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# Ag/g-$C_3N_4$ composite nanosheets: Synthesis and enhanced visible photocatalytic activities

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ABSTRACT

A simple photodeposition method was presented for synthesis of novel Ag/g-$C_3N_4$ composite nanosheets (AGCNs) where Ag nanoparticles with diameters of 5 to 20 nm were evenly loaded onto g-$C_3N_4$ nanosheets forming a heterogeneous structure. Compared to the pure g-$C_3N_4$ nanosheets, more intensive absorption within the visible light range and lower recombination probability of photogenerated charge carriers were observed in AGCNs. Photocatalytic activities of the as-prepared samples were evaluated by the photocatalytic oxidation decomposition of Rhodamine B (RhB) under visible light irradiation. The experimental results showed that AGCNs (8 wt%) exhibited the highest photocatalytic activity and the corresponding degradation rate was 7 times as much as that of pure g-$C_3N_4$ nanosheets.

## 1. Introduction

Photocatalysis has been proved to be a promising strategy for clean energy production and environmental remediation using solar energy [1,2]. Among various semiconductors investigated, graphitic carbon nitride (g-$C_3N_4$) has attracted much attention in the photocatalytic field due to its remarkable properties such as metal-free, suitable bandgap, and low cost [3]. Bulk g-$C_3N_4$, typically prepared by polycondensation of organic precursors containing both carbon and nitrogen such as cyanamide, dicyandiamide and melamine, exhibits low photocatalytic activities owing to the limited specific surface area and the fast recombination of photo-generated charge carriers [4,5]. To solve this problem, many attempts were explored to enhance the photocatalytic activity. For example, Liu synthesized thin layered g-$C_3N_4$ nanosheets with high specific surface areas by thermal oxidation etching of the bulk g-$C_3N_4$ and observed a much higher hydrogen evolution rate under visible light irradiation [6]. Cheng fabricated heterogeneous structures by loading Au NPs onto g-$C_3N_4$ nanosheets and demonstrated enhanced photocatalytic activities for the decomposition of methyl orange [7]. However, combining thin layered g-$C_3N_4$ nanosheets which are advantageous of large specific surface area with fine Ag NPs through a simple and green photodepositing method has not been reported.

In this work, novel Ag/g-$C_3N_4$ composite nanosheets (AGCNs) were synthesized by photodepositing Ag NPs onto g-$C_3N_4$ nanosheets. The structures, morphologies and optical properties of the products were studied. Subsequently, the photocatalytic activity of AGCNs is evaluated through the photocatalytic degradation of RhB under visible-light irradiation.

## 2. Experimental

Synthesis of AGCNs: The bulk g-$C_3N_4$ photocatalysts were synthesized by directly heating melamine in a semi-closed alumina crucible with a cover according to the literature [5]. The g-$C_3N_4$ nanosheets were prepared by exfoliation of as-prepared bulk g-$C_3N_4$ in deionized water. In brief, 5 g of bulk g-$C_3N_4$ power was dispersed in 500 mL of water, then the mixture was ultrasonically treated for 12 h. The resulting suspension was centrifuged at 3000 rpm to remove the residual unexfoliated g-$C_3N_4$. A certain quantity of $AgNO_3$ (0.1 mol/L) aqueous solution and 10 ml of the above suspension were added into a quartz tube with stirring. Then, the mixture was irradiated by 800 W Xenon lamp with continuous stirring for 0.5 h. After that, the mixture was collected for further study. According to this method, the AGCNs samples with different weight ratios were obtained.

Characterization: The crystalline phases of the samples were examined by an X-ray diffraction (XRD) instrument (Rigaku, D/max-2500) using Cu $K\alpha$ radiation. X-ray photoelectron spectroscopy (XPS) measurements were done on a PHI Quantum 1600 XPS instrument. Morphological analysis and product compositions were investigated by transmission electron microscope (JEM-2100). UV–vis diffuse reflection spectra were recorded on a Shimadzu UV-3100 spectrophotometer. The photoluminescence (PL) spectra of photocatalysts

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were detected on a Varian Cary Eclipse spectrometer with excitation wavelength of 325 nm.

