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Article (Special Issue on Photocatalysis in China)

Photocatalytic degradation of sulfamethazine by graphitic carbon nitride-modified zinc molybdate: Effects of synthesis method on performance, degradation kinetics, and mechanism

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ARTICLE INFO

Article history:

Received 11 September 2017

Accepted 19 October 2017

Published 5 December 2017

Keywords:

Zinc molybdate

Graphitic carbon nitride

Photocatalysis

Sulfamethazine

Water treatment

ABSTRACT

In the present study, zinc molybdate (β -ZnMoO₄) and graphitic carbon nitride (g-C₃N₄)-modified β -ZnMoO₄ (β -ZnMoO₄/g-C₃N₄) were prepared to decontaminate aqueous solutions from the antibiotic sulfamethazine (SMZ). Our results revealed that the hydrothermal synthesis method greatly influenced the photocatalytic activity of the resultant catalysts. The pristine β -ZnMoO₄ samples obtained under more intensive synthesis conditions (24 h at 280 °C) showed higher photocatalytic activity than that prepared for 12 h at 180 °C (denoted β -ZnMoO₄-180). In the case of in situ hydrothermal synthesis of β -ZnMoO₄/g-C₃N₄, a surface-modified sample was only obtained under the reaction conditions of 180 °C for 12 h. Compared with the sheet-like β -ZnMoO₄-180 sample, the β -ZnMoO₄-180/g-C₃N₄ composite showed enhanced photocatalytic activity for the degradation of SMZ. By contrast, the hydrothermal reaction at 280 °C caused the gradual decomposition of g-C₃N₄. It is believed that the structural incorporation of g-C₃N₄ into β -ZnMoO₄ at 280 °C might disrupt the crystal growth, thereby deteriorating the performance of the composite catalysts formed at this temperature. For the composite catalysts prepared by the ultrasonic method, a remarkable increase in the degradation rate of SMZ was only observed at a high g-C₃N₄ content of 8 mol%. The photocatalytic degradation of SMZ by β -ZnMoO₄-180/g-C₃N₄ composite catalysts followed pseudo-first-order kinetics. Further study of the photocatalytic mechanism revealed that holes and superoxide radicals were the dominant oxidative species in the photodegradation process. The enhanced photocatalytic performance of the composites was attributed to the higher separation efficiency of the photogenerated electron-hole pairs at heterogeneous junctions. The degradation intermediates of SMZ were detected by liquid chromatography-mass spectrometry, from which plausible reaction pathways for the photodegradation of SMZ were proposed. Our results indicated that the synthesis method for g-C₃N₄ composites should be carefully selected to achieve superior photocatalytic performance.

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This work was supported by the National Natural Science Foundation of China (51778505) and the grants from Hubei Province of China (Special Grant for Technological Innovation [2016ACA162], and the Natural Science Foundation, 2015CFA017).

DOI: 10.1016/S1872-2067(17)62935-8 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 12, December 2017

