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Ag-Doped g-C₃N₄ film electrode: fabrication, characterization and photoelectrocatalysis property†

Fanjing Qi,^{ab} Yibing Li,^b Yanbin Wang,^a Yan Wang,^a Shanshan Liu^a and Xu Zhao^{*a}

Ag-Doped graphitic carbon nitride films (Ag/g-C₃N₄) were synthesized easily onto ITO substrates by a liquid-based reaction process. Ag/g-C₃N₄ films were comprehensively characterized by SEM, HRTEM, XRD, UV/vis DRS, and XPS. The results indicated that Ag and Ag₂O disperse homogeneously in the matrix of the g-C₃N₄ film. The photocurrent response of the Ag/g-C₃N₄ films increased remarkably with increasing Ag content and the best performance was observed with the sample of Ag/g-C₃N₄ (1 : 10). The Ag/g-C₃N₄ films exhibited a high photoelectrocatalytic activity for the degradation of methylene blue. The enhancement of photoelectrocatalysis owing to more visible light could be harvested and photogenerated electron and interfacial electron could transfer more easily after modifying Ag in the g-C₃N₄ film. Thus, a possible photoelectrocatalysis mechanism was proposed. Beside g-C₃N₄, electron–hole pairs could be generated by Ag under visible light irradiation, and the photogenerated electron was captured by O₂ or [•]O₂[−] and then forms [•]OH radicals.

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1. Introduction

Polymeric graphitic carbon nitride (g-C₃N₄) has attracted considerable attention as a potential material recently.^{1,2} It has two-dimensional planes of tri-s-triazine and π -conjugated phase between the layers and shows photocatalytic, electrocatalytic, and heterogeneous catalytic activities.^{3–5} g-C₃N₄ can be simply synthesized from a certain amount of nitrogen- as well as carbon-rich precursors such as urea,⁴ dicyandiamide⁵ or melamine.^{6,7} With an optical band gap of 2.70 eV, g-C₃N₄ showed a response to visible-light up to 460 nm.^{8–10}

Most of the researches focus on the g-C₃N₄ powders. For the electrochemical or photoelectrochemical applications, including water electrosplitting, fuel cells, and solar cells, a direct and continuous g-C₃N₄ layer is preferred. Recently, numerous studies have been devoted to the synthesis of a g-C₃N₄ thin film, including bubble template method,^{11,12} sol–gel techniques,¹³ chemical exfoliation method,¹⁴ deposition method,^{15,16} as well as spin-coating method.¹⁷

It was recognized that the photocatalytic activity of g-C₃N₄ is limited by its high recombination probability of

photogenerated electron–hole pairs. Therefore, a great deal of effort has been made, which include coupling with other semiconductors (*e.g.*, C₃N₄/TiO₂,¹⁸ C₃N₄/BiPO₄,¹⁹ metal or nonmetal doping (*e.g.*, Fe,²⁰ Ag,²¹ Bi²² and P,²³ S,²⁴ F²⁵), and other chemical doping. Metal doping is an effective strategy to tune the electronic and optical properties, as well as the conduction band edge of the semiconductors and their surface properties. Ag is an ideal dopant to improve the photoelectrocatalytic abilities followed by the enhancement of the visible light response and the improvement of the charge separation and transfer. Ag/g-C₃N₄ powder materials were synthesized with a metallic silver content in the 1–10 wt% range through a microemulsion method; the introduction of silver in the 1–10 wt% range enhanced the g-C₃N₄ photocatalytic activity.²⁶

Herein, we report a Ag doped g-C₃N₄ film electrode with an remarkable enhancement of photoelectrochemical properties afforded by a mixture of AgNO₃, cyanuric acid, benzoguanamine and grown thin films using the supramolecular approach on the ITO substrate by a liquid-based reaction. The Ag species on the g-C₃N₄ film were analyzed and a proposed mechanism of the photoelectrochemical response enhancement was proposed.

2. Experimental

2.1 Materials

Cyanuric acid (>98%) and benzoguanamine (>98%) were purchased from Tokyo Kasei Kogyo Co., Ltd. AgNO₃ (AR) was provided by Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). All the reagents were used without further purification.

