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Construction of carbon dots modified $MoO_3/g\text{-}C_3N_4$ Z-scheme photocatalyst with enhanced visible-light photocatalytic activity for the degradation of tetracycline

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ABSTRACT

Carbon quantum dots (CDs) have been frequently used for broadening spectrum light response due to their superior up-conversion photoluminescence (UPPL) property and effective charge separation capacity. In this study, a novel CDs modified Z-scheme photocatalyst ($CDs/g\text{-}C_3N_4/MoO_3$) was successfully constructed. The morphologies, chemical compositions, and optical properties of the prepared catalysts were investigated via a series of characterization techniques. Systematic studies indicated that the $CDs/g\text{-}C_3N_4/MoO_3$ photocatalyst exhibited remarkably enhanced visible-light photocatalytic activity for the degradation of tetracycline (TC) compared to pristine $g\text{-}C_3N_4$ and $MoO_3/g\text{-}C_3N_4$ composite. Doping 0.5% CDs resulted in the highest TC degradation rate, which was 3.5 and 46.2 times higher than that of $MoO_3/g\text{-}C_3N_4$ and $g\text{-}C_3N_4$, respectively. The enhanced photocatalytic performance of $CDs/g\text{-}C_3N_4/MoO_3$ can be attributed to the synergistic effects of CD properties (i.e., excellent UPPL activity and high charge separation capacity and the Z-scheme heterojunction structure). Reactive species scavenging experiments revealed that photogenerated holes are the main active species during the photocatalytic process. Possible photocatalytic degradation pathways of TC were proposed through the identification of intermediates using HPLC-MS and the frontier electron density calculation. Experimental results showed that the newly fabricated Z-scheme $CDs/g\text{-}C_3N_4/MoO_3$ is a promising photocatalyst for the removal of TC from the environment.

1. Introduction

In the past decades, tetracycline (TC) has been widely used to treat human and animal infections [1]. It has been frequently detected in various environmental matrices. The presence of TC in the environment could cause antibiotic resistance problem, which poses a serious threat to the well-being of human and animals. However, due to the stable chemical structure and recalcitrance to biological degradations, TC cannot be effectively removed through conventional wastewater treatment processes [2,3]. Therefore, new techniques for the treatment of TC in wastewater are required. Recent years, photocatalytic degradation of TC from wastewater has received a lot of attention due to its high efficiency and long-term reliability. Some of traditional photocatalysts, e.g., TiO_2 [4], have been proven to have the ability to degrade TC under UV light irradiation. However, the poor utilization of solar light energy of these photocatalysts hindered their practical application. Therefore, the sunlight -driven photocatalysts are needed for the photocatalytic treatment of TC.

Graphitic carbon nitride ($g\text{-}C_3N_4$) as a new visible light-driven photocatalyst has attracted enormous attention due to its low toxicity, high stability, and low cost [5]. As a metal-free polymeric semiconductor, $g\text{-}C_3N_4$ has a narrow band gap of ca. 2.7 eV and thus has a strong visible-light response. This property results in electrons and holes easily produced under visible-light excitation [6]. However, the high recombination rate of the photogenerated electron-hole pairs and the low specific area of pure $g\text{-}C_3N_4$ greatly limited its photocatalytic activity [7,8]. Therefore, various methods have been developed to improve the photocatalytic performance of the pure $g\text{-}C_3N_4$, including nonmetal doping [9,10], metal deposition [11], coupling with other materials to form hybrids [12,13], and using nano-sized structures $g\text{-}C_3N_4$ [14,15]. In particular, combining $g\text{-}C_3N_4$ with other semiconductors to form the Z-scheme heterostructured photocatalyst would efficiently separate the photogenerated electrons and holes, thus enhance the photocatalytic activity of $g\text{-}C_3N_4$ under visible light.

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MoO_3 is a well-known p-type metal oxide semiconductor and has been considered to be a promising candidate to form the Z-scheme heterostructured photocatalyst due to its unique energetic and electrical properties [16]. It has been demonstrated that combining MoO_3 with other photocatalyst, such as TiO_2 [17], CdS [18], and polyimides [19], enabled the composites with the excellent photocatalytic activity through the hindering of charge recombination and improving of charge transfer processes. Recent studies also found that the combination of MoO_3 with g-C_3N_4 could form the Z-scheme photocatalyst with enhanced photocatalytic performance [16,20]. Because of the suitable band gaps between the two semiconductors, the photogenerated charge carrier can be effectively separated and hence generated more reactive species. Nevertheless, it is still needed to improve the visible light absorption of the composites to achieve their high photocatalytic activity in their practical applications.

Carbon quantum dots (CDs), as a new discovered carbon-based nanomaterial, displayed the excellent up-conversion photoluminescence feature, as well as the outstanding photoinduced electron transfer and reservoir properties, all of which enabled the photocatalysts to utilize the sunlight efficiently [21]. Due to these remarkable properties, CDs have been successfully integrated with many semiconductors to improve their photocatalytic activities by decreasing electron-hole recombination and broadening the photo-absorption region. Our former studies also found that CDs could effectively improve the photocatalytic performances of TiO_2 [22], $BiPO_4$ [23], and g-C_3N_4 [24] for the degradation of PPCPs in water. Therefore, we are motivated to rationally design the carbon dots modified MoO_3/g-C_3N_4 Z-scheme photocatalyst with enhanced visible-light photocatalytic activity for potential practical application.