1. Introduction

In the past several decades, the use of molybdates as functional materials has been attracting great attention because of their favorable properties and complex chemistry. A variety of molybdates have been synthesized for different purposes. For example, divalent transition metal molybdates NiMoO_4 and CoMoO_4 demonstrated excellent good rate capability and high specific capacitances when used as electrodes for electrochemical capacitors [1,2]. Meanwhile, divalent metal molybdates with the general formula MMoO_4 ($\text{M} = \text{Ca}, \text{Mg}, \text{Zn}$) are semiconductors that have drawn considerable interest because of their potential applications in luminescence, catalysis, capacitors, and scintillation detectors [3–5]. Among divalent metal molybdates, the synthesis and use of zinc molybdates are attractive because zinc cations are recognized as ‘inorganic nodes’ for the design of porous inorganic compounds and metal semiconductors [6]. Zinc molybdates possess complex structures and their general chemical formula can be expressed as $n\text{ZnO} \cdot m\text{MoO}_3$ ($n = 3, 2$, or 1 and $m = 2, 3$, or 1), in which the molybdenum cation has a valence of $+6$ or $+4$. Compounds with different stoichiometric ratios, including ZnMoO_4 , $\text{Zn}_2\text{Mo}_3\text{O}_8$, and $\text{Zn}_3\text{Mo}_2\text{O}_9$, have also been reported [7]. In particular, ZnMoO_4 crystals show similarities with Aurivillius-type compounds, and have different crystalline phases, such as $\alpha\text{-ZnMoO}_4$ (JCPDS No. 35-0765), $\beta\text{-ZnMoO}_4$ (JCPDS No. 25-1024), and $\text{ZnMoO}_4 \cdot 0.8\text{H}_2\text{O}$ (JCPDS No. 25-1025). Among the three phases, $\alpha\text{-ZnMoO}_4$ has a triclinic structure and is characterized by the structural group $[\text{ZnO}_6/\text{MoO}_4]$ with tetrahedral MoO_4^{2-} anions. The other two phases possess monoclinic structures described by distorted $[\text{ZnO}_6]/[\text{MoO}_6]$ groups with octahedral MoO_6^{6-} anions [8]. These materials are semiconducting; triclinic $\alpha\text{-ZnMoO}_4$ was reported to have a bandgap of 3.3 eV, while monoclinic $\beta\text{-ZnMoO}_4$ was characterized with bandgaps of around 3.13–3.51 eV [9] and 2.74–2.85 eV [8]. To date, ZnMoO_4 has been used to effectively treat methyl orange [10], Victoria blue R, and phenol [8] under visible or ultraviolet (UV) light.

China has the largest source of molybdenum in the world (>19.6 Mt) [11]. The vast majority of the molybdenum is used in the production of high-strength steels employed in bridges, power plants, and pipelines. An alternative value-added use of molybdenum is in decontamination materials. In the present study, $\beta\text{-ZnMoO}_4$ and graphitic carbon nitride ($\text{g-C}_3\text{N}_4$)-modified $\beta\text{-ZnMoO}_4$ are synthesized to explore the feasibility of using these materials for the photocatalytic degradation of organic pollutants. We combine $\beta\text{-ZnMoO}_4$ with $\text{g-C}_3\text{N}_4$ because it is a low-cost light-active material that has been reported to enhance the photocatalytic performance of composites via a type II or Z-scheme mechanism [12]. Meanwhile, $\text{g-C}_3\text{N}_4$ itself is a photocatalyst that is responsive to visible light. The introduction of $\text{g-C}_3\text{N}_4$ to $\beta\text{-ZnMoO}_4$ may improve the photocatalytic performance of the resulting $\text{ZnMoO}_4/\text{g-C}_3\text{N}_4$ composite in the visible light region via the formation of heterogeneous junctions. Multiple approaches to synthesize $\text{g-C}_3\text{N}_4$ composites have been reported, including in situ hydrothermal treatment [13–16], ultrasonication [17–20], one-step heating

[21–28], and precipitation [29,30]. Han *et al.* [31] prepared $\text{g-C}_3\text{N}_4$ -hybridized TiO_2 nanofibers by an electrospinning process combined with a heat-etching method. Liao and colleagues fabricated a graphene oxide/ $\text{g-C}_3\text{N}_4$ composite photocatalyst using a sonochemical approach [19]. Although various $\text{g-C}_3\text{N}_4$ -based composites have been prepared by the above-mentioned methods, few studies have investigated the effect of the synthesis method on the performance of the resulting materials.

Therefore, in the present study, we use different methods to synthesize composite catalysts, and explore the effect of synthesis method on the performance of catalysts in which $\beta\text{-ZnMoO}_4$ and $\text{g-C}_3\text{N}_4$ serve as the host material and dopant material, respectively. Sulfamethazine (SMZ), as one of the most commonly used antibiotics, is selected as a model pollutant because of its presence in natural water streams and adverse effects on living beings [32,33]. The performance of the composite photocatalysts is tested by SMZ degradation experiments. The kinetics and degradation pathways of SMZ over the course of degradation are accordingly studied. We hope that this study will not only deepen our understanding of ZnMoO_4 -based photocatalysts, but also give clues to find simple and effective strategies to obtain high-performance composite photocatalysts.