^aKey Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P. O. Box 2871, 18 Shuangqing Road, Haidian District, Beijing 100085, China. E-mail: zhaoxu@rcees.ac.cn; Tel: +86-010-62849667

^bSchool of Civil Engineering and Transportation, Hebei University of Technology, Tianjin 300401, China

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ITO (Indium-Tin Oxide) conductive film glasses with a size of $10 \times 2.5 \times 0.2$ cm were provided by Shenzhen Jingweite Technology Co., Ltd. (Shenzhen, China).

2.2 Preparation of the film electrode

The precursor powder was prepared by a concussion-hybrid method and the film electrodes were afforded by liquid-based growth reaction, as described by Xu *et al.*¹⁵ In a typical process, 4 g of a mixture of cyanuric acid and benzoguanamine (molar ratio of 1 : 1) and the required amount of AgNO_3 were dispersed in 40 mL deionized water and stirred continuously for 6 hours. The white suspension was then centrifuged at about 7500 rpm and the sediment was freeze-dried for 24 h.

One piece of ITO glass was placed in a quartz crucible with the conducting side up, and then an adequate amount of precursor powder was transferred to the crucible, totally covering the substrate placed at the bottom. The crucible was then capped and heated at 500 °C for 2 h with a ramp rate of about 3°C min^{-1} for both the heating and cooling process in a nitrogen atmosphere. In all cases, continuous $\text{g-C}_3\text{N}_4$ and $\text{Ag/g-C}_3\text{N}_4$ film electrodes were obtained, demonstrating complete coverage across the substrate. $\text{Ag/C}_3\text{N}_4$ film electrode with different Ag contents were denoted as $\text{Ag/g-C}_3\text{N}_4$ (1 : 10), $\text{Ag/g-C}_3\text{N}_4$ (1 : 25), and $\text{Ag/g-C}_3\text{N}_4$ (1 : 50), where the number denotes the AgNO_3 to $\text{g-C}_3\text{N}_4$ molar ratios.

2.3 Characterization

The surface morphology was characterized on a Hitachi SU-8020 scanning electron microscope (SEM, Hitachi Ltd., Japan). Powder and film X-ray diffraction (XRD) patterns were recorded on an X'pert PRO MPD PC system, utilizing Cu $K\alpha$ radiation at a scan rate (2θ) of 0.5° s^{-1} . The accelerating voltage and applied current were 40 kV and 80 mA, respectively. Fourier transform infrared (FT-IR) spectra were obtained on a Nicolet 8700 spectrometer (Thermo Fisher Scientific) in the frequency range of 4000–800 cm^{-1} . X-ray photoelectron spectroscopy (XPS) was measured using a PHI Quantera SXM instrument (ULVAC-PHI, Japan). The binding energies were calibrated with $\text{C } 1s = 284.8$ eV.

2.4 Photoelectrochemical measurements

Photoelectrochemical measurements were performed in a three-electrode experimental system using the CHI660D Electrochemical Workstation (Shanghai Chenhua Instrument Co., Ltd., Shanghai, China). The prepared photoelectrodes ($10 \times 2.5 \times 0.2$ mm), saturated calomel electrode, and Pt electrode acted as the working, reference, and counter electrodes, respectively. The electrolyte was 0.05 mol L^{-1} Na_2SO_4 . The photocurrent density with time (i - t curve) was performed at 1 V bias potential under visible light irradiation. The photons generated by a 300 W Xe arc lamp (PLS-SXE500, BoPhilae technology co., LTD, Beijing, China) passed through a quartz reactor, equipped on the side of the three-electrode cell, and irradiated the backside of the photoelectrode. Visible light was obtained by placing a 400 nm cutoff filter to remove the UV irradiation. Electrochemical

impedance spectroscopy (EIS) was performed at the open circuit potential over the frequency range between 10^6 and 10^{-2} Hz, with an AC voltage magnitude of 5 mV, using 12 points per decade.

In the case of the photoelectrocatalytic degradation experiment, 10 mg L^{-1} MB was added to the quartz reactor with a three-electrode experimental system. The prepared photoelectrodes ($10 \times 2.5 \times 0.2$ mm), saturated calomel electrode, and Pt electrode acted as the working, reference, and counter electrodes, respectively. The electrolyte was 0.05 mol L^{-1} Na_2SO_4 . The absorbance of the reaction solution was measured by a UV-vis spectrophotometer (U-3010, Hitachi Ltd., Japan).

