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Fabrication of TiO_2/MoS_2@zeolite photocatalyst and its photocatalytic activity for degradation of methyl orange under visible light

Weiping Zhang, Xinyan Xiao*, Lili Zheng, Caixia Wan

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, China

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ABSTRACT

TiO_2/MoS_2@zeolite composite photocatalysts with visible-light activity were fabricated via a simple ultrasonic-hydrothermal synthesis method, using $TiCl_4$ as Ti source, MoS_2 as a direct sensitizer, glycerol water solution with certain dispersion agent as hydrolytic agent, and zeolite as carrier. The structure, morphology, composition, optical properties, and specific surface area of the as-prepared photocatalysts were characterized by using XRD, FTIR, SEM–EDS, TEM, XPS, UV–vis, PL and BET analyzer, respectively. And the photocatalytic degradation of methyl orange (MO) in aqueous suspension has been employed to evaluate the photocatalytic activity and degradation kinetics of as-prepared photocatalysts with xenon lamp as irradiation source. The results indicate that: (1) TiO_2/MoS_2@zeolite composite photocatalysts exhibit enhanced photocatalytic activities for methyl orange (MO) degradation compared to Degussa P25; (2) photocatalytic degradation of MO obeys Langmuir–Hinshelwood kinetic model (pseudo-first order reaction), and its degradation rate constant (k_{app}) (2.304 h^{-1}) is higher than that of Degussa P25 (0.768 h^{-1}); (3) the heterostructure consisted of zeolite, MoS_2 and TiO_2 nanostructure could provide synergistic effect for degradation of MO due to the efficient electron transfer process and better absorption property of TiO_2/MoS_2@zeolite composite photocatalyst.

1. Introduction

Solar energy semiconductor photocatalysis, as a potential photocatalysis technology, has important research significance for solving environmental and energy problems. Numerous attempts have been made to develop the semiconductor photocatalytic materials which have wider light absorption range for more effectively utilizing the solar energy. Titanium oxide (TiO_2)-based nanomaterials are generally considered to be the most reliable photocatalytic materials for the decomposition of toxic and hazardous organic pollutants. However, TiO_2 can absorb only a small portion of the solar spectrum in the ultraviolet region because of the wide band gap energy (TiO_2, 3.2 eV), and meanwhile, the fast recombination of the photogenerated electron/hole (e^-/h^+) reduces the photonic efficiency and represents the major drawback of photocatalytic applications [1–4]. So, a single-component photocatalyst could not fulfill the practical application. To enhance the photocatalytic activities of TiO_2 under solar light, multiphase photocatalyst system has been developed by shifting the wavelengths of light the photocatalysts absorb to the visible portion of the spectrum [5]. Nowadays, significant interest has been devoted to designing TiO_2-semiconductor multiphase photocatalyst system [6–8], aiming at a synergetic combination of their intrinsic outstanding properties and, thus, enhanced performance to meet requirements imposed by environmental applications, such as water purification, detoxification of heavy metal ions. In this area, All-solid-state Z-scheme photocatalytic systems as a promising composite-type were extensively studied, which has become an important strategy to achieve high-efficiency photocatalyst [9,10]. Z-scheme photocatalytic system has a novel photoexcitation mechanism due to its distinctive structure. In TiO_2/CdS Z-scheme system (Fig. 1), the electrons of TiO_2 and CdS are photoexcited from the VB to the CB, respectively, leaving the holes in their VB. The electrons in the CB of TiO_2 migrate to VB of CdS through a solid-state electron mediator, and consume the holes in the VB of CdS. As a result, the electrons and the holes can be completely separated in space, leading to an enhanced photocatalytic activity of TiO_2/CdS [11].

Molybdenum dichalcogenides (MoS_2), as a potential semiconductor, has been extensively studied in photocatalysis and electrochemical solar energy conversion because of its excellent

Abbreviations: MO, methyl orange; MoS_2, molybdenum dichalcogenides; TiO_2, titanium dioxide; XRD, X-ray diffraction; FTIR, Fourier transform infrared spectroscopy; SEM, scanning electron microscope; TEM, transmission electron microscope; PL, photoluminescence; UV–vis, ultraviolet visible.

* Corresponding author.
E-mail address: cexyxiao@scut.edu.cn (X. Xiao).

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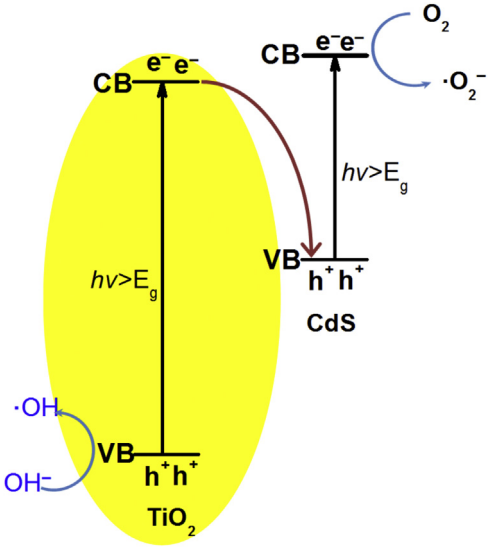

Fig. 1. Schematic illustration of charge transfer route in the CdS/TiO_2 nanocomposite system.

performance such as matching the solar spectrum and stability against the photocorrosion [12–15]. However, the conduction band energy level of bulk MoS_2 is less negative than that of TiO_2. Fortunately, nanoscale MoS_2 exhibited quantum confinement effects as some research reported [16–19]. Owing to the confinement effects, the band gap of nanoscale MoS_2 can be increased significantly and the energy level of conduction band is higher than that of TiO_2. As a graphite-like layered-structure material, commercial MoS_2 is usually the aggregation of three-dimensional multilayer structure, which is bound through Van der Walls force between layers and the multilayer structure MoS_2 can be peeled off and formed nanoscale structure by using mechanically or chemically exfoliated method [20,21]. Hence, commercial MoS_2 can be used as sensitizer for synthesis of Z-scheme TiO_2/MoS_2 photocatalyst.

