



Ag modified g-C₃N₄ composites with enhanced visible-light photocatalytic activity for diclofenac degradation



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ABSTRACT

Highly efficient visible-light-driven Ag/g-C₃N₄ heterostructured photocatalysts with different Ag amount were prepared by photodeposition under ambient condition. The composition, structure, morphology, and optical properties of the photocatalysts were characterized by X-ray powder diffraction (XRD), Fourier transform-infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), Transmission electron microscopy (TEM), UV–vis diffuse reflectance spectroscopy (DRS), and Photoluminescence Spectroscopy (PL), respectively. The results showed that photocatalytic activity of the heterostructured photocatalysts was higher than that of pure g-C₃N₄ through the comparison of photodegradation rates of diclofenac under visible light irradiation. When the mass ratio of Ag was 54%, the kinetic constant of diclofenac degradation over Ag/g-C₃N₄(54%) was 0.0429 min⁻¹, which was almost 3.1 times higher than that of the pure g-C₃N₄ ($k=0.0141$ min⁻¹), showing the highest activity. Reactive species in DCF degradation were pinpointed by adding a series of scavengers into the photocatalytic reaction. Photo-generated hole was the main reactive species in diclofenac degradation. In addition, the photocatalysts showed excellent stability for the degradation of diclofenac over multiple reaction cycles. The enhanced photocatalytic activity for the photocatalyst originated from the close contact between Ag and g-C₃N₄, and the localized surface plasmon resonance (SPR) effect of Ag. The possible photocatalytic mechanism of the charge transfer in Ag/g-C₃N₄ composites was analyzed and proposed to shed into the visible light driven photocatalysis on g-C₃N₄ for the degradation of diclofenac.

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1. Introduction

Diclofenac (DCF) is a synthetic non-steroidal anti-inflammatory drug (NSAD), mostly used as its sodium salt for medical applications. Since the conventional wastewater treatment processes cannot completely degrade DCF, it has been widely detected in raw water and treated water with concentration reaching up to 28.4 μg/L in surface water and 0.59 μg/L in groundwater [1,2]. Nowadays, adverse impacts of DCF (even as low as 1 μg/L) on different organisms in aquatic environments have been observed [3–7]. To effectively remove DCF, many novel DCF treatment methods such as Fenton reactions under UV-light irradiation in the presence of H₂O₂ or ozone have been proposed [8–10]. Photocatalytic degradation and disinfection, particularly under visible light irradiation, has always remained the focus of this field due to the potential solar energy utilization and efficient reaction [11,12]. Plenty of semiconductor materials have been exploited as photocatalysts.

Graphitic carbon nitride (g-C₃N₄) is one of the most popular photocatalysts due to its unique character. The relatively low band gap of g-C₃N₄ ca. 2.70 eV effectively permits visible-light degradation absorbance. Besides, g-C₃N₄ has a similar two dimensional layered structure to graphene, where there are strong covalent C–N bonds instead of C–C bonds, unique electronic properties, large specific surface area and environmental benignity make it a superior candidate for the construction of catalyst [13,14]. After Wang et al. [15] first reported the use of g-C₃N₄ as a stable photocatalyst for H₂ production from water splitting under visible light irradiation in 2009, many further research also demonstrated the promising photocatalytic performance in water splitting and the degradation of organic pollutions [16–19]. However, the photocatalytic performances of g-C₃N₄ are still limited due to low quantum efficiency and fast recombination of photogenerated electron-hole pairs [20]. To resolve these problems, many strategies have been carried out to improve the photocatalytic performance of g-C₃N₄, such as hybridization with semiconductor cocatalysts [21,22], non-metal doping [23], noble metal deposition [24–27], and the creation of mesoporous g-C₃N₄ [13,28–30]. Among these approaches, noble metal deposition shows a great potential to promote the pho-

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photocatalytic activity of $g\text{-C}_3\text{N}_4$. The photogenerated electron can migrate from the surface of catalyst to the solution through metal nanoparticles, which restrain the recombination of photogenerated electron-hole pairs. Furthermore, when $g\text{-C}_3\text{N}_4$ contact with metal, a metal-semiconductor heterojunction will be formed. The type of the heterojunction (Schottky barrier or ohmic contact) depends on the relative levels of semiconductor band structures and metal work functions. The potential well on the metal-semiconductor interface can capture electrons, which will promote the separation of electron-hole pairs and thus improve the photocatalytic performance of the hybrid catalyst [31].

As a famous noble metal, Ag has been widely studied for its potential applications in catalysis, biosensors, and biomedicine [32–37]. Ag nanoparticles exhibit characteristic optical and physical properties because of their unique size and distribution, morphology, and interparticle distance in comparison with the bulk counterparts [38–44]. However, the high surface energy of the Ag nanoparticles makes them prone to aggregation, which could deteriorate their unique chemical properties and decrease the overall performance. Therefore, the stability of Ag nanoparticles is an important factor for their practical applications. As photodeposition is an appropriate approach to prevent nanoparticles from aggregation, it can be used to prepare supported metal catalyst with highly dispersed active sites [45].

In this work, a series of Ag/ $g\text{-C}_3\text{N}_4$ nanocomposites with different percent of Ag was successfully fabricated by a photodeposition method, followed by extensive characterization. Furthermore, the stability of the prepared photocatalyst was investigated by repeated experiment. Finally, the mechanism for DCF photodegradation was discussed based on experimental results.

2. Experimental

2.1. Materials

Melamine ($\text{C}_3\text{H}_6\text{N}_6$) and silver nitrate (AgNO_3) were obtained from Sinopharm Chemical Reagent Corp, P. R. China. Diclofenac sodium (DCF) was purchased from Sigma chemical Reagent Co. USA. All chemicals were used as received prepared without further purification, and all aqueous solution were prepared with deionized water.

