



Preparation and enhanced visible-light photocatalytic activity of silver deposited graphitic carbon nitride plasmonic photocatalyst



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ABSTRACT

A series of silver deposited g-C₃N₄ (Ag/g-C₃N₄) plasmonic photocatalysts with Ag loading from 0.1 to 5 wt% are prepared by thermal polymerization of urea precursor combined with the photodeposition method. The phase and chemical structure, electronic and optical properties as well as morphologies of Ag/g-C₃N₄ heterostructures are well-characterized. Subsequently, the photocatalytic activity of Ag/g-C₃N₄ is evaluated by the degradation of methyl orange (MO) and *p*-nitrophenol (PNP) under visible-light irradiation. The enhanced photocatalytic activity of Ag/g-C₃N₄ compared with g-C₃N₄ itself is obtained and explained in terms of the efficient visible-light utilization efficiency due to the SPR absorption of silver nanoparticles as well as fast generation, separation and transportation of the photogenerated carriers, evidenced by photoelectrochemical tests, photoluminescence measurements and free radical and hole scavenging experiments. Finally, the reusability of the catalyst is evaluated by five consecutive catalytic runs.

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1. Introduction

The growing concerns about environmental and energy crises have stimulated intense research on solar energy utilization [1]. In the field of the elimination of organic pollutants, solar photocatalysis by semiconductors has emerged as one of the most promising technologies [2–5]. Nevertheless, wide bandgap and low quantum efficiency are still the “bottleneck” of the photocatalysts to meet the requirement of practical applications. For example, the most common TiO₂ is not an ideal photocatalyst because it performs rather poorly in the processes associated with solar photocatalysis. As a result, it is an urgent issue to search for efficient sunlight- or visible-light-driven photocatalysts. For this purpose, the modified TiO₂ and TiO₂-alternative photocatalysts have been developed [6–17]. However, it still remains a challenge to design stable photocatalysts that are abundant and facile preparation besides high visible-light efficiency.

In the search for robust and stable visible-light-driven photocatalysts, a polymeric semiconductor, graphitic carbon nitride (g-C₃N₄), has recently attracted a great deal of interest in photocatalytic applications. The heptazine ring structure and high degree of condensation make metal-free g-C₃N₄ possess many advantages such as good chemical stability as well as an appealing electronic structure with a medium-bandgap (2.7 eV). In addition, g-C₃N₄ is abundant and easily-synthesized *via* one-step polymerization of the cheap feedstocks like cyanamide [18,19], dicyandiamide [20–22], melamine [23–25], thiourea [20,26] and urea [20,27–29]. These unique properties make g-C₃N₄ a promising candidate for applications in solar photocatalysis. However, metal-free g-C₃N₄ suffers from disadvantages such as rapid recombination of the photogenerated electrons (e_{CB}⁻) and holes (h_{VB}⁺), low visible-light utilization efficiency and small BET surface area [18–26]. Accordingly, the development of reliable and facile strategies to fabricate the modified g-C₃N₄-based photocatalysts with unique physicochemical properties and photocatalytic performances is of growing interests. For this purpose, g-C₃N₄-based heterostructured photocatalysts such as g-C₃N₄/ZnO [30,31], g-C₃N₄/Fe₂O₃ [32], g-C₃N₄/ZnWO₄ [33], g-C₃N₄/Bi₂WO₆ [34], g-C₃N₄/BiOBr [35], g-C₃N₄/SmVO₄ [36] and g-C₃N₄/AgX (X=Br, I) [37] have been constructed. Among these materials, the conduction band (CB) of g-C₃N₄ (N 2p orbitals) is more negative than that of the coupled

