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Short communication

Ag/g-C_3N_4 photocatalysts: Microwave-assisted synthesis and enhanced visible-light photocatalytic activity

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ABSTRACT

Ag/g-C_3N_4 photocatalysts were synthesized by a rapid microwave-assisted polyol process. The characterization results showed monodisperse Ag nanoparticles with diameters of a few nanometers closely attached to the edges of g-C_3N_4. The presence of Ag nanoparticles in Ag/g-C_3N_4 photocatalysts enhanced the visible-light absorption and suppressed the recombination of photogenerated electron/hole pairs. The Ag/g-C_3N_4 photocatalysts exhibited the superior visible-light responsive photocatalytic activity for rhodamine B degradation. The mechanism of visible-light induced photocatalysis over Ag/g-C_3N_4 photocatalysts was also discussed.

1. Introduction

Graphitic carbon nitride (g-C_3N_4), a new-type polymeric semiconductor material with narrow bandgap, is widely used in photocatalytic degradation of organic pollutants, hydrogen production, oxygen evolution and CO_2 reduction due to its visible-light responsive activity, stability, low-cost and environmental friendliness [1–4]. However, the photocatalytic activity of pristine g-C_3N_4 is still not satisfactory under visible-light irradiation because of rapid recombination of photogenerated electron/hole pairs, low absorption in visible-light region and small specific surface area [5]. These drawbacks seriously hinder its applications in visible-light driven photocatalysis. Therefore, the design and synthesis of modified g-C_3N_4 photocatalysts have attracted intensive research interests recently [6,7].

Up to now, various strategies including fabrication of nanostructures [8] or porous structures [9], bandgap tuning [10], noble metal deposition [11], metal [12] or non-metal [13,14] doping, coupling with other semiconductor [15–20] and acid treatment [21,22] have been applied in order to enhance visible-light induced photocatalytic activity of g-C_3N_4. Among these modified approaches, noble metal deposition, especially the deposition of Ag nanoparticles, has received extensive attention owing to stronger electron storage capacity, lower cost and nontoxic [5,23–31]. To date, Ag-deposited g-C_3N_4 photocatalysts have been synthesized using various synthesis methods, including photoreduction [5,27,29,31], $NaBH_4$ reduction [24,26,28], dimethylformamide (DMF) reduction [30], citrate reduction [25], calcination [23], and so on. However, to the best of our knowledge, no research has been done in the synthesis of Ag/g-C_3N_4 photocatalysts by a microwave-assisted protocol with polyol as solvent.

Herein, we reported a rapid microwave-assisted synthesis of Ag/g-C_3N_4 photocatalysts in ethylene glycol (EG). The Ag/g-C_3N_4 photocatalysts exhibit the superior visible-light responsive photocatalytic activity. The microwave-assisted polyol system provides a facile and efficient way to synthesize Ag/g-C_3N_4 photocatalysts, which have potential applications in photocatalytic degradation of organic pollutants, hydrogen production, disinfection and other fields.

2. Experimental

g-C_3N_4 was synthesized by thermal polycondensation using thiourea as the precursor. Ag/g-C_3N_4 was synthesized by a microwave-assisted route in EG. Ag/g-C_3N_4 photocatalysts with nominal x wt.% were denoted as Ag/g-C_3N_4-x. Photocatalytic degradation of rhodamine B (RhB) using Ag/g-C_3N_4 photocatalysts was investigated under visible-light irradiation. The detailed experimental procedures see Supplementary material.

3. Results and discussion

Unlike previous reports, we choose a microwave-assisted polyol synthesis route in this work, mainly because it combines the advantages of microwave-assisted synthesis and polyol reduction simultaneously. Microwave-assisted synthesis is a rapid and energy saving method [32]. EG acts both as an eco-friendly solvent and a safe reducing agent during reaction. So, the process is suitable for the facile synthesis of the Ag/g-C_3N_4 photocatalysts.