2. Experimental

2.1. Chemicals

Analytical-grade chemicals including zinc nitrate hexahydrate, sodium molybdate dihydrate, *p*-benzoquinone (BQ), triethanolamine (TEOA), sodium azide (NaN_3), *t*-butanol (TBA), formic acid, and ethanol, along with methanol (high-performance liquid chromatography (HPLC) grade) were all purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. Melamine (99%) and SMZ (99%) were purchased from Shanghai Aladdin Industrial Corporation. Ultrapure water was used throughout this work.

2.2. Catalyst preparation

$\beta\text{-ZnMoO}_4$ powder was synthesized by hydrothermal reaction under various conditions [8]. For the $\beta\text{-ZnMoO}_4$ powder obtained at 180 °C (denoted $\beta\text{-ZnMoO}_4\text{-180}$), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ with a molar ratio of 1:1 were used as the starting materials, which were separately dissolved in ultrapure water and then mixed under constant stirring. The mixture was transferred to a Teflon-lined autoclave and heated at 180 °C for 12 h. The crude powder was collected, washed with water and ethanol several times, and then dried at 60 °C for 12 h to give $\beta\text{-ZnMoO}_4\text{-180}$. For the $\beta\text{-ZnMoO}_4$ powder obtained at 280 °C ($\beta\text{-ZnMoO}_4\text{-280}$), a 1:2 molar ratio of Mo to Zn was used and the hydrothermal conditions were 280 °C for 24 h. We obtained $\text{g-C}_3\text{N}_4$ by a thermal polycondensation process in a tube furnace [34]. The precursor melamine powder was transferred into a ceramic crucible and heated at a rate of 5 °C/min to 300 °C for 2 h; further deammoniation treatment

was subsequently performed at 520 °C for 2 h.

The g-C₃N₄-modified ZnMoO₄ (β-ZnMoO₄/g-C₃N₄-X%) samples were prepared by in situ hydrothermal synthesis. In this case, g-C₃N₄ powder was added to the Na₂MoO₄ solution with a g-C₃N₄/Mo molar ratio of 1:100, 2:100, 3:100, 4:100, 5:100, or 8:100, and then the subsequent steps were the same as those used to synthesize β-ZnMoO₄. In addition, β-ZnMoO₄/g-C₃N₄-X%-U samples were also prepared by an ultrasonication method. An appropriate amount of g-C₃N₄ was completely dispersed in methanol assisted by ultrasonication. The as-prepared β-ZnMoO₄ powder was subsequently added and the mixture was stirred in a fume hood for 24 h. The resulting powder was collected by centrifugation and then dried at 60 °C for 12 h.

2.3. Photocatalytic degradation of SMZ

The photocatalytic experiments were carried out under the irradiation of an 18-W light-emitting diode (LED). The central wavelength of the LED was 380 nm, and it was placed at the bottom of a double-jacketed glass reactor. A given amount of catalyst (100 mg) was added to SMZ aqueous solution (200 mL, 2 mg/L), and the mixture was mechanically stirred at 25 °C. Prior to irradiation, the mixture was constantly stirred under dark conditions for 30 min to ensure the adsorption equilibrium was reached. At specific time intervals, 2 mL aliquots were withdrawn. To remove the particles, each sample was filtered through a 0.45 μm filter. To investigate the photodegradation mechanism, inhibition tests were carried out using different radical scavengers. BQ (0.2 mmol/L), TBA (0.2 mol/L), NaN₃ (0.012 mol/L), and TEOA (0.1 mol/L) were used as scavengers for superoxide radicals ($\bullet\text{O}_2^-$), hydroxyl radicals ($\bullet\text{OH}$), singlet oxygen ($^1\text{O}_2$), and holes (h^+), respectively [22].