In this study, we reported the facile fabrication of CDs/g-C_3N_4/MoO_3 composites, which showed excellent visible-light photocatalytic performance compared to that of the pristine g-C_3N_4, MoO_3, and g-C_3N_4/MoO_3 hybrids. The microstructures, morphologies, phases, and optical properties of the samples were investigated via a series of characterization. Tetracycline (TC), as one of the most widely used antibiotics, was used to evaluate the photocatalytic activities of the prepared composites. The influences of MoO_3 and CDs contents on the photocatalytic performance of the CDs/g-C_3N_4/MoO_3 composite were systematically evaluated. Electron spin resonance (ESR) and the reactive species trapping experiments were conducted to qualitatively detect the roles of the different active species during TC degradation. Subsequently, possible photocatalytic transformation pathway and mechanisms for TC degradation were proposed. Finally, the reduction of antibacterial activity of TC during the photocatalytic process was evaluated.

2. Experimental section

2.1. Catalyst preparation

All reagents (Taitan Company, China) employed for catalyst preparation were analytical grade and used without further purification. Deionized (DI) water from a Milli-Q apparatus (> 18 mΩ cm, Germany) was used. MoO_3 powder was synthesized through the solid-state decomposition reaction of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ at 500 °C for 4 h in ambient air condition. The obtained product was then washed with DI water three times and dried at 60 °C for 5 h.

Graphitic carbon nitride (g-C_3N_4) was synthesized by directly heating dicyandiamide [24]. Typically, 3.0 g of dicyandiamide was introduced into a covered alumina crucible, and then heated to 550 °C for 3 h at a heating rate of 2.8 °C min^{-1}. After cooling to room temperature, the obtained bulk g-C_3N_4 was milled into powders.

Carbon dots (CDs) were prepared by a hydrothermal method [24,25]. Briefly, citric acid (3.0 g) and urea (1.0 g) were dissolved in DI water by ultrasound for 2 h. The mixture was then transferred into a 50 mL Teflon-lined stainless steel autoclave at 180 °C for 5 h. After cooling to room temperature, the obtained black solution was centrifuged at 10,000 rpm for 30 min to remove large particles. Finally, the supernatant was collected and reconstituted to 100 mL with DI water for storage.

CDs/g-C_3N_4/MoO_3 composite was synthesized through a facile calcination method [26]. In a typical procedure, 1.97 g of g-C_3N_4 and predetermined amounts of carbon dots and MoO_3 were co-dispersed in 50 mL ethanol through ultrasound for 2 h. The mixture was then carefully vaporized at 75 °C by magnetic stirring to remove ethanol and was subsequently dried at 100 °C for 12 h. The obtained powder was grounded and then calcined at 300 °C for 4 h in a muffle furnace. After cooling to room temperature, the product of interest was obtained. For comparison, a series of MoO_3/g-C_3N_4 composites with different mass contents of MoO_3 were also prepared using the same method, which are named as g-C_3N_4/MoO_3-*x* (CM*x*), where *x* represents the mass fractions of MoO_3. As can be seen in Text S1 of the Supplementary Materials (SM), the g-C_3N_4/MoO_3-3 with weight contents of 3% MoO_3 has the highest photocatalytic activity. Thus, a series of CDs/g-C_3N_4/MoO_3 composites with different mass contents of CDs were prepared and named as *y*-CDs/g-C_3N_4/MoO_3-3 (*y*CCM3), where *y* represents the mass fractions of CDs.

2.2. Characterization

The microstructures of the synthesized catalyst were observed by a JSM-6700 scanning electron microscope (SEM) and a JEM-2100HR transmission electron microscope (TEM). The elemental compositions of samples were characterized by an energy dispersive spectroscopy (EDS) equipped on the SEM. X-ray diffraction (XRD, Bruker-D8-Advanced X-ray diffractometer) with Cu Kα radiation source was used to characterize the crystal structure of samples, with the scanned area of 2θ from 10° to 80°. The chemical components and valence states of the catalyst were analyzed using X-ray photoelectron spectroscopy (XPS) on a Thermo VG ESCALAB 250 spectrometer with Al Kα radiation as the excitation source. The Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 spectrometer with the samples dispersed in KBr. The UV–vis spectra were measured by an UV2450 UV–vis spectrometer (Shimadzu) using the $BaSO_4$ powder as the reference. The photoluminescence (PL) emission spectra were measured by a FlouroMax-4 fluorescence spectrophotometer. The electron spin resonance (ESR) acquired on a Bruker A200-9.5/12 spectrometer was used to detect the radical intermediates.

2.3. Photocatalytic performance tests

Photocatalytic performances of the synthesized catalysts were evaluated by the photocatalytic degradation of tetracycline (TC) under visible light. TC (98% purity) was purchased from TCI Reagent Co. Ltd. (Shanghai, China). Visible-light irradiation was achieved by a 350 W xenon lamp with a 420 nm cutoff filter. A water circulation system was used to maintain the temperature at 25 °C. In each test, 30 mg of catalysts were firstly dispersed in 50 mL of 20 mg L^{-1} TC aqueous solution, and then the mixture was stirred in dark for 30 min to reach the adsorption-desorption equilibrium before the light irradiation. During the reaction process, 2 mL of suspension was collected at predetermined time intervals, and filtered through 0.22-μm Millipore filters to remove the catalysts. The residue TC in solution was analyzed by high performance liquid chromatography (HPLC). HPLC was performed on a Waters e2968 instrument equipped with a UV detector and a 4.6 × 250 mm Zorbax Eclipse XDB C18 reverse-phase column (Agilent, USA) at 25 °C. The detection wavelength of the UV detector was 355 nm and the injection volume was 20 μL. The isocratic mobile phase was made up of 25% methanol and 75% water (with 0.2% formic acid) with a flow rate of 1.0 mL min^{-1}.