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3.1. Photocatalyst characterization

Fig. 1 displays the X-ray diffraction (XRD) patterns of the samples. For all samples, the distinct diffraction peaks at around 13.2 and 27.7° correspond to the (100) and (002) planes of g-C_3N_4, respectively [31]. The intensities of diffraction peak at around 27.7° gradually are reduced with the increase of Ag loading amounts. In addition to the diffraction peaks of g-C_3N_4, no apparent diffraction peaks of metallic Ag appear in the patterns of Ag/g-C_3N_4 photocatalysts. This may be due to the low loading amounts and high dispersion of Ag in the composite photocatalysts. As shown in Fig. S1, X-ray photoelectron spectroscopy (XPS) analysis reveals the surface chemical states of Ag/g-C_3N_4–2 photocatalysts and indicates the presence of metallic Ag^0 species.

Fig. S2 and Fig. 2 are the typical transmission electron microscopy (TEM) images of g-C_3N_4 and Ag/g-C_3N_4–2, respectively. Fig. S2 displays that the primary g-C_3N_4 consists of nanosheets in the range of 300 nm to 1 μm. As shown in Fig. 2, fine and monodisperse Ag nanoparticles with a size of a few nanometers are closely attached to the edges of g-C_3N_4 nanosheets. Higher surface energy on the edges of g-C_3N_4 nanosheets may lead to the site-selective attachment of Ag nanoparticles [33]. The nanoscale crystallite size of Ag particles and strong coupling between Ag nanoparticles and g-C_3N_4 nanosheets may result in superior photocatalytic activity of Ag/g-C_3N_4 photocatalysts.

Fig. 3 displays optical properties of the samples. The UV-vis diffuse reflectance spectroscopy (UV-vis DRS) of the samples are shown in Fig. 3a. Obviously, the primary g-C_3N_4 exhibits strong visible-light absorption bands in the range from 450 to 800 nm, which is distinctly different from g-C_3N_4 prepared using dicyandiamide or melamine as starting materials in previous literatures [2,3]. The enhanced visible-light absorption of primary g-C_3N_4 could be attributed to the modified band structure of g-C_3N_4 by enriched nitrogen [3]. More importantly, visible-light absorption intensities of Ag/g-C_3N_4 photocatalysts have been further enhanced compared with the pristine g-C_3N_4 due to surface plasmon resonance (SPR) of Ag nanoparticles [5]. The intense visible-light response will promote the photocatalytic activities of Ag/g-C_3N_4 photocatalysts. Fig. 3b shows the photoluminescence (PL) spectra of the samples. The pristine g-C_3N_4 exhibits strong PL intensity, indicated that the rapid recombination of photogenerated electron/hole pairs is presented in photocatalytic process of g-C_3N_4. However, the PL intensities of all Ag/g-C_3N_4 photocatalysts decline significantly, suggested that the recombination of photogenerated electron/hole pairs has been effectively suppressed by Ag nanoparticles. Moreover, the change of PL intensities of the Ag/g-C_3N_4 photocatalysts is divided into two stages. The PL intensities first decrease with the increase of Ag content from Ag/g-C_3N_4–1 to Ag/g-C_3N_4–2, then increase when Ag content

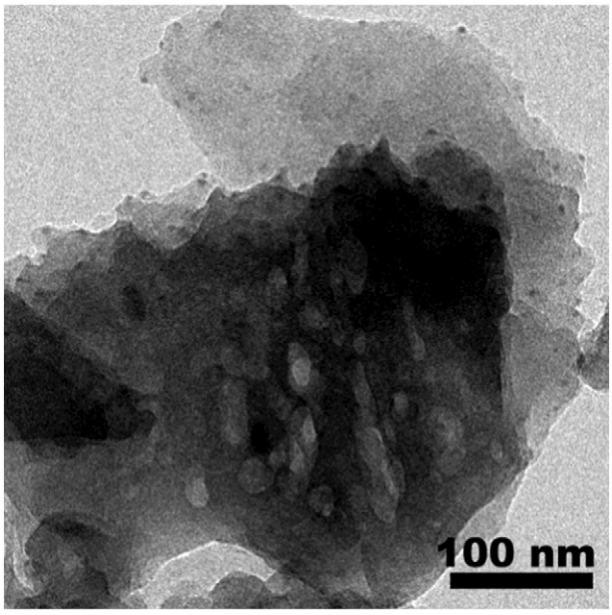

Fig. 2. TEM image of Ag/g-C_3N_4–2.

