Ag Loading Enhanced Photocatalytic Activity of g-C$_3$N$_4$ Porous Nanosheets for Decomposition of Organic Pollutants

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The g-C$_3$N$_4$ porous nanosheets with different loading amount of Ag nanoparticles (NPs) are successfully prepared by a simple liquid-phase reduction method. These Ag/g-C$_3$N$_4$ composites have an improved photocatalytic performance for decomposing organic pollutants compared with that of pure g-C$_3$N$_4$ nanosheets. Many measurements have been used for characterizing the samples, such as XRD, FTIR, UV-Vis DRS, PL, XPS, EDS, SEM, and TEM. In Ag/g-C$_3$N$_4$, the Ag NPs are uniformly coated on the g-C$_3$N$_4$ surface, the diameter is mainly in the range of 8~18 nanometers. Loading of Ag NPs expand the response to the visible light for g-C$_3$N$_4$ and increasing the producing rate of photogenerated e$^-$-h$^+$ pairs. The loading of silver NPs obviously enhances the photocatalytic activity of C$_3$N$_4$ nanosheets toward the Rhodamine B (RhB) decomposition under the simulated sunlight irradiation. With different loading amounts of Ag NPs, Ag/g-C$_3$N$_4$ (3 wt% of Ag) showed the highest photocatalytic activity for RhB decomposition among these as-prepared samples, which is 10 times of the rate of pure C$_3$N$_4$. Based on the experimental results, a possible photocatalytic mechanism for Ag/g-C$_3$N$_4$ is proposed.

Keywords: Ag nanoparticles, Ag/g-C$_3$N$_4$, photocatalytic activity, organic pollutant, electron-hole separation, modification

INTRODUCTION

The organic pollutants in waste water has become a serious problem that threatens human health (Zhang and Wen, 2008). Solar energy, as a clean energy, has been widely concerned. It is a very effective way to solve the problem of water pollution by using solar energy (George et al., 2015; Wang et al., 2017, 2018a; Qi et al., 2018a; Shi et al., 2018; Wei et al., 2018; Yan et al., 2018a,b; Zhong et al., 2018). Since Fujishima et al. reported the phenomenon of water splitting for hydrogen production on TiO$_2$ photoanode (Fujishima and Honda, 1972), the study of semiconductor photocatalysts has become very popular (Tao et al., 2014; Wei et al., 2015; Wen et al., 2015; Park et al., 2016; Qi et al., 2017b, 2018b; Xia et al., 2017).
The photocatalysis technology has been widely used to treat the organic polluted waste water because of its simpler equipment, convenient operation, energy saving, environmental protection, and strong oxidizing ability. Semiconductor photocatalysts mainly include graphite nitride (g-C₃N₄) (Cao et al., 2015), metal oxide (Qi et al., 2017a), and metal sulfide (Hong et al., 2015). Among these materials, g-C₃N₄, as an important photocatalyst, has received widespread attention, because of its unique characteristics, including metal free, non-toxic, easy preparation, suitable band gap, and cheap (Cao and Yu, 2014). However, the photocatalytic activity of g-C₃N₄ is still very low, it is difficult to use in real life, due to the low utilization efficiency of sunlight and the fast recombination of photogenerated e⁻-h⁺ pairs (Martha et al., 2013; Zhu et al., 2018). Up to now, many efforts have been devoted to improve the photocatalytic performance of g-C₃N₄ (Xiang et al., 2011; Akple et al., 2015; Xu et al., 2018; Fu et al., 2019). For example, Liu et al. used metal doping to enhance the visible light adsorption of g-C₃N₄ and found that it enhanced the photocatalytic activity in the photocatalysis of water splitting for hydrogen production (Niu et al., 2012). Cheng et al. demonstrated that through building heterojunction of ZnO/g-C₃N₄, the photocatalytic activity for the decomposition of organic dyes is enhanced (Cheng et al., 2013). Fina et al. reported that loading Pt nanoparticles (NPs) can enhance activity of g-C₃N₄ photocatalytic water splitting into H₂ production (Fina et al., 2015). In these methods, depositing noble metals (Au, Ag, Pt, or Pd) on the g-C₃N₄ surface is useful to enhance the photocatalytic activity of g-C₃N₄ (Wen et al., 2017; Tong et al., 2018; Wang et al., 2018b). However, the mechanism of interaction between the loading noble metals and C₃N₄, and how they work to enhance the photocatalytic activity of g-C₃N₄ are limited to know.