Measurements of photocatalytic activity: The photocatalytic activities of the samples were evaluated by degradation of RhB (10 mg/L) under visible light irradiation. The light source was an 800 W Xe lamp with a 420 nm cutoff filter. Prior to irradiation, the mixture (1 g/L) were magnetically stirred in the dark for 30 min to achieve adsorption equilibrium. At irradiation time intervals of every 5 min, a certain volume of suspensions were collected and then analyzed by checking the absorbance at 553 nm with UV–vis spectrophotometer.

## 3. Results and discussion

To confirm the phase structures of g-$C_3N_4$ nanosheets and AGCNs in which the weight ratio of Ag was 8%, XRD was performed. As shown in Fig. 1A, two distinct peaks could be observed for g-$C_3N_4$ nanosheets, which were indexed to graphite carbon nitride (JCPDS 87-1526). Compared with the pure g-$C_3N_4$ nanosheets, the spectrum of AGCNs (8 wt%) exhibited three additional peaks corresponding to the face-centered cubic (fcc) metallic Ag (JCPDS 04-0783), confirming the formation of Ag NPs on the composite nanosheets.

The chemical composition and chemical states of AGCNs (8 wt%) were also analyzed using XPS, as shown in Fig. 1B. The C, N, Ag, and O peaks were clearly observed. The C1s (Fig. 1C) spectra of AGCNs (8 wt%) could be fitted to four peaks at 284.6, 285.1, 288.0, and 288.5 eV, corresponding to the $sp^2$ C–C bonds, C–$NH_2$ species, N=C–N coordination and the N–C–O groups, respectively [8,9]. The O1s XPS spectrum (Fig. 1D) could be fitted to two peaks at 532.3 and 533.4 eV, which were associated with O–H in the water and N–C–O groups [10]. In addition, the sample exhibited N 1s in Fig. 1E profiles with core levels at around 398.5, 399.1, 400.1 and 401.1 eV, which could be attributed to $sp^2$-hybridized nitrogen (C–N=C), $sp^3$-hybridized nitrogen (N–$C_3$), $sp^2$-hybridized nitrogen (N–C–O) and amino functional groups with a hydrogen atom (C–$NH_2$), respectively [8]. The XPS data confirmed the existence of graphite-like $sp^2$-bonded structure in graphitic carbon nitride. Fig. 1F showed the characteristic Ag3d peak that had a 6.0 eV splitting of the 3d doublet, corresponding to the metallic Ag0 species [5].

The morphologies of the as-prepared g-$C_3N_4$ nanosheets and AGCNs (8 wt%) were investigated by TEM. Fig. 2A showed the TEM image of the pure g-$C_3N_4$ nanosheets. It could be seen that the free-standing g-$C_3N_4$ nanosheets with sub-micrometer size had a tow-dimensional structure consisting of sheets stacking together. Fig. 2B showed the TEM image of AGCNs (8 wt%). A large amount of black colored dots corresponding to Ag NPs were evenly dispersed on the g-$C_3N_4$ nanosheets. Diameters of the Ag NPs mainly distributed in the range of 5–20 nm.

Optical absorption spectra were used to study the effects of Ag loading on g-$C_3N_4$ nanosheets. As shown in Fig. 3A, the obtained samples presented the typical absorption patterns of semiconductors. Compared with pure g-$C_3N_4$ nanosheets, the UV–vis diffuse reflection spectra of AGCNs (8 wt%) showed an additional wide absorption peak arrange from 450 nm to 600 nm characteristic of the colloidal silver surface plasmon resonance band [11]. Besides, the composites also showed increased absorption both in UV and visible light region, which could be attributed to the absorption of Ag NPs [5]. Fig. 3B showed the PL spectra of g-$C_3N_4$ nanosheets and AGCNs (8 wt%). It could be observed that there was a significant decrease in the PL intensity of AGCNs compared to that of g-$C_3N_4$ nanosheets. A weaker intensity of the peak represents that the Ag NPs dispersed on the surface of g-$C_3N_4$ nanosheets could effectively inhibit the recombination of photogenerated charge carriers, which is helpful for the separation of photogenerated electron–hole pairs in g-$C_3N_4$ nanosheets.

