicating that ·O₂⁻ has less photocatalytic effect on the sample g-C₃N₄/Ag-ID8, which is due to the fact that Ag nanoparticles act as an electron sink to capture photogenerated electrons in the CB, promoting...

Figure 8. The cyclic experiments of the degradation of MB solution (20 mg l⁻¹) over g-C₃N₄/Ag-ID8 under visible light irradiation.

Figure 9. X-ray diffraction spectroscopy for g-C₃N₄/Ag-ID8 composite before and after photocatalytic reaction.
the separation of photogenerated electron-hole pairs and decreasing the photogenerated electron-hole pairs recombination, thereby enhancing the photocatalytic activity [19]. Consequently, $h^+$, $\cdot$OH and $\cdot$O$_2^-$ are the main reactive species of g-C$_3$N$_4$/Ag-ID8 composites in the process of photocatalytic degradation of MB.

4. Conclusion

In summary, this work successfully deposited Ag nanoparticles on pure g-C$_3$N$_4$ by direct heating and indirect heating, and forming g-C$_3$N$_4$/Ag-DX and g-C$_3$N$_4$/Ag-IDX visible light-driven photocatalysts, respectively. The results of photocatalytic degradation experiments showed that the photocatalytic activity of g-C$_3$N$_4$/Ag-DX and g-C$_3$N$_4$/Ag-IDX both increase with the increase of Ag nanoparticles content and are stronger than pure g-C$_3$N$_4$.

It was worth noting that g-C$_3$N$_4$/Ag-ID8 has outstanding photocatalytic activity. This may be attributed to the fact that indirect heating makes the specific surface area of g-C$_3$N$_4$/Ag-ID larger and the band gap energy narrower. Meanwhile, the cyclic degradation experiment suggested that g-C$_3$N$_4$/Ag-ID8 has excellent stability and can be recycled in photocatalytic experiments. Moreover, the free radical scavenging experiments proved...
that $H^+$, $-OH$ and $-O_2^-$ are the main reactive species for the photocatalytic degradation of MB in the g-C$_3$N$_4$/Ag-ID8 composite.