This work reports a simple liquid-phase reduction method to prepare the Ag/g-C₃N₄ composites. The structure, morphology, optical property, and photocatalytic activity of the as-prepared Ag/g-C₃N₄ samples are investigated. The effects of loading content of Ag on the light absorbency and photocatalytic activity of C₃N₄ are studied. Under the simulated sunlight, the photocatalytic performance of g-C₃N₄ for Rhodamine B (Rhb) photodegradation is obviously improved after loading Ag NPs. Finally, a possible photocatalytic mechanism of the Ag/g-C₃N₄ composite is given.

EXPERIMENTAL

Synthesis

The g-C₃N₄ nanosheet was prepared via thermal polycondensation of urea. Fifteen grams urea was placed into a covered ceramic crucible and heated to 500°C for 5 h in air, at the heating rate of 10°C min⁻¹. After the reaction, it cooled down to room temperature naturally, the product was collected and grind to powder. The Ag/g-C₃N₄ composite was synthesized by a liquid-phase reduction method. First 0.5 g of g-C₃N₄ was put in 50 mL of water and ultrasonic treated for 5 min. Second, a certain amount of AgNO₃ (5 mM) aqueous solution was put into the above solution and maintain stirring. Third, a certain amount of NaBH₄ [the molar ratio of n( AgNO₃):n( NaBH₄) = 1:5] dissolved in 30 mL of water, and then put into the above solution, stirring for 1 h. Following, the product was centrifuged and washed with absolute ethanol and distilled water, respectively. Finally, these samples are dried in vacuum oven at 70°C for 5 h. By varying the amount of using AgNO₃, a series of samples with different ratios of Ag to g-C₃N₄ [m( Ag):n( g-C₃N₄) = 1, 2, 3, 4, and 5%] were prepared and labeled as 1%-Ag/g-C₃N₄, 2%-Ag/g-C₃N₄, 3%-Ag/g-C₃N₄, 4%-Ag/g-C₃N₄, and 5%-Ag/g-C₃N₄, respectively.

Characterization

The crystal phases of products were studied by X-ray diffraction (XRD) (X-ray diffractometer, Cu Kα, λ = 1.54056 Å) (Bruker D5005, Germany). Fourier transform infrared (FT-IR) spectra were conducted using a Nicolet Magna 560 (US) spectrophotometer. X-ray photoelectron spectroscopy (XPS) was measured on a PHiQ 1,600 XPS (US) instrument. The weight percentages of Ag in the Ag/g-C₃N₄ photocatalysts was studied by inductively coupled plasma atomic emission spectrometry (ICP-AES, Shimadzu ICP-7510, Japan). High resolution transmission electron microscopy (HRTEM) was taken by a JEOL JEM-2100F (Japan) electron microscope. UV–vis absorbance spectra were collected on a Shimadzu UV-3100 (Japan) spectrophotometer, using BaSO₄ as reference. The photoluminescence (PL) spectra of g-C₃N₄ and Ag/g-C₃N₄ samples were studied on a Varian Cary Eclipse (US) spectrometer equipped with an excitation wavelength of 325 nm.

Photocatalytic Performance

The photocatalytic activity of pure g-C₃N₄ and Ag/g-C₃N₄ samples was examined by photodegradation of RhB under the simulated sunlight irradiation, which was obtained from an 500 W Xe lamp. Milligram of samples were dispersed in 25 mL of RhB aqueous solution (10 mg/L RhB aqueous solution). Prior to the irradiation, the reaction solution was magnetically stirred in the dark for 30 min to get adsorption-desorption equilibrium for the dyes on photocatalyst surface. During the photocatalytic degradation, 2 mL of the sample was withdrawn from the reaction solution at the time intervals of every 15 min and then centrifuged to remove the particles. Then the concentration of RhB was examined by UV–vis spectrophotometer, at the absorbance wavelength of 553 nm. The photodegradation rate of RhB was calculated by the formula: D = C/C₀ × 100%, where C₀ is the initial concentration of RhB, and C is the concentration of RhB at a time t.