The comparison of photocatalytic degradation curves of RhB in the pure Ag, g-$C_3N_4$ nanosheets and AGCNs (8 wt%) aqueous suspensions under visible light irradiation was demonstrated in Fig. 4A. It could be seen that the degradation of RhB over pure Ag

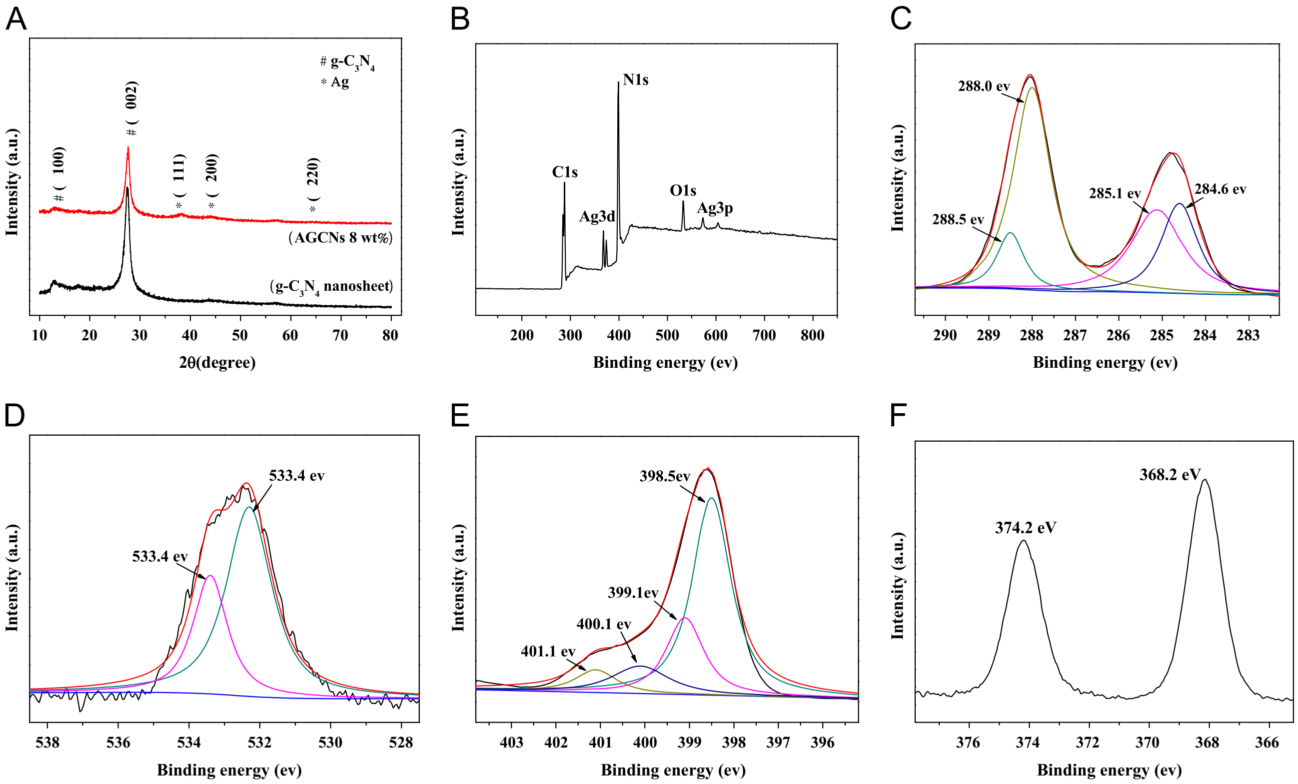

**Fig. 1.** XRD pattern (A) and XPS spectra of AGCNs (8 wt%): (B) survey XPS spectrum; (C) C1s; (D) O1s; (E) N1s; (F) Ag3d.