2.2. Preparation of the photocatalyst

$g\text{-C}_3\text{N}_4$ was prepared by directly heating sulfuric acid treated melamine precursor in a muffle furnace [46]. The ramping rate was $4^\circ\text{C}/\text{min}$ from room temperature to 550°C , and keep at 550°C for 4 h. The obtained yellow product was collected and ground into powder in an agate mortar. The $g\text{-C}_3\text{N}_4$ nanosheets were obtained by liquid exfoliation of the as-synthesized bulk $g\text{-C}_3\text{N}_4$ in methanol [47]. Briefly, 0.3 g bulk $g\text{-C}_3\text{N}_4$ powder was dispersed in 100 mL methanol and then ultrasonicated for 10 h. The formed suspension was centrifuged at 4000 rpm for 20 min to remove aggregates. The resulting pale yellow colored products were $g\text{-C}_3\text{N}_4$ nanosheets.

Ag modified $g\text{-C}_3\text{N}_4$ composite photocatalysts were synthesized by photodeposition. 0.1 g $g\text{-C}_3\text{N}_4$ nanosheets and different amount of AgNO_3 were added in 100 mL deionized water, and the suspension was stirred for 4 h at room temperature. 10 mL methanol was added into the beaker as the sacrificial agent. Then, the beaker was covered with a glass disc and sealed with parafilm, a Teflon hose was inserted through a small hole in parafilm to perform N_2 for purging for 30 min to remove O_2 in the suspension. The suspension was illuminated under Xenon lamp for 90 min. After filtrating, washing and drying, the Ag/ $g\text{-C}_3\text{N}_4$ (X) (X represents the mass ratio of Ag, X was 10%, 19%, 32%, 54%, and 70%) was prepared.

2.3. Characterization

Phase purity and crystal structure of the obtained samples were examined by X-ray diffraction (XRD) using a Bruker D8 Advance X-ray diffractometer equipped with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$), at a scanning rate of $10^\circ \text{ min}^{-1}$ in the 2θ range of $10\text{--}80^\circ$. The chemical structures of the photocatalysts were confirmed by a Nicolet 5700 Fourier transform infrared (FTIR) spectrometer (Thermo Fisher Scientific). Surface composition and chemical bonds were examined by a PHI 5000C ESCA X-ray photoelectron spectroscopy (XPS). UV–vis diffuse reflectance spectra (UV–vis DRS) were obtained on an UV–vis spectrophotometer (UV-2550, Shimadzu, Japan). BaSO_4 was used as a reflectance standard in the UV–vis diffuse reflectance experiments. The Photoluminescence Spectroscopy (PL) of photocatalysts was investigated using a Horiba FL-3000 equipped, and the excitation wavelength was set at 368 nm. Transmission electron microscopy (TEM) observation was performed by a CM200FEG field emission transmission electron microscope with an accelerating voltage of 200 kV.

2.4. Evaluation of photocatalytic activity

The photocatalytic activities of the as-prepared materials were evaluated by the degradation of diclofenac (DCF) under visible light irradiation. The light source was a 300 W Xenon lamp (BL-GHX-Xe-300) with an optical cut-off filter ($\lambda \geq 400 \text{ nm}$), the intensity was $100 \text{ mW}/\text{cm}^2$. In a typical experiment, 10 mg of the photocatalyst powder was suspended in 100 mL of 100 mg/L DCF aqueous solution in a quartz reactor. During the reaction, the irradiated chamber was cooled by water circulation, and the temperature was maintained at 25°C . The aqueous samples were collected at the given time intervals and filtrated through $0.45 \mu\text{m}$ membranes. The photolysis experiment of DCF was carried out without the presence of the photocatalyst under the same condition.

The concentration of DCF was measured by a reversed-phase high-performance liquid chromatography system (Agilent 1200). The analytical column was a C18 column (Gemini $5 \mu\text{m}$, $150 \text{ mm} \times 4.6 \text{ mm}$, from Phenomenex). The injection volume was $50 \mu\text{L}$. The mobile phase was a mixture of 80% HPLC-grade methanol and 20% MilliQ-water (containing 0.1% formic acid) at a constant flow rate of $1.0 \text{ mL}/\text{min}$, and the detection wavelength was set at 276 nm. Total organic carbon (TOC) measurements at certain time intervals were carried out by a TOC analyzer (TOC-L, Shimadzu, Japan).

2.5. Evaluation of reactive oxygen species

In a typical photocatalytic process, a large number of reactive species including photogenerated holes (h^+), hydroxyl radicals ($\bullet\text{OH}$), superoxide anion radicals ($\bullet\text{O}_2^-$), and singlet oxygen ($^1\text{O}_2$) may be directly involved [48]. To determine the effect of reactive species in photodegradation, corresponding scavengers were introduced to quench the specific reactive species, the scavengers used in this study are isopropanol (10 mM) for $\bullet\text{OH}$, benzoquinone ($0.5 \mu\text{M}$) for $\bullet\text{O}_2^-$, sodium azide ($0.5 \mu\text{M}$) for $^1\text{O}_2$, and EDTA disodium ($5 \mu\text{M}$) for h^+ [49]. As a consequence of quenching, photocatalytic oxidation reaction will be partly suppressed, and the extent of decrease indicates the importance of the corresponding oxidization species.

3. Results and discussion

3.1. Structure and composition of Ag/ $g\text{-C}_3\text{N}_4$ photocatalysts

The structure and composition of the as-prepared samples were characterized by XRD, FTIR and XPS, respectively.

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