2.4. Characterization and analytical methods

Phase identification of samples was conducted by X-ray diffraction (XRD; Shimadzu X-ray 6000). The morphologies of samples were obtained by field-emission scanning electron microscope (FE-SEM; Zeiss SIGMA) and transmission electron microscopy (TEM; JEOL JEM-2010). Fourier transform infrared (FTIR) spectra were acquired by a Nicolet Avatar 360 spectrometer with KBr pellets in the 4000–400 cm⁻¹ region. Specific surface areas were determined with the Brunauer-Emmett-Teller (BET) equation using an adsorption apparatus (Micromeritics ASAP2460, USA). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific Escalab 250Xi spectrometer. The granulometric distribution of each sample was determined by a particle size analyzer (Microtrac S3500). UV-vis diffuse reflection spectroscopy (DRS) was performed on a Shimadzu UV-2550 spectrophotometer using BaSO₄ as the reference. The concentration of ammonia nitrogen (NH₄⁺-N) in each sample was measured by Nessler's reagent spectrophotometry. The Mott-Schottky analysis and electrochemical impedance spectroscopy (EIS) were performed with a three-electrode configuration in 0.1 mol/L Na₂SO₄ solutions, with a saturated calomel electrode (SCE) as the reference

electrode. For these measurements, working electrodes were prepared by mixing and kneading the as-prepared catalysts with acetylene black (8:1) and binder (polytetrafluoroethylene, 35 wt%) along with several drops of ethanol. The resulting slurry was rolled into film using a rolling machine. The film was cut into a square (1×1 mm), which was then pressed onto a titanium mesh. Measurements were performed on an electrochemical workstation (CHI-660b, Shanghai Chenhua Co., Ltd, China).

The degradation products of SMZ were determined by HPLC (LC-15C, Shimadzu) using a system equipped with a UV absorbance detector. HPLC was conducted on a C18 reversed-phase column using a mobile phase of 30:70 methanol:water (containing 0.1% formic acid), with a flow rate of 1 mL/min, and detection wavelength of 270 nm. The identification of intermediates was performed by liquid chromatography-mass spectrometry (LC-MS; Agilent 6460 triple quadrupole mass spectrometer) with an electrospray ionization source. A reversed-phase column (Agilent Eclipse Plus C18) was used with a flow rate of 0.3 mL/min, and the elution was accomplished with 20:80 methanol:water (containing 0.1% formic acid). The total organic carbon (TOC) decay of solutions was determined on an Elementar Vario TOC analyzer. The inorganic ions in the solutions during photocatalytic degradation were measured by ion chromatography (Metrohm 930).

3. Results and discussion

3.1. Materials characterization

Fig. 1(a) presents the XRD patterns of ZnMoO₄ crystals prepared under different conditions. All peaks were indexed to the crystalline structure of β-ZnMoO₄ (JCPDS No. 25-1024) [8]. No diffraction peaks from other crystalline phases were detected, indicating that β-ZnMoO₄ of good quality was successfully synthesized by the two hydrothermal procedures used. Fig. 1(b) shows the XRD patterns of the β-ZnMoO₄/g-C₃N₄ composites prepared with different g-C₃N₄/Mo molar ratios. The pure g-C₃N₄ sample presented two obvious peaks consistent with g-C₃N₄. The (002) peak was typical of interplanar stacking in conjugated aromatic systems, and the other one at 13° (100) was associated with the in-plane structural packing motif of the tri-s-triazine units [35]. For the β-ZnMoO₄-180/g-C₃N₄ composites, the main peak at 27.5° from g-C₃N₄ was observed, and the intensities of the peaks increased with the g-C₃N₄/Mo ratio. Compared with that of the pristine g-C₃N₄, the main (002) peak of g-C₃N₄ in the composite shifted slightly (by 0.3°), indicating the interlayer spacing decreased. This observation was also reported by other scholars [31]; a plausible reason for this phenomenon is that the interaction of g-C₃N₄ with ZnMoO₄ influences its interplanar spacing.

