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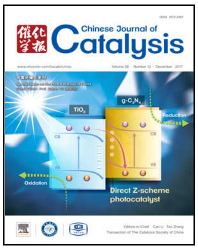

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Construction of carbon nitride and MoS_2 quantum dot 2D/0D hybrid photocatalyst: Direct Z-scheme mechanism for improved photocatalytic activity

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Graphite-like carbon nitride (g-C_3N_4)-based compounds have attracted considerable attention because of their excellent photocatalytic performance. In this work, a novel direct Z-scheme system constructed from two-dimensional (2D) g-C_3N_4 nanoplates and zero-dimensional (0D) MoS_2 quantum dots (QDs) was prepared through the combination of a hydrothermal process and microemulsion preparation. The morphologies, structures, and optical properties of the as-prepared photocatalysts were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, atomic force microscopy, transmission electron microscopy, and UV-vis diffuse reflectance spectroscopy. In addition, the photocatalytic performances of the prepared 2D/0D hybrid composites were evaluated based on the photodegradation of rhodamine B under visible-light irradiation. The results demonstrated that the introduction of MoS_2 QDs to g-C_3N_4 greatly enhanced the photocatalytic efficiency. For the optimum 7% MoS_2 QD/g-C_3N_4 photocatalyst, the degradation rate constant was 8.8 times greater than that of pure g-C_3N_4 under visible-light irradiation. Photocurrent and electrochemical impedance spectroscopy results further demonstrated that the MoS_2 QD/g-C_3N_4 composites exhibited higher photocurrent density and lower chargetransfer resistance than those of the pure g-C_3N_4 or MoS_2 QDs. Active species trapping, terephthalic acid photoluminescence, and nitro blue tetrazolium transformation experiments were performed to investigate the evolution of reactive oxygen species, including hydroxyl radicals and superoxide radicals. The possible enhanced photocatalytic mechanism was attributed to a direct Z-scheme system, which not only can increase the separation efficiency of photogenerated electron-hole pairs but also possesses excellent oxidation and reduction ability for high photocatalytic performances. This work provides an effective synthesis approach and insight to help develop other C_3N_4-based direct Z-scheme photocatalytic systems for environmental purification and energy conversion.

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1. Introduction

In recent decades, photocatalysis technology has been proven to be a green method for resolving environmental issues and the energy crisis [1–5]. In particular, the development of novel visible-light-driven photocatalysts with low cost, excellent stability, and high activity has attracted considerable attention [6–8]. Graphitic carbon nitride (g-C_3N_4) with a two-dimensional (2D) nanosheet structure is a new type of metal-free semiconductor for visible-light photocatalysts and has attracted significant attention because of its suitable band gap (E_g = 2.7 eV), excellent chemical stability, and low cost [9–12]. However, the photocatalytic efficiency of g-C_3N_4 is limited by the low quantum efficiency and fast recombination of photo-generated charges [13–15]. Thus, developing novel g-C_3N_4-based photocatalysts with high quantum efficiency is highly desirable, and various strategies have been developed, including heterojunction construction [16,17], surface deposition of noble metals [18,19], and nonmetal doping [20–22]. However, these techniques cannot overcome the inherent deficiencies, such as the high recombination rate and low separation efficiency of photogenerated electron-hole pairs [23,24]. Therefore, finding a new route to improve the photocatalytic performance of g-C_3N_4 remains a great challenge.

It is well known that a Z-scheme photocatalytic system possesses enhanced separation efficiency of photoinduced electrons and holes on different semiconductors as well as strong redox ability [25,26]. Unfortunately, traditional Z-scheme systems consist of two individual semiconductors with noble metals or the electron acceptor/donor pairs as the electron mediator [27–29], and this type of structure has some drawbacks such as backward reactions and the reduction of light absorption, consequently inhibiting practical application. The construction of mediator-free direct Z-scheme systems only containing two semiconductor components has thus become promising and important. Recently, many g-C_3N_4-based photocatalytic systems with a direct Z-scheme mechanism have been constructed, such as g-C_3N_4/TiO_2 [30,31], g-C_3N_4/$BiVO_4$ [32], and g-C_3N_4/Ag_2CrO_4 [33], with enhanced separation efficiency of photoinduced electrons and holes. Therefore, it is a great challenge to design a novel and highly efficient direct Z-scheme g-C_3N_4-based photocatalytic system.