Photoelectrochemical Measurement

The photoelectrochemical performance was studied on a CHI 660D electrochemical work station with a standard three-electrode system. Put g-C₃N₄ or Ag/g-C₃N₄ on the ITO glass surface as the working electrode. A piece of Pt wire and a calomel electrode were used as the counter electrode and reference electrode, respectively. The electrolyte is 0.1 mol/L Na₂SO₄ aqueous solution. Five milligram photocatalysts were mixed with 1 mL ethanol and then the mixture was coated on 2 × 4 cm ITO glass for use as an electrode. Photoelectrochemical impedance spectroscopy (EIS) Nyquist plots were conducted at an open
current potential with an amplitude of 5 mV and the frequency range was from $10^2$ to 1 Hz.

RESULTS AND DISCUSSION

XRD Patterns

The crystal phase of as-prepared samples is studied by XRD measurements, and the XRD patterns are shown in Figure 1. The pure g-C$_3$N$_4$ nanosheets and Ag/g-C$_3$N$_4$ nanocomposites have two dominant peaks at 13.1° and 27.5°, indexed to g-C$_3$N$_4$ (JCPDS87-1526) (Yang et al., 2013b). The peak at 27.5° is ascribed to the typical (002) plane with planar distance of 0.33 nm corresponding to interlayer-stacking of aromatic segments. The peak at 13.1° with distance of 0.675 nm is indexed to the (100) plane corresponding to in-plane structural packing (Dong et al., 2011; Liu et al., 2011). Compared with the pure g-C$_3$N$_4$ nanosheets, the intensity of the diffraction peak at 27.5° becomes weaker with increasing content of loading Ag NPs. The diffraction peak related to Ag NPs is not found, because of the low Ag loading amount and the high dilution effect of Ag NPs on the g-C$_3$N$_4$ surface (Zhou et al., 2014; Fu et al., 2015). As follows, the XPS and EDS data demonstrate the existence of Ag loading on the g-C$_3$N$_4$ surface.

FTIR Analysis

The FTIR spectra are similar between the pure g-C$_3$N$_4$ nanosheets and Ag/g-C$_3$N$_4$ composites with different Ag loading amounts (Figure 2). The peak at 1,639 cm$^{-1}$ can be ascribed to the stretching vibration of C-N groups, and the peaks at 1,242, 1,327, 1,568 and 1,408 cm$^{-1}$ can be attributed to the aromatic C-N stretching vibration (Aghdam et al., 2017). The peak at 809 cm$^{-1}$ corresponds to the breathing mode of triazine units (Sun et al., 2012). The peak at 3171 cm$^{-1}$ is attributed to the stretching vibration of N-H group (Yang et al., 2013a). All these characteristic FTIR peaks suggest that the overall structure of g-C$_3$N$_4$ maintains the original form after Ag NPs loading.

TEM Images

The morphology and microstructure of the pure g-C$_3$N$_4$ and 3%-Ag/g-C$_3$N$_4$ samples were investigated by TEM measurements. The TEM image of pure g-C$_3$N$_4$ shows that it is a two-dimensional nanosheet with some holes in the size range of 10–30 nm (Figure 3A). TEM image of the 3%-Ag/g-C$_3$N$_4$ sample (Figure 3B) shows that Ag NPs, observed as black dots, uniformly disperse on g-C$_3$N$_4$ surfaces. The size of Ag NPs is from 6 to 20 nm, indicating that these Ag NPs are Ag clusters on the surface of g-C$_3$N$_4$. The size distribution of Ag NPs on 3%-Ag/g-C$_3$N$_4$ is presented in Figure 3C, which is mainly in the range of 8–18 nm. The energy dispersive X-ray spectrum (EDS) also confirms that Ag NPs exist on the surface of g-C$_3$N$_4$ (Figure 3D). Also, it shows that the 3%-Ag/g-C$_3$N$_4$ sample is consisted of C, N, and Ag elements, which confirms that Ag NPs successfully adsorbed on the g-C$_3$N$_4$ surface.