SEM images of the samples revealed that the β-ZnMoO₄-180 sample produced using a 1:1 Mo/Zn molar ratio had a sheet-like structure, and the sheets further assembled into flower-like shapes (Fig. 2(a)). Meanwhile, β-ZnMoO₄-280 prepared with a 1:2 Mo/Zn molar ratio has an irregular shape with larger corners (Fig. 2(d)), which is similar to the morphology of

Fig. 1. XRD patterns of ZnMoO₄ crystals prepared under different hydrothermal conditions (a) and g-C₃N₄-modified ZnMoO₄ prepared by in situ hydrothermal synthesis (b).

Fig. 2. SEM images, SAED patterns, and HRTEM images of β -ZnMoO₄-180 (a–c), β -ZnMoO₄-280 (d–f), and g-C₃N₄ (g, h).

β -ZnMoO₄ crystals reported by Jiang *et al.* [8]. The different initial contents of the starting materials and the varied hydrothermal conditions affected the rate and direction of crystal growth in the samples, leading to the formation of β -ZnMoO₄ crystals with dissimilar morphologies. In addition, the surfaces of these microcrystals are very smooth, with low BET surface areas of 0.883 m²/g for β -ZnMoO₄-180 and 0.491 m²/g for β -ZnMoO₄-280. Fig. 2(b) and (c) show a selected-area electron diffraction (SAED) pattern and high-resolution transmission electron microscopy (HRTEM) image of the β -ZnMoO₄-180 sample, respectively. The lattice spacings in Fig. 2(c) are 0.56, 0.47, and 0.34 nm, which correspond to the lattice spacings of the (010), (100), and (110) planes of the β -ZnMoO₄ crystals,

respectively. The corresponding SAED pattern demonstrates that the β -ZnMoO₄-180 sample is monocrystalline. The SAED pattern of β -ZnMoO₄-280 (Fig. 2(e)) indicates this sample has a polycrystalline nature, and its HRTEM image (Fig. 2(f)) has lattice spacings of 0.36, 0.24, and 0.23 nm, corresponding to the lattice spacings of the (110), (002), and (200) planes, respectively. These results are in good accordance with those of the XRD pattern in Fig. 1(a). Fig. 2(g) and (h) show the morphology of the g-C₃N₄ prepared in this study. The pristine g-C₃N₄ existed in the form of small lumps, and its lamellar structure can be observed. This kind of structure makes g-C₃N₄ easy to split into smaller blocks during ultrasonication.

Fig. 3 illustrates the morphologies of g-C₃N₄-modified

Fig. 3. SEM images of β -ZnMoO₄-180/g-C₃N₄-2% (a), β -ZnMoO₄-180/g-C₃N₄-2%-U (b), β -ZnMoO₄-180/g-C₃N₄-5% (c), β -ZnMoO₄-180/g-C₃N₄-5%-U (d), β -ZnMoO₄-280/g-C₃N₄-2% (e) and β -ZnMoO₄-280/g-C₃N₄-2%-U (f).

β -ZnMoO₄ prepared with different methods. For the samples prepared by the in situ hydrothermal method (Fig. 3(a), (c), and (e)), g-C₃N₄ particles were successfully loaded onto the surface of β -ZnMoO₄-180, whereas no g-C₃N₄ particles were observed for the β -ZnMoO₄-280/g-C₃N₄ sample. The FTIR spectra (see Fig. S1 in Supporting Information (SI)) of the β -ZnMoO₄-280/g-C₃N₄ samples also suggested that no g-C₃N₄ could be detected on the surface of the β -ZnMoO₄-280 crystals. This result is contradictory to the results of XRD in Fig. 1(b), in which the β -ZnMoO₄-280/g-C₃N₄ sample showed the characteristic peak of g-C₃N₄ at 27.5°. This observation suggests that the detected g-C₃N₄ might be incorporated into the structure of the composite, rather than modifying its surface. For the composites prepared by the ultrasonic method (Fig. 3(b), (d), and (f)), g-C₃N₄ particles were observed on the surface of the β -ZnMoO₄ crystals, and the loading of g-C₃N₄ particles increased with the g-C₃N₄/Mo ratio. This experimental result suggests that the g-C₃N₄ particles can attach to the surface of β -ZnMoO₄ crystals through the ultrasonic method. Therefore, extra experiments were carried out to examine why g-C₃N₄ was not observed on the β -ZnMoO₄-280/g-C₃N₄ sample. Fig. S2 in the SI shows the concentrations of NH₄⁺-N in the solutions after the hydrothermal treatment of g-C₃N₄ suspension for different periods. The inset in Fig. S2 reveals that suspended g-C₃N₄ par-