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**References**

[1] Safarik I and Safariková M 2002 Detection of low concentrations of malachite green and crystal violet in water Water Res. 36 196–200
[2] Yang F et al 2008 Progress in study of determination thionine dyes and metabolize of animal in vitro Journal of Pharmaceutical Analysis. 8 1395–400
[3] Disanto A R and Wagner J G 1972 Pharmacokinetics of highly ionized drugs I: methylene blue—whole blood, urine, and tissue assays J. Pharm. Sci. 61 598–602.
[4] Chung K T, Fulk G E and Andrews A W 1981 Mutagenicity testing of some commonly used dyes Appl. Environ. Microbiol. 42 641–8
[5] Peter C et al 2000 Pharmacokinetics and organ distribution of intravenous and oral methylene blue Eur. J. Pharm. Sci. 56 247–50
[6] Patnaik S, Martha S, Acharya S and Parida K M 2015 An overview on modification of the g-C$_{3}$N$_{4}$ with high carbon containing materials for photocatalytic applications Inorganic Chemistry Frontiers. 30 336–47
[7] Le T M O, Lam T H, Pham T N, Ngo T C, Lai N D, Do Danh B and Van Minh N 2018 Enhancement of rhodamine B degradation by Ag nanoclusters-loaded g-C$_3$N$_4$ nanosheets Polymers. 10 633
[8] Liu Z Y, Zhang M Y and Wu J L 2018 Enhanced Visible-Light Photocatalytic and Antibacterial Activities of Ag-Doped g-C$_3$N$_4$ Nanocomposites Chemistry Select. 3 10630–6
[9] Su F Y and Zhang W D 2017 Carbonyl-Grafted g-C$_3$N$_4$ porous nanosheets for efficient photocatalytic hydrogen evolution Chem. Asian J. 12 515–23
[10] Xu W et al 2020 Visible light photocatalytic degradation of tetracycline with porous Ag/graphite carbon nitride plasmonic composite: degradation pathways and mechanism J. Colloid Interface Sci. 574 110–21
[11] Tian H Y et al 2019 Gold nanorods/g-C$_3$N$_4$ heterostructures for plasmon-enhanced photocatalytic H$_2$ evolution in visible and near-infrared light J. Colloid Interface Sci. 557 700–8
[12] Xu X L et al 2018 Unprecedented catalytic performance in amine syntheses via Pd/g-C$_3$N$_4$ catalyst-assisted transfer hydrogenation Green Chem. 20 2038–46
[13] Xue J J et al 2015 Facile photochemical synthesis of Au/Pt/g-C$_3$N$_4$ with Plasmon-enhanced photocatalytic activity for antibiotic degradation ACS Applied Materials & Interfaces. 7 9630–7
[14] Fan M S et al 2016 Visible-light-driven high photocatalytic activities of Cu/g-C$_3$N$_4$ photocatalysts for hydrogen production RSC Adv. 6 34633–40
[15] Chen X F et al 2016 Growth of g-C$_3$N$_4$ on mesoporous TiO$_2$ spheres with high photocatalytic activity under visible light irradiation Appl. Catalysis B 188 342–50
[16] Kuang J Y et al 2019 Surface plasma Ag-decorated single-crystalline TiO$_2$-x(B) nanorod/defect-rich g-C$_3$N$_4$ nanosheet ternary superstructure 3D heterojunctions for enhanced visible-light-photocatalyst J. Colloid Interface Sci. 542 63–72
[17] Li F X et al 2020 TiO$_2$-on-g-C$_3$N$_4$ double-shell microtubes: in situ fabricated heterostructures toward enhanced photocatalytic hydrogen evolution J. Colloid Interface Sci. 572 22–30
[18] Uma R et al 2017 Cost-effective fabrication of ZnO/g-C$_3$N$_4$ composite thin films for enhanced photocatalytic activity against three different dyes (MB, MG and RB) Mater. Chem. Phys. 201 147–55
[19] Mott D et al 2010 Aqueous synthesis and characterization of Ag and Ag-Au nanoparticles: addressing challenges in size, monodispersity and structure Philosophical Transactions of The Royal Society A-Mathematical Physical and Engineering Sciences. 368 4275–92
[20] Liu Y et al 2015 Generation of oxygen vacancy and OH radicals: a comparative study of Bi$_2$WO$_6$ and Bi$_2$WO$_6$-x nanophases Chem Cat Chem. 7 4076–84
[21] Li G S et al 2016 Nanotube confinement induced size-controllable g-C$_3$N$_4$ quantum dots modified single-crystalline TiO$_2$ nanotube arrays for stable synergetic photoelectrocatalysis Nano Energy. 19 446–54
[22] Sun J X et al 2012 Fabrication of composite photocatalyst g-C$_3$N$_4$/ZnO and enhancement of photocatalytic activity under visible light Dalton Trans. 41 6756–63
[23] Kang S B et al 2015 Critical influence of g-C$_3$N$_4$ self-assembly coating on the photocatalytic activity and stability of Ag/AgCl microspheres under visible light Appl. Catalysis B 168–169 472–82
[24] Xu J et al 2019 Enhanced visible-light-induced photocatalytic degradation and disinfection activities of oxidized porous g-C$_3$N$_4$ by loading Ag nanoparticles Catal. Today 332 227–35
[25] Niu P et al 2018 Distinctive defects engineering in graphitic carbon nitride for greatly extended visible light photocatalytic hydrogen evolution Nano Energy. 44 73–81
[26] Christoforidis K C et al 2018 Metal-free dual-phase full organic carbon nanotubes/g-C$_3$N$_4$ heteroarchitectures for photocatalytic hydrogen production Nano Energy. 50 468–78
[27] Wang J F et al 2018 Robust photocatalytic hydrogen evolution over amorphous ruthenium phosphate quantum dots modified g-C$_3$N$_4$ nanosheets Appl. Catalysis B 239 578–85
[28] Lin X et al 2015 Ternary heterostructured Ag–BiVO$_4$/InVO$_4$ composites: synthesis and enhanced visible-light-driven photocatalytic activity J. Alloys Compd. 635 256–64
[29] Ren H T, Jia S Y, Wu Y, Wu S H, Zhang T H and Han X 2014 Improved Photochemical Reactivities of Ag2O/g-C$_3$N$_4$ in Phenol Degradation under UV and Visible Light Ind. Eng. Chem. Res. 53 17645–53
[30] Zhang Y F et al 2015 A polymer-metal-polymer-metal heterostructure for enhanced photocatalytic hydrogen production Journal of Materials Chemistry A. 3 109–15
[31] Zhang S S et al 2018 Facile synthesis of Pt assisted Bi-Bi2WO6-x with oxygen vacancies for the improved photocatalytic activity under visible light Appl. Surf. Sci. 459 363–75
[32] Huo W C et al 2019 Synthesis of Bi2WO6 with gradient oxygen vacancies for highly photocatalytic NO oxidation and mechanism study Chem. Eng. J. 361 129–38
[33] Zhang X G et al 2018 Carbon Nitride Bimetallic Ag-Ni/g-C3N4 catalysts for photocatalytic degradation of methylene blue under visible-light irradiation Journal of the Chinese Ceramic Society. 46 85–92
[34] Xu H et al 2013 Novel visible-light–driven AgX/graphitic-like C3N4 (X = Br, I) hybrid materials with synergistic photocatalytic activity Appl. Catalysis B 129 182–93
[35] Zhang S et al 2017 Enhanced photocatalytic activity in Ag-nanoparticle-dispersed BaTiO3 composite thin films: role of charge transfer Advances in Applied Ceramics. 6 1–10
[36] Meng A Y et al 2019 Dual cocatalysts in TiO2 photocatalysis Adv. Mater. 31 1807660