There are several limitations to use nano-TiO_2 with high surface activity as photocatalyst in the photocatalytic reactor. One is fast aggregation of TiO_2 in suspension leads to effective surface area decreased and furthers its catalytic efficiency reduction. Furthermore, a filtration step after photocatalytic reaction is required because of TiO_2 suspension. Attempts have been made to immobilize TiO_2 on different supports like zeolites [22], clays [23], fiberglass [24], activated carbon [25], and carbon nanotube [26]. Incorporation of adsorbent into TiO_2 has been considered a practical way to enhance the activity. It not only collects pollutants from dilute solution or open air to the vicinity active site of TiO_2, but also retains them to be degraded by additional illumination. Zeolites have high surface area and porous structure, which have been used as conventional adsorbents. The fine titanium oxide photocatalysts loaded on zeolite have opened possibilities for photocatalytic degradation of various organic pollutants with low concentration [27,28].

Herein, a novel approach for the synthesis of TiO_2/MoS_2@zeolite photocatalyst was developed by ultrasonic-assisted hydrothermal method using micro-MoS_2 as the photosensitizer. In this fabrication process, the formation method of TiO_2/MoS_2 contact interface use bulk MoS_2 as the substrate by chemical reaction and followed by in situ condensation load on the surface of zeolite, and the Z-scheme TiO_2/MoS_2 photocatalyst can be formed on the zeolite. The morphology, optical property and physical and chemical structures of TiO_2/MoS_2@zeolite nanocomposites were characterized. The photocatalytic activities of as-prepared photocatalyst were evaluated using degradation of methyl orange (MO) under visible-light irradiation. The photocatalytic degradation mechanism was also tentatively analyzed.

2. Experimental

2.1. Materials

All of the chemicals used for synthesis of the catalysts were of analytical grade and were used as-received without any further purification. Titanium tetrachloride ($TiCl_4$), molybdenum disulfide (MoS_2, 3 μm) and zeolite (20–40 mesh) were obtained from Tianjin Fuchen Chemical Reagent Factory (China); Degussa P25 was obtained from Evonik Industries (German); ethanol (C_2H_5OH) was obtained from Nanjing Chemical Reagent Co., Ltd. (China); both glycerol ($C_3H_8O_3$) and sodium hexametaphosphate ($(NaPO_3)_6$) were obtained from Tianjin Kemiou Chemical Reagent Co., Ltd. (China).

2.2. Fabrication of TiO_2/MoS_2@zeolite photocatalyst

First, 4 mL of titanium tetrachloride ethanol solution ($TiCl_4$, 2 mol/L) and certain MoS_2 powders was added to a beaker, and the homogeneous dispersion solution was obtained by ultrasound method for 10 min at room temperature. Then, 5.6 mL glycerol aqueous solution containing certain dispersant as hydrolytic agent was added to the dispersion, and the TiO_2–MoS_2 vitreosol was obtained. Subsequently, the obtained solution vitreosol and certain zeolite (based on mass ratio of (TiO_2–MoS_2)/zeolite) were transferred into 25 mL stainless steel autoclave. The hydrothermal synthesis was performed at 413 K for 3 h. TiO_2/MoS_2@zeolite

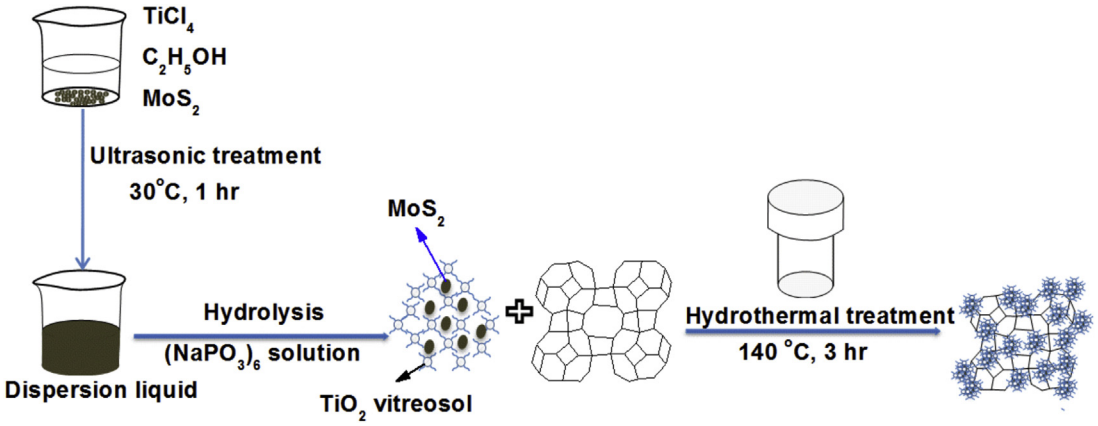

Fig. 2. Schematic illustration for the preparation of TiO_2/MoS_2@zeolite photocatalyst.

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