ticles still existed in the solution after treatment at 280 °C for 0.5 h, and the solution became clear after treatment for 1 h. Meanwhile, the NH₄⁺-N concentration in the solutions increased, indicating some of the nitrogen in g-C₃N₄ was converted into dissolved NH₄⁺-N. The inset proves that during hydrothermal treatment at 280 °C, the decomposition of g-C₃N₄ particles progressed. Some of the particles might be incorporated into β -ZnMoO₄ crystals in the early stage of the hydrothermal process, while the rest of the g-C₃N₄ particles eventually decomposed, preventing the existence of surface-attached g-C₃N₄ particles. This may explain why the characteristic diffraction peak of g-C₃N₄ was observed in the XRD pattern of the β -ZnMoO₄-280/g-C₃N₄ sample (Fig. 1(b)), but g-C₃N₄ particles were not observed on the surface of the samples in the SEM images (Fig. 3(e)).

XPS analysis was used to investigate the chemical composition of the as-prepared β -ZnMoO₄ and β -ZnMoO₄/g-C₃N₄ composites. As shown in Fig. 4, the spin-orbit splitting of the Mo 3d level gave rise to 3d_{5/2} and 3d_{3/2} levels with an energy separation of 3.2 eV, and the binding energies of 232.6 and 235.8 eV corresponded to Mo 3d_{5/2} and Mo 3d_{3/2}, respectively. The Mo 3d_{5/2} peak revealed that Mo possessed a hexavalent oxidation state and the Zn 2p_{3/2} peak at 1021.3 eV revealed Zn had a divalent oxidation state [36]. The characteristic binding energy of 530.1 eV for O 1s revealed O was present as a metal oxide. Regarding the g-C₃N₄-modified β -ZnMoO₄ prepared by the in situ hydrothermal synthesis method, there was no evident difference between the binding energies of Zn, Mo, and O with or without g-C₃N₄. In Fig. 4(c) and (d), the small deviation of Mo 3d and O 1s may be caused by the different experimental conditions. Jiang *et al.* [8] reported a similar observation in their XPS analysis of different β -ZnMoO₄ samples.

The particle size distribution curves of β -ZnMoO₄ with different morphologies are shown in Fig. 5. Based on the distribution curves, the β -ZnMoO₄ samples prepared under different hydrothermal reaction conditions with flower-like and irregular shapes possessed very similar average particle sizes (*D*₅₀) of 15.02 and 17.80 μm, respectively. Finer particles were found for the β -ZnMoO₄-280 sample, as can also be observed in the SEM images (Fig. 2). The β -ZnMoO₄-180 sample had a narrower size distribution than that of β -ZnMoO₄-280 because of its more regular sheet-like structure.

3.2. Removal of SMZ by photocatalytic degradation

The adsorption and photodegradation of SMZ by pristine β -ZnMoO₄ samples were studied. Fig. 6(a) reveals that the two kinds of β -ZnMoO₄ show very weak capability to uptake SMZ in the dark. The small BET surface area of the β -ZnMoO₄ particles explains their poor SMZ adsorption ability. Fig. 6(b) shows the photocatalytic activities of the β -ZnMoO₄ and g-C₃N₄ particles for SMZ degradation. After irradiation for 3 h, the degradation efficiencies of the β -ZnMoO₄-180 sample with flower-like morphology, β -ZnMoO₄-280 crystals with irregular corners, and g-C₃N₄ were 71%, 93%, and 100%, respectively. With increasing reaction temperature and time, the crystallinity of β -ZnMoO₄ increased and its defect content decreased, leading

Fig. 4. XPS analysis of the β -ZnMoO₄ and β -ZnMoO₄/g-C₃N₄-2% samples. β -ZnMoO₄-180 (1); β -ZnMoO₄-280 (2); β -ZnMoO₄-180/g-C₃N₄-2% (3); and β -ZnMoO₄-280/g-C₃N₄-2% (4).