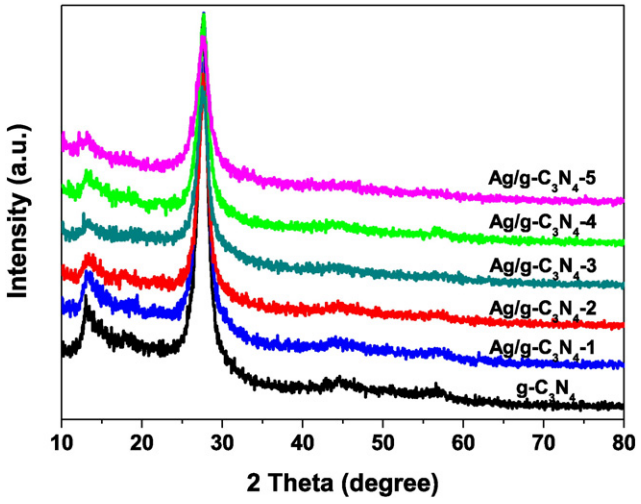

Fig. 1. XRD patterns of samples.

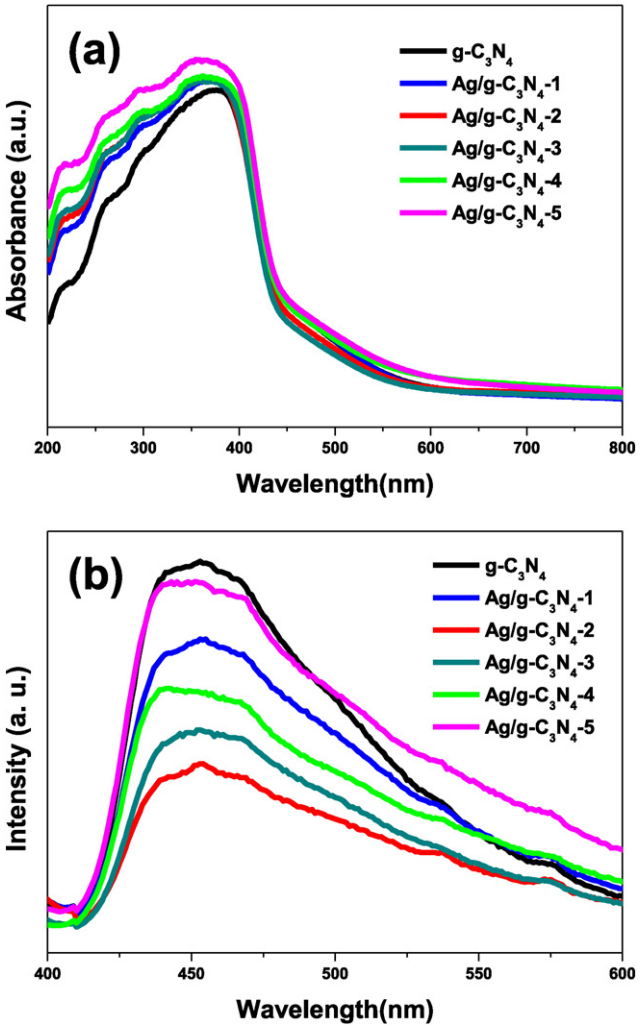

Fig. 3. (a) UV–vis DRS and (b) PL spectra of samples.