XPS Analysis

The surface elemental composition and chemical states of Ag/g-C$_3$N$_4$ are studied by XPS, here 3%-Ag/g-C$_3$N$_4$ is selected for study (Figure 4). The elements C, N, O, and Ag are clearly observed in the survey spectrum (Figure 4A). The peak located at 531 eV is assigned to O, which may be the water molecules at the sample surface (Hu et al., 2015). Two C 1s peaks locate at 284.8 eV and 288.3 eV (Figure 4B). The peak located at 284.8 eV is assigned to sp$^2$-hybridized C atoms, and the 288.3 eV peak can be assigned as N-C=N groups (Wu et al., 2015). As shown in Figure 4C, the peaks of N 1s locate at 398.8, 400.5, and 401.5 eV, which can be ascribed to sp$^2$ bonded nitrogen C-N-C groups, sp$^3$ tertiary nitrogen N-(C)$_3$ and amino functional groups (C-N-H), respectively (Qi et al., 2019). The spectrum of Ag 3d (Figure 4D) shows that the peaks located at 367.4 and 374.0 eV can be assigned as Ag 3d$^{5/2}$ and Ag 3d$^{3/2}$, respectively (Yang et al., 2016). This confirms that Ag NPs are successfully coated on g-C$_3$N$_4$ surfaces. The peak at 368.1 eV is assigned as Ag(I), which indicates the formation of Ag$_2$O on the surface of metallic Ag (Tian et al., 2015). The actual content of Ag in the Ag/g-C$_3$N$_4$
FIGURE 3 | TEM images of (A) pure g-C$_3$N$_4$ and (B) 3%-Ag/g-C$_3$N$_4$. (C) size distribution of Ag NPs on 3%-Ag/g-C$_3$N$_4$. (D) EDX mapping of 3%-Ag/g-C$_3$N$_4$.

FIGURE 4 | XPS spectra of 3%-Ag/g-C$_3$N$_4$ composites: (A) survey XPS spectrum, high resolution of (B) C1s spectra, (C) N1s spectrum, (D) Ag 3d spectrum.
composites was studied by ICP-AES analysis. The result shows that the weight percentages of Ag in 1%-Ag/g-C$_3$N$_4$, 2%-Ag/g-C$_3$N$_4$, 3%-Ag/g-C$_3$N$_4$, 4%-Ag/g-C$_3$N$_4$, and 5%-Ag/g-C$_3$N$_4$ were measured to be 0.72, 1.43, 2.09, 2.74, and 3.55, respectively. The measured value by ICP-AES is a little smaller than the theoretical value for the weight percentages of Ag in Ag/g-C$_3$N$_4$ composites, but both of the two changing trends are the same.

UV-vis Diffuse Reflectance Spectra

The UV-DRS measurement is used to study the optical adsorption property of the pure g-C$_3$N$_4$ nanosheets and Ag/g-C$_3$N$_4$ composites (Figure 5). Figure 5A shows that the light absorption edge of the pure g-C$_3$N$_4$ is at 440 nm, which agrees with the intrinsic band gap of bulk g-C$_3$N$_4$ (Chen et al., 2016). Compared with pure g-C$_3$N$_4$ nanosheets, Ag/g-C$_3$N$_4$ composites have an additional weak and broad absorption peak around 450–600 nm, which is characteristic of the silver surface plasmon resonance band (Liu et al., 2013). The Ag/g-C$_3$N$_4$ composite shows similar light absorption range with that of pure g-C$_3$N$_4$, but the visible light adsorption is increased, as shown in Figure 5B. Thus, the samples with the increasing of Ag loading amount change the color from yellow to dark gray.