Fig. 5. Particle size distributions of the pristine β -ZnMoO₄ samples. β -ZnMoO₄-180 (a); β -ZnMoO₄-280 (b).

to the enhanced photocatalytic activity of the β -ZnMoO₄-280 sample over that of β -ZnMoO₄-180 [8,37–39].

The photocatalytic activities of the β -ZnMoO₄/g-C₃N₄ composites are presented in Fig. 6(c) and (d). The photocatalytic degradation of SMZ by the composites follows pseudo-first-order kinetics. In the case of g-C₃N₄-modified

β -ZnMoO₄-180 (Fig. 6(c)), the photodegradation experiments revealed that this composite showed higher photocatalytic activity than that of β -ZnMoO₄-180. When the g-C₃N₄/Mo ratio was 3:100, the maximum photodegradation rate was achieved. Fig. 6(d) illustrates that the β -ZnMoO₄-280/g-C₃N₄ composites showed lower photocatalytic activities than that of

Fig. 6. Adsorption (a) and photocatalytic degradation (b) of SMZ by β -ZnMoO₄. The photocatalytic degradation of SMZ by β -ZnMoO₄-180/g-C₃N₄ (c), β -ZnMoO₄-280/g-C₃N₄ (d), β -ZnMoO₄-180/g-C₃N₄-U (e), and β -ZnMoO₄-280/g-C₃N₄-U (f). For (e) and (f), the photocatalytic experiments were performed by adding 200 mg of catalyst to 200 mL of SMZ solution.

β -ZnMoO₄-280; namely, the introduction of g-C₃N₄ lowered the performance of this catalyst. Fig. 6(e) and (f) show the photocatalytic activities of β -ZnMoO₄ and g-C₃N₄-modified β -ZnMoO₄ photocatalysts prepared by the ultrasonic method. With increasing g-C₃N₄ content, the photodegradation abilities of the two kinds of β -ZnMoO₄ improved slightly. For the β -ZnMoO₄-180/g-C₃N₄-U samples (Fig. 6(e)), considerably enhanced degradation of SMZ was only observed for the composite sample with 8% g-C₃N₄. For the β -ZnMoO₄-280 samples (Fig. 6(f)), modification with g-C₃N₄ by the ultrasonic method only weakly influenced the photocatalytic degradation of SMZ. The above results reveal that all the surface-modified β -ZnMoO₄/g-C₃N₄ samples were better than the pristine β -ZnMoO₄ samples at SMZ photodegradation. In particular, the β -ZnMoO₄-180/g-C₃N₄ sample with 3% g-C₃N₄ prepared by the in situ hydrothermal method exhibited high photodegradation efficiency, indicating this synthesis method allowed good bonding between the β -ZnMoO₄ and g-C₃N₄ particles. Retardation of photoactivity following g-C₃N₄ addition was only found for the β -ZnMoO₄-280/g-C₃N₄ sample prepared by the in-situ hydrothermal method. Different from the surface-attached g-C₃N₄, the structural incorporation of g-C₃N₄ into β -ZnMoO₄-280 may decrease its crystallinity, resulting in its poor photocatalytic activity.

The growth mechanism of the β -ZnMoO₄ and β -ZnMoO₄/g-C₃N₄ composites synthesized by the hydrothermal method are shown in Fig. 7. The growth of zinc molybdate crystals mainly involves the following stages [8,40]: (a) nucleation of the first clusters or nuclei, (b) self-assembly of small crystallites, and (c) crystal growth. The electrostatic attraction

between Zn²⁺ and MoO₄²⁻ promotes the nucleation process that produces the initial β -ZnMoO₄ precipitates or nuclei. The hydrothermal conditions increase the effective collision frequency of the nanoparticles in the suspension. At a reaction temperature of 180 °C, the nanoparticles aggregate to form plate-like β -ZnMoO₄ microcrystals. At 280 °C, the intensified self-aggregation of particles compared with that at 180 °C resulted in the formation of β -ZnMoO₄ microparticles with irregular shape. When using the in situ hydrothermal method to synthesize the g-C₃N₄-modified β -ZnMoO₄ composites, temperature-dependent results were obtained because of the different