3. Results and discussion

3.1 SEM-EDS analysis of $\text{g-C}_3\text{N}_4$ and $\text{Ag/g-C}_3\text{N}_4$ composites

Fig. 1 shows SEM images of $\text{g-C}_3\text{N}_4$ film (a) and $\text{Ag/g-C}_3\text{N}_4$ films (b–d). As observed in Fig. 1(a), pure $\text{g-C}_3\text{N}_4$ shows a typical flat layer structure with a size of several micrometers. For $\text{Ag/g-C}_3\text{N}_4$ films (Fig. 1(b–d)), Ag particles with a polyhedral structure could be seen on the surface of the $\text{Ag/g-C}_3\text{N}_4$ films and linked with $\text{g-C}_3\text{N}_4$, indicating that Ag and Ag_2O disperse homogeneously in the matrix of the $\text{g-C}_3\text{N}_4$ film. To further confirm the existence of Ag nanoparticles, EDS was performed and the result is shown in Fig. 2(b). 47.93 wt% of Ag was observed in the partial area of the $\text{Ag/g-C}_3\text{N}_4$ (1 : 10) film electrode, suggesting Ag with a polyhedral structure was introduced to the $\text{g-C}_3\text{N}_4$ film (Table 1).

3.2 HRTEM-STEM analysis of $\text{g-C}_3\text{N}_4$ and $\text{Ag/g-C}_3\text{N}_4$

Fig. 3 shows the HRTEM images of $\text{Ag/g-C}_3\text{N}_4$ and the corresponding selected area electron diffraction (SAED). As seen in Fig. 3(a–c), the morphology of $\text{Ag/g-C}_3\text{N}_4$ (1 : 10) exhibits a disordered state and a lamellar structure with no lattice fringes. However, the diffraction ring was observed in Fig. 3(d), which corresponds to (002) of the $\text{g-C}_3\text{N}_4$ layered structure

Fig. 1 SEM images of $\text{g-C}_3\text{N}_4$ and $\text{Ag/g-C}_3\text{N}_4$ with different doping ratios: (a) $\text{g-C}_3\text{N}_4$; (b) $\text{Ag/g-C}_3\text{N}_4$ (1 : 50); (c) $\text{Ag/g-C}_3\text{N}_4$ (1 : 25); (d) $\text{Ag/g-C}_3\text{N}_4$ (1 : 10).

Fig. 2 EDS image of the Ag/g-C₃N₄ (1 : 10) sample.

Table 1 Atomic ratio of the Ag/g-C₃N₄ sample (1 : 10) sample

Element	Intensity (c/s)	Atomic%	Conc.	Units
C	59.36	31.769	16.63	wt%
N	55.90	58.037	35.43	wt%
Ag	177.51	10.194	47.93	wt%
Total		100.000	100.00	wt%

Fig. 3 HRTEM images of Ag/g-C₃N₄ (1 : 10) and the corresponding selected area electron diffraction pattern.

formed by accumulation. The STEM-EDS of Ag/g-C₃N₄ (1 : 10) are shown in Fig. S1.† Since a heavier element is indicated as a brighter image in the STEM result, the brighter parts are supposed to be Ag nanoparticles. Furthermore, as shown in Fig. S1(c),† the percentage of Ag is 39.5 wt% for the brighter parts, further confirming that the brighter parts are Ag particles. In addition, the STEM and corresponding element mappings in Fig. S2† detect the presence of Ag in addition to C, N, and O and the size of Ag is about 1 micrometer, proving the existence of Ag in Ag/g-C₃N₄ (1 : 10) and that this method can successfully fabricate a Ag/g-C₃N₄ film.

3.3 XRD patterns of Ag/g-C₃N₄

The X-ray diffraction pattern for the pure g-C₃N₄ film has two distinct peaks at 13.2° and 27.3°, corresponding to the (100) and (002) planes of g-C₃N₄, respectively. The peak at 27.3° is due to the stacking of the conjugated aromatic system, which was consistent with the reported literature.^{27,28} As shown in Fig. 4, the relative intensity of the peak at 27.3° decreased with increasing Ag contents, suggesting that the diffracted intensity of graphite with tri-s-triazine-based connection sheet became weaker after doping with Ag. For the Ag/g-C₃N₄ (1 : 10) sample, five peaks at 38.1°, 44.3°, 64.4°, 77.4°, and 81.5° were observed, corresponding to the (111), (200), (220), (311), and (222) planes of the face-centered cube structure of Ag,^{29,30} respectively. However, no significant diffraction peaks of Ag were observed for Ag/g-C₃N₄ (1 : 25) and Ag/g-C₃N₄ (1 : 50) owing to the low Ag content of these samples.