PL Spectra

Photoluminescence measurement is an useful method to analyze the separation efficiency and the life time of photogenerated carriers, as shown in Figure 6. PL spectra of pure g-C$_3$N$_4$ and Ag/g-C$_3$N$_4$ are taken by the exciting light of 325 nm. A strong broad peak at ~460 nm is observed. Compared with pure g-C$_3$N$_4$, the PL intensity of Ag/g-C$_3$N$_4$ composites decreases significantly. The weaker peak intensity of PL results in a slower recombination rate of photogenerated carriers (Ong et al., 2014). In Ag/g-C$_3$N$_4$ composites, Ag NPs combine with the g-C$_3$N$_4$ surface strongly, and effectively reduce the recombination rate of e$^-$-h$^+$ pairs. This improved separation efficiency of photogenerated carriers leads to increasing e$^-$ and h$^+$ to join the photocatalytic process of Ag/g-C$_3$N$_4$. However, over loading of Ag on g-C$_3$N$_4$, such as 5%-Ag/g-C$_3$N$_4$, the PL intensity is getting increase again, indicating the increase of the combination of photogenerated carriers. It clearly sees that the Ag/g-C$_3$N$_4$ composites with proper loading amounts of Ag have a potential for using as photocatalysts with high activity.

Photocatalytic Activity

The photocatalytic activity of pure g-C$_3$N$_4$ and Ag/g-C$_3$N$_4$ for photodecomposition of RhB is tested under the simulated sunlight irradiation. As shown in Figure 7A, compared with that of pure g-C$_3$N$_4$, the Ag nanoparticle modified g-C$_3$N$_4$ shows an improved photocatalytic performance for decomposition of RhB aqueous. After irradiation for 100 min, the degradation of RhB is about 20% for pure g-C$_3$N$_4$ nanosheets and almost 100% for 3%-Ag/g-C$_3$N$_4$. Figure 7B shows the apparent reaction rate constant (k) of RhB photodegradation, which shows that the kinetic constant of 3%-Ag/g-C$_3$N$_4$ is almost 10 times higher than that of pure g-C$_3$N$_4$. When the mass ratio of Ag is in the range of 1–5 wt%, the enhanced photocatalytic activity is observed, due to effective enhanced the separation efficiency of photogenerated e$^-$-h$^+$ pairs at the Ag/g-C$_3$N$_4$ interface and the surface plasmon resonance (SPR) effect of Ag NPs (Duan et al., 2014), which are

![Figure 5](image1.png)  
**Figure 5** | (A) UV-Vis diffuse reflectance absorption spectra of the pure g-C$_3$N$_4$ and Ag/g-C$_3$N$_4$ samples. (B) Magnify the square apart of picture (A).

![Figure 6](image2.png)  
**Figure 6** | PL spectra of the pure g-C$_3$N$_4$, 1%-Ag/g-C$_3$N$_4$, 3%-Ag/g-C$_3$N$_4$, and 5%-Ag/g-C$_3$N$_4$ sample.
also supported by PL and UV-vis DRS results. Obviously, 3%-Ag/g-C3N4 has the highest photocatalytic activity, which may be due to that the excess Ag NPs will be working as recombination centers, or the active site on g-C3N4 surface is blocked (Ge et al., 2011). The photocatalytic activity of as-prepared Ag/g-C3N4 composites is compared to the typical photocatalysts including TiO2 and ZnO. The photocatalytic activity of 3%-Ag/g-C3N4 (k = 0.0326 min⁻¹) in this work is higher than TiO2 (k = 0.0084 min⁻¹) and ZnO (k = 0.0062 min⁻¹) reported previously (Carvalho et al., 2015; Hao et al., 2019). In order to check the reusability of as-prepared Ag/g-C3N4 photocatalysts, the recycling test was carried out. As shown in Figure 7C, the photodegradation percentage of RhB is >90% after six cycles, which indicates the as-prepared photocatalysts owns a good stability. A gradually decreased photocatalytic activity is due to the loss of photocatalyst in the recovery process.

**Photoelectrochemical Performance**

The charge separation efficiency is studied by using the photoelectrochemical measurements. Figure 8A shows that the photocurrent response of pure g-C3N4, 1%-Ag/g-C3N4, 3%-Ag/g-C3N4, and 5%-Ag/g-C3N4 samples under the simulated sunlight irradiation, which shows stable reproducible photocurrent responses over five on-off cycles. The photocurrent starts when the light was turned on, the photocurrent is close to zero when the light was turned off. The photocurrent density

![FIGURE 7](image-url) | (A) photodegradation of RhB using pure g-C3N4, Ag/g-C3N4 with different Ag contents under simulated sunlight irradiation. (B) kinetic data for the degradation of RhB. (C) the photodegradation rate of RhB for six cycles using 3%-Ag/g-C3N4.