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semiconductor, accordingly, the photoexcited e_{CB}^- generated on $g\text{-C}_3\text{N}_4$ or both components are effectively collected in the CB of the coupled semiconductor; meanwhile, the photoexcited h_{VB}^+ are effectively collected in the valence band (VB) of $g\text{-C}_3\text{N}_4$ ($C\ 2p$ orbitals) since VB of $g\text{-C}_3\text{N}_4$ is more negative than that of the coupled semiconductor. The above procedures facilitate the efficient separation of the photogenerated carriers, leading to the enhanced photocatalytic activity compared with $g\text{-C}_3\text{N}_4$ itself. However, the reducibility of e_{CB}^- decreases obviously owing to the transportation of e_{CB}^- from the CB of $g\text{-C}_3\text{N}_4$ to that of the coupled semiconductor, giving a negative influence on the photocatalytic activity of $g\text{-C}_3\text{N}_4$ /semiconductor. For example, under the visible-light irradiation of the heterostructured $g\text{-C}_3\text{N}_4$ /BiOBr photocatalyst, the e_{CB}^- are injected into the CB of BiOBr (0.3 V vs. NHE) from that of $g\text{-C}_3\text{N}_4$ (−1.3 V vs. NHE) [18]. Owing to much positive CB edge of BiOBr compared with the standard redox potential of $O_2/\cdot O_2^-$ (−0.046 V vs. NHE), the number of the generated superoxide radicals ($\cdot O_2^-$) decreases, which limits the enhancement of the photocatalytic activity of $g\text{-C}_3\text{N}_4$ /BiOBr.

Herein, a series of silver deposited $g\text{-C}_3\text{N}_4$ heterostructures ($Ag/g\text{-C}_3\text{N}_4$) are prepared by thermal polymerization of urea precursor combined with photodeposition. Owing to utilization of the plasmonic nanostructure as the sensitizer for $g\text{-C}_3\text{N}_4$, as-prepared $Ag/g\text{-C}_3\text{N}_4$ are expected to improve the visible-light photocatalytic activity of $g\text{-C}_3\text{N}_4$ -based materials significantly [38]. On the one hand, the surface plasmon resonance (SPR) effect of silver nanoparticle causes the intense local electromagnetic fields, which can speed the formation rate of h_{VB}^+ and e_{CB}^- within $g\text{-C}_3\text{N}_4$ [39]. Additionally, the favorable Fermi level of silver facilitates the separation of e_{CB}^- and h_{VB}^+ , which in turn enhances the quantum efficiency of $g\text{-C}_3\text{N}_4$ [40]. Moreover, the transferred e_{CB}^- shift the Fermi level to more negative potential, and thereby keeping the reducibility of e_{CB}^- in the Fermi level close to that in the CB of $g\text{-C}_3\text{N}_4$ [41]. On the other hand, the efficient utilization of sunlight can be realized due to SPR absorption in the visible-light region as well as UV light response of the interband transition of silver nanoparticles.

The phase and chemical structure, optical absorption properties as well as morphologies of $Ag/g\text{-C}_3\text{N}_4$ are well characterized, and the visible-light photocatalytic activity of $Ag/g\text{-C}_3\text{N}_4$ is evaluated by the degradation of two typical organic pollutants, methyl orange (MO) and *p*-nitrophenol (PNP). Meanwhile, the separation and transportation of the photogenerated carriers in the visible-light-irradiating $Ag/g\text{-C}_3\text{N}_4$ system is studied by photoluminescence (PL) spectroscopy measurements and photoelectrochemistry experiments, and the active species generated during the process of photodegradation are investigated by free radical and hole scavenging experiments. On the basis of the above results, mechanism of visible-light photocatalytic degradation of aqueous organic pollutants over $Ag/g\text{-C}_3\text{N}_4$ plasmonic photocatalyst is revealed, which is one of the most important issues for the TiO_2 -alternative photocatalysts but is seldom studied up till now.

2. Experimental

2.1. Catalyst preparation

2.1.1. Graphitic C_3N_4

Urea (50 g) was put into an alumina crucible with a cover under ambient pressure in air, and then the crucible was heated in a muffle furnace to 250 °C for 1 h, 350 °C for 2 h and a final temperature 550 °C for 2 h at a heating rate of 2 °C min^{−1}. The yielded yellow powder was washed with nitric acid (0.1 mol L^{−1}) and distilled water to remove any residual alkaline species (e.g. ammonia)

adsorbed on the surface of the product, and then the product was dried at 80 °C for 12 h.