3.4 FT-IR analysis of Ag/g-C₃N₄

Fig. 5 represents the FT-IR spectra of g-C₃N₄ and Ag/g-C₃N₄ with different Ag ratios. Three main absorption regions are observed for the pure g-C₃N₄. The broad peak at 3000–3500 cm^{−1} was ascribed to the stretching vibration of N–H and O–H in physically

Fig. 4 XRD patterns of g-C₃N₄ and Ag/g-C₃N₄ with different Ag content.

Fig. 5 FT-IR spectra of the prepared g-C₃N₄ and Ag/g-C₃N₄ samples.

adsorbed water.³¹ The intensity of this broad peak decreases with increasing Ag content, which can be attributed to the destruction part of N-H and O-H by inserting Ag atoms. The bands at 1407, 1320 and 1240 cm⁻¹ are assigned to the typical stretching vibration of aromatic C-N, whereas the bands at 1640 and 1567 cm⁻¹ are ascribed to the C=N vibration.^{30,32} The intensity of these peaks does not change obviously, indicating that Ag/g-C₃N₄ has a reservation of aromatic CN heterocycles. In addition, the intensity of the peak at 808 cm⁻¹, which was assigned to the breathing mode of the triazine units, decreased with the decreasing of g-C₃N₄ content. However, the triazine rings still remain even at the highest doping level, indicating that the lattice changes are only partial. In particular, the peaks at 2160 and 2340 cm⁻¹ can be assigned to C≡C and C≡N triple bonds, respectively. Their intensity increases with increasing Ag content, indicating that new C≡C and C≡N triple bonds are formed in place of the typical stretching vibration of aromatic C-N stretching. These results imply that some triazine rings of g-C₃N₄ framework were broken and sp² C-N bonds transformed into C≡C and C≡N triple bonds upon the introduction of Ag.

3.5 UV/vis diffuse densities of Ag/g-C₃N₄ composite

Fig. 6 shows the UV/vis diffuse reflectance spectra of pure g-C₃N₄ and Ag/g-C₃N₄ with different Ag contents. The maximum

Fig. 6 UV/vis diffuse reflectance spectra of the g-C₃N₄ and Ag/g-C₃N₄ samples.

absorption wavelength can be obtained by drawing tangent along the critical fall part of the UV/vis diffuse reflectance spectrum and extending to the horizontal axis. The maximum absorption wavelength of g-C₃N₄ was estimated to be about 462 nm, which indicates that g-C₃N₄ responds to visible light. In contrast, with increasing Ag doping ratio, the maximum absorption wavelengths of Ag/g-C₃N₄ are approximately 521, 595 and 602 nm, respectively. The band gap of g-C₃N₄ calculated based on the Oregan and Gratzel method is 2.68 eV, which accorded well with previous reports.^{33,34} The band gap of Ag/g-C₃N₄ with a Ag : g-C₃N₄ ratio of 1 : 50, 1 : 25, and 1 : 10 are 2.38, 2.08, and 2.05 eV, respectively. These results demonstrate the existence of strong interactions between Ag and nitrogen, which alter the electronic structure of g-C₃N₄. This phenomenon suggests that more visible light can be harvested with increasing Ag doping content.