![FIGURE 8](image-url) | (A) photocurrent response and (B) electrochemical impedance spectroscopy of the pure g-C3N4, 1%-Ag/g-C3N4, 3%-Ag/g-C3N4, and 5%-Ag/g-C3N4 samples.
(0.50 μA/cm²) of 3%-Ag/g-C_3N_4 is bigger than the pure g-C_3N_4 (0.07 μA/cm²) and the 5%-Ag/g-C_3N_4 (0.38 μA/cm²). The stronger photocurrent is due to the higher separation efficiency of the photogenerated e^-·h^+ pairs of Ag/g-C_3N_4, which is consistent with its higher activity on photocatalytic decomposition of organic dyes.

In order to study the charge separation efficiency, the electrochemical impedance spectroscopy (EIS) Nyquist plots are used, and the EIS Nyquist plot of pure g-C_3N_4, 1%-Ag/g-C_3N_4, 3%-Ag/g-C_3N_4, and 5%-Ag/g-C_3N_4 sample is as shown in Figure 8B. Usually, the smaller the radius of EIS Nyquist plots is, the higher the separation efficiency of charge carriers is (Li et al., 2015). The radius on the EIS Nyquist plot of C_3N_4 is getting smaller after Ag modification, the order is 3%-Ag/g-C_3N_4 < 5%-Ag/g-C_3N_4 < 1%-Ag/g-C_3N_4 < g-C_3N_4, indicating that Ag modification indeed reduces the recombination of charge carriers and increase the separation efficiency of photogenerated e^-·h^+ pairs, 3%-Ag/g-C_3N_4 is the best, which agrees well with PL spectra.

**Photocatalytic Mechanism**

Figure 9 shows the photocatalytic mechanism of Ag/g-C_3N_4 composites during RhB decomposition under sunlight irradiation. Ag nanoparticle modification enhances the photocatalytic performance of g-C_3N_4 due to the synergistic effect of two aspects, one is the SPR effect of metal Ag, another is the decrease of the recombination rate of photogenerated e^-·h^+ pairs (Ingram et al., 2011). When Ag/g-C_3N_4 is irradiated by the simulated sunlight irradiation, the e^-·h^+ pairs are separated, e^- is excited to CB of g-C_3N_4, h^+ remains at VB of g-C_3N_4. Then e^- transfers to Ag NPs due to the high Schottky barrier of Ag, finally, transfers to the photocatalyst surface to join the reduction reaction. The generated e^- from two routes one from the plasmon excited Ag NPs and the other from the photoexcited g-C_3N_4 nanosheets. These e^- react with O_2 to generate O_2•-, and O_2•- radicals can decompose of RhB molecules to CO_2 and H_2O. Thus it is concluded that the adsorbed silver NPs have two functions, one is as the electron pool and the other is capture of the photoinduced electrons.

**CONCLUSION**

In this work, Ag NPs modified g-C_3N_4 nanosheets are successfully prepared by a simple liquid-phase reduction method. In the Ag/g-C_3N_4 composites, the Ag NPs uniformly coated on the g-C_3N_4 surface with the diameter range of 6-20 nm. After Ag loading, the Ag/g-C_3N_4 composites expand the visible light response and show an enhanced photocatalytic activity on RhB decomposition. The enhanced photocatalytic activity of Ag/g-C_3N_4 is due to the two reasons, one is the SPR effect of metal Ag, and another is the decrease of the recombination of the photogenerated e^-·h^+ pairs. Especially, 3%-Ag/g-C_3N_4 demonstrates the highest photocatalytic activity among the as-prepared samples for RhB decomposition, which is 10 times faster than the pure g-C_3N_4 nanosheet for decomposition of RhB. This work indicates that the Ag/g-C_3N_4 photocatalyst is one of promising candidates to treat organic pollutants in the waste water.

**AUTHOR CONTRIBUTIONS**

All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication.

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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