2.1.2. Ag deposited $g\text{-C}_3\text{N}_4$

As-prepared $g\text{-C}_3\text{N}_4$ powder (0.7 g) was dispersed into an aqueous $AgNO_3$ solution (90 mL) with the concentration of 0.08, 0.4, 0.8, 1.6, and 4 mmol L^{−1}, respectively, to obtain Ag deposited $g\text{-C}_3\text{N}_4$ materials with various Ag loadings (0.1, 0.5, 1, 2, and 5 wt%). The resulting suspension was irradiated under a 300 W Xe lamp (PLS-SXE300, Beijing Trusttech Co., Ltd.) for 2 h. The separated powder was washed with distilled water to remove the adsorbed Ag^+ ions, and then the product was dried at 80 °C for 12 h. The products are denoted as $Ag(x)/g\text{-C}_3\text{N}_4$, where x represents Ag deposited level (wt%) in the products.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were obtained on a Japan Rigaku D/max 2000 X-ray diffractometer (Cu K α , $\lambda = 1.5418 \text{ \AA}$). Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Magna 560 IR spectrophotometer. X-ray photoelectron spectroscopy (XPS) was performed on a VG-ADES 400 instrument with Mg K-ADES source. Transmission electron microscope (TEM) was recorded on a JEM-2100F high resolution transmission electron microscope at an accelerating voltage of 200 kV. Nitrogen porosimetry measurement was performed on a Micromeritics ASAP 2020M surface area and porosity analyzer. UV–vis diffuse reflectance spectra (UV–vis/DRS) were recorded on a Cary 500 UV–vis–NIR spectrometer. PL of the samples was obtained using a Varian Cary Eclipse spectrometer.

2.3. Photocatalytic tests

The adsorption and photocatalytic activity of as-prepared photocatalysts were evaluated by the degradation of MO and PNP under visible-light irradiation by a 300 W Xe lamp with an IR cut filter to remove IR irradiation from 680 nm to 1100 nm and a 400 nm cut filter to remove the UV irradiation. For all adsorption and photocatalysis experiments, 100 mL of aqueous MO or PNP solution with the initial concentration of 10 mg L^{−1} was used, and the catalyst amount was 100 mg. All experiments were performed in a self-made quartz photoreactor fitted with a circulation water system to maintain a constant temperature. Prior to irradiation, the adsorption–desorption equilibrium between the target compound and the catalyst was monitored by the determination of the concentrations of the target compound at a certain time interval. During the photocatalytic tests, fixed amounts of the reaction solution were taken out at given time intervals, followed by centrifugation to remove the photocatalyst completely. The concentrations of MO during the degradation procedures were determined by a Cary 60 UV–vis–NIR spectrometer at $\lambda = 464 \text{ nm}$, and the concentrations of PNP were determined at $\lambda = 317 \text{ nm}$ and a Agilent 1200 high performance liquid chromatography: C18 column, UV detector ($\lambda = 320 \text{ nm}$) and methanol/water (60/40, v/v) was used as a mobile phase at a flow rate of 1.0 mL min^{−1}. Final products such as NO_3^- and SO_4^{2-} ions were analyzed by a Metrohm 881 Compact ion chromatography (IC) equipped with a Metrosep A SUPP 4 anion column and conductivity detector. Na_2CO_3 (1.8 mmol L^{−1}) and $NaHCO_3$ (0.17 mmol L^{−1}) were used as the mobile phase, and the detection limit of NO_3^- and SO_4^{2-} is lower than 0.05 mg L^{−1}.

2.4. Photocurrent (PC) measurements

The working electrode was prepared on the rectangle titanium (Ti) sheets (size 10 mm × 50 mm, thickness 140 μm , purity > 99.6%), which was cleaned by sonication in water and alcohol for 10 min,

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