3.6 XPS analysis of Ag/g-C₃N₄ composite samples

The surface elemental composition and valence state of g-C₃N₄ and Ag/g-C₃N₄ were investigated by XPS. Fig. S3† shows the survey spectrum and high resolution XPS spectra of C 1s, N 1s and Ag 3d. As shown in Fig. 7(a), two peaks centered at 284.6 and 288.0 eV were observed, which can be ascribed to the C-C bond of carbon species adsorbed on the surface of g-C₃N₄^{12,34} and N-C=N species,^{35,36} respectively. The ratio of the intensity between C-C and N-C=N decreases with the increasing Ag doping. Moreover, the signal of N-C=N slightly shifts to a higher binding energy, indicating that the chemical environment changed due to the interaction between Ag and g-C₃N₄. The N 1s XPS spectrum of g-C₃N₄ is shown in Fig. 7(b), which can be deconvoluted into four peaks that correspond to nitrogen atoms in different functional groups: sp² hybridized aromatic N bonded to carbon atoms of C-N=C at 398.5 eV,³⁷ tertiary N bonded to carbon atoms in the form of N-C₃ at 399.7 eV, amino functional groups with hydrogen (C-N-H) at 401.2 eV,³⁸ and π-excitations at 404.3 eV.^{3,35} The N 1s XPS spectrum of Ag/g-C₃N₄ is shown in Fig. 7(c); remarkable shifts to lower binding energy are observed, suggesting that the electronic structure of g-C₃N₄ is changed by Ag modification. In the high-resolution Ag 3d XPS spectrum (Fig. 7(d), two major peaks with binding energies of Ag/g-C₃N₄ (1 : 10 and 1 : 25) at 367.9 and 374.0 eV are fitted to Ag 3d_{5/2} and Ag 3d_{3/2}, respectively, suggesting that the major phase are Ag⁰. The two peaks at 368.2 and 273.9 eV of Ag/g-C₃N₄ (1 : 50) indicate Ag₂O to be the major phase.

3.7 Photoelectrochemical response of Ag/g-C₃N₄

EIS was used to investigate the migration ability of the electrons, which was related to the photocatalytic and photoelectrochemical properties of semiconductor materials. The Nyquist plots of g-C₃N₄ and Ag/g-C₃N₄ photoanodes are shown in Fig. 8. The diameter of the semicircular Nyquist plot was significantly smaller compared to pure g-C₃N₄ with the introduction of Ag, suggesting a faster charge transfer rate and more effective separation of the photogenerated electron-hole pairs.³⁹

Fig. 7 High-resolution XPS spectra of C 1s region (a), N 1s region of pure g-C₃N₄ (b), N 1s region of Ag/g-C₃N₄ (c), and Ag 3d region (d).

Fig. 8 EIS spectra of g-C₃N₄ and Ag/g-C₃N₄ photoelectrodes ($\lambda > 400$ nm, [Na₂SO₄] = 50 mM, applied bias = 1.0 V).

Fig. 9 Photocurrent response of g-C₃N₄ and Ag/g-C₃N₄ photoelectrodes under visible light ($\lambda > 400$ nm, [Na₂SO₄] = 50 mM, $U = 1.0$ V) (a), g-C₃N₄; (b), Ag/g-C₃N₄ (1 : 50); (c), Ag/g-C₃N₄ (1 : 25); (d), Ag/g-C₃N₄ (1 : 10).

The photocurrent response of g-C₃N₄ and Ag/g-C₃N₄ photoelectrodes under visible light irradiation are shown in Fig. 9. The photogenerated current density is 0.93 $\mu\text{A mm}^{-2}$ for g-C₃N₄ under visible light irradiation and it increases with increasing Ag content. For example, the photogenerated current density was 1.93, 3.86, 6.40 $\mu\text{A mm}^{-2}$ for the Ag/g-C₃N₄ (1 : 50), Ag/g-C₃N₄ (1 : 25) and Ag/g-C₃N₄ (1 : 10) samples, respectively. The photocurrent results confirm the more efficient separation of photogenerated electron-hole pairs for the Ag/g-C₃N₄ samples than that of pure g-C₃N₄. It indicates that Ag has been combined effectively with Ag/g-C₃N₄, which leads to efficient separation of the photogenerated electron-hole pairs in the g-C₃N₄.

To evaluate the photoelectrocatalytic activities of the Ag/g-C₃N₄ samples, photoelectrocatalytic degradation of MB using the Ag/g-C₃N₄ film as a photoanode under visible light irradiation ($\lambda > 400$ nm) with a bias potential of 1.0 V was performed. As shown in Fig. 10(a), the MB degradation efficiency was 38.96%, 45.66%, 64.23%, and 72.90% for g-C₃N₄, Ag/g-C₃N₄ (1 : 50), Ag/g-C₃N₄ (1 : 25), and Ag/g-C₃N₄ (1 : 10), respectively. Compared with the g-C₃N₄ case, it is clearly seen that the degradation efficiency for MB was improved using Ag/g-C₃N₄.