Compared with bulk materials, zero-dimensional (0D) quantum dots (QDs) possess unique advantages for application in photocatalysis, such as band gap tunability, strong light harvesting capability in the visible and near-infrared region, and large surface-to-volume ratios [34]. Recently, great developments of carbon, graphene, and MoS_2 QDs combined with layered materials as 0D/2D composite photocatalysts have been achieved [35–37]. Interactions between the 0D QD and 2D nanoplate moieties can make QDs more dispersive and stable, and the accelerated charge transfer from 2D nanoplates can inhibit the recombination of photoexcited charges, thereby resulting in greatly promoted photocatalytic activity [38,39]. For example, Fang et al. [40] introduced CdS QDs on the surface of graphene, leading to enhanced photocatalytic and photoelectric performance. MoS_2 QDs are potentially applicable in catalysis, fluorescence sensing, and bio-imaging because of their excellent optical and electronic properties [41]. Li and coworkers [42] loaded MoS_2 QDs on graphene nanoplates, which displayed excellent hydrogen evolution reaction activity. Inspired by the aforementioned reports, an effective strategy of coupling MoS_2 QDs with other 2D layered materials was unveiled for the development of new visible-light-driven photocatalysts for environmental decontamination.

Herein, we developed a combined route using a hydrothermal process and microemulsion preparation to synthesize 2D/0D hybrid composites constructed from 2D carbon nitride nanoplates and 0D MoS_2 QDs. The as-obtained hybrid composites exhibited distinctly enhanced photocatalytic activity compared with that of pure g-C_3N_4 under visible-light irradiation. The enhanced photocatalytic activity was mainly attributed to the formation of a Z-scheme system in the 2D/0D hybrid composite. In addition, a possible Z-scheme photocatalytic mechanism for enhancing photocatalytic activity was also proposed.

2. Experimental

2.1. Catalyst preparation

Ammonium tetrathiomolybdate ($(NH_4)_2MoS_4$), hydrazine hydrate ($N_2H_4 \cdot H_2O$, 85%), and rhodamine B (RhB) were obtained from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. Pure g-C_3N_4 nanosheets were prepared according to the procedures described in previous reports [43].

2.1.1. Synthesis of MoS_2 QDs

In this process, 0.1 g $(NH_4)_2MoS_4$ was dispersed in 20 mL of deionized water and 20 mL of ethanol, and the solution was mixed and sonicated for 30 min. Then, 1.5 mL of $N_2H_4 \cdot H_2O$ was added dropwise to the above solution with stirring. Subsequently, the mixture was poured into a stainless-steel-lined Teflon autoclave and heated at 200 °C for 16 h. After the solution cooled naturally, it was filtered through a 0.22-μm microporous membrane and dialyzed with water. The solid samples were then obtained by evaporating the solvents.

2.1.2. Synthesis of MoS_2 QD/g-C_3N_4 composites

MoS_2 QD/g-C_3N_4 composite materials were prepared by applying a microemulsion method using hexanol (85/10 *V*/*V* versus H_2O, Aldrich), Triton X-100 (Aldrich), and *n*-heptane (105/100 *V*/*V* with surfactant Scharlau) as the cosurfactant, surfactant, and organic medium, respectively [44]. The g-C_3N_4 (0.1 g) was introduced into the microemulsion and sonicated for 10 h for further experiments. Different volumes of the MoS_2 QD aqueous solution were added dropwise into the above suspension and stirred for 24 h. The MoS_2 QD/g-C_3N_4 composites were collected by centrifugation and washed with absolute ethanol, deionized water, and acetone and then dried at 70 °C for 12 h. The MoS_2 QD/g-C_3N_4 composites were marked as x% MoS_2 QD/g-C_3N_4, where x indicates the mass fraction of the MoS_2 QDs (1%, 5%, 7%, and 10%).