Fig. 10 (a) MB degradation curves of g-C₃N₄ and Ag/g-C₃N₄ under visible light irradiation at 1.0 V; (b) effect of the applied voltages on the degradation rate of MB with Ag/g-C₃N₄ (1 : 10) ($\lambda > 400$ nm, initial concentration of MB = 10 mg L⁻¹, [Na₂SO₄] = 50 mM).

and increased with increasing Ag content. Among these photoanodes, Ag/g-C₃N₄ (1 : 10) shows the best photoelectrocatalytic activity. This shows that doping with Ag can increase the photo response ability of the g-C₃N₄ film electrode and enhance the photoelectrocatalytic activity. As shown in Fig. 10(b), the rate of MB degradation with Ag/g-C₃N₄ (1 : 10) as the photoanode increases with increasing voltage in the range of 0–1.0 V. The degradation efficiency of MB was the highest at a bias potential of 1.0 V and reached up to 72.90% in 2.5 h. A possible reason is that the higher applied bias, the greater level of electron transfer.

3.8 Mechanism considerations

To investigate the main reactive oxidative species involved in the photoelectrocatalytic process, reactive oxidative species trapping experiments were performed. Ethanol, EDTA, and N₂ were used as hydroxyl radical ($\cdot\text{OH}$), hole (h^+) and superoxide radical ($\cdot\text{O}_2^-$) scavenger, respectively. Fig. 11(a) presents the effects of various scavengers on the degradation of MB in the g-C₃N₄ photoelectrocatalysis system. The removal of MB decreased from 48.21% to 28.54% and 38.96% with N₂ and ethanol added, respectively, implying that $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ are involved in the photoelectrocatalysis process and $\cdot\text{O}_2^-$ is the major reactive oxidative species for the degradation of MB.

Fig. 11 Influence of various scavengers on the PEC processes of (a) pure g-C₃N₄ and (b) Ag/g-C₃N₄ (1 : 10) toward the degradation of MB ($\lambda > 400$ nm, initial concentration of MB = 10 mg L⁻¹, [Na₂SO₄] = 50 mM).

However, the degradation of MB improved with the addition of EDTA, indicating that the photogenerated hole was captured by EDTA and the recombination of electron–hole pairs was inhibited. Therefore, more e^- can react with O₂ to form $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ (eqn (1)–(3)), which enhances the photoelectrocatalytic performance. As for Ag/g-C₃N₄ (1 : 10) system (Fig. 11(b)), the inhibition performance followed the order: ethanol > N₂ > EDTA. The results suggest that $\cdot\text{OH}$ radicals are not only formed from $\cdot\text{O}_2^-$ (eqn (1)–(3)), but are also formed from the reaction between h^+ and OH⁻ (eqn (4)). However, when enriched electrons gathered on the Ag connect with other semiconductors, a multiple-electron reduction reaction of oxygen will occur.³⁷

Based on the abovementioned results and analysis, a possible mechanism for the enhanced photoelectrocatalytic performance of the Ag/g-C₃N₄ (1 : 10) film electrode was proposed, and the scheme is shown in Fig. 12. The band gap of

Fig. 12 Proposed mechanism of the photoelectrocatalytic degradation of MB with the Ag/g-C₃N₄ (1 : 10) photoanode.

Ag/g-C₃N₄ (1 : 10) was smaller than that of the pure g-C₃N₄ film photoelectrode and more light could be harvested. In addition, a faster charge transfer rate and more effective separation of the photogenerated electron-hole pairs could be achieved according to EIS. Therefore, the photogenerated electron could transfer easily to the Pt electrode and be captured by O₂, leading to the generation of $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ radicals. Finally, MB can be degraded by $\cdot\text{OH}$ radicals. In addition, the Ag metal also can generate electron-hole pairs under visible light irradiation, which also can capture O₂ molecules to form $\cdot\text{O}_2^-$ radicals, leaving behind holes (Ag⁺) that can be filled by electrons from Ag/g-C₃N₄ (1 : 10).³⁰

4. Conclusions

Ag-Modified g-C₃N₄ film electrodes were prepared by a liquid-based reaction onto an ITO substrate during the calcination treatment. The characterized results indicated that metallic silver and Ag₂O exist in the Ag/g-C₃N₄ film electrode. The photoelectrochemical response of the g-C₃N₄ film electrode increased after the modification of Ag, because of the enhanced migration rate of the photogenerated electrons and interfacial electron. The Ag/g-C₃N₄ (1 : 10) film electrode showed the best performance and its photocurrent density was approximately 6.8 times greater than that of the pristine g-C₃N₄ film electrode. The involved active radicals including $\cdot\text{O}_2^-$ and $\cdot\text{OH}$ were confirmed for the degradation of MB.

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