Fig. 7. Schematic illustration of the growth mechanism of β -ZnMoO₄ and β -ZnMoO₄/g-C₃N₄ composites prepared by the hydrothermal method.

growth pathways of β -ZnMoO₄ crystals at different temperatures. While g-C₃N₄ bound to the surface of flower-like β -ZnMoO₄-180, it was included inside the β -ZnMoO₄-280 crystals of the β -ZnMoO₄-280/g-C₃N₄ sample. The structural incorporation of g-C₃N₄ into the composite may lower the crystallinity of β -ZnMoO₄-280, resulting in its decreased photodegradation ability.

3.3. Photodegradation mechanism of SMZ

To elucidate the photodegradation mechanism of SMZ by β -ZnMoO₄ and the β -ZnMoO₄/g-C₃N₄ composites, photocatalytic experiments were carried out in the presence of different radical scavengers (Fig. 8). First, TBA, a widely used $\bullet$ OH scavenger, was added to investigate whether it affected the degradation of SMZ. For both β -ZnMoO₄-180 and β -ZnMoO₄-180/g-C₃N₄ samples, TBA caused only a slight decrease of photocatalytic ability. When a scavenger for $^1\text{O}_2$ (NaN₃) was added to the photocatalytic experiments, similar results were obtained. These results indicated that $\bullet$ OH and $^1\text{O}_2$ were not the primary oxidative species in the photodegradation of SMZ. By contrast, the addition of TEOA or BQ markedly retarded SMZ photodegradation. TEOA and BQ are scavengers for h^+ and $\bullet\text{O}_2^-$, respectively, indicating that the photodegradation mechanism of the samples was mainly associated with h^+ and $\bullet\text{O}_2^-$.

UV-vis DRS of β -ZnMoO₄ are presented in Fig. 9(a). The absorption edge of ZnMoO₄ was in the visible region, corresponding to band gaps (E_g) of 3.078 eV for β -ZnMoO₄-180 and 3.038 eV for β -ZnMoO₄-280. The conduction band (CB) of the β -ZnMoO₄ samples was determined by Mott-Schottky analysis. As shown in Fig. 9(b), the flat-band (FB) potential of β -ZnMoO₄-180 was estimated to be -1.08 V vs. SCE, and the positive slope of this linear plot suggests the n-type character of this sample. It has been reported that the CB potentials of n-type semiconductors are 0.1–0.2 V more negative than their FB potential [41]. Assuming that the CB edge is 0.1 V more negative than the FB potential, the estimated CB edge for β -ZnMoO₄-180 is -1.18 V vs. SCE (-0.94 V vs. normal hydrogen

electrode (NHE)), and the estimated valence band (VB) is 1.90 V vs. SCE (2.14 V vs. NHE). Likewise, the estimated CB edge for β -ZnMoO₄-280 is -1.27 V vs. SCE (-1.03 V vs. NHE), and its VB is 1.77 V vs. SCE (2.01 V vs. NHE). UV-vis DRS and Mott-Schottky plots for g-C₃N₄ are shown in Fig. S3 and S4 in the SI; its determined CB and VB positions are -1.04 and 1.77 V vs. NHE, respectively. The band structures of β -ZnMoO₄ and g-C₃N₄ are summarized in Fig. 9(c).

The EIS analysis of β -ZnMoO₄-180 and β -ZnMoO₄-180/g-C₃N₄-3% was performed to investigate the effect of g-C₃N₄ modification on electrode behavior. Generally, a smaller arc size in a Nyquist plot indicates lower charge transfer resistance on an electrode surface [15,42]. The arc radius of the Nyquist plot of β -ZnMoO₄-180/g-C₃N₄-3% was smaller than that of the β -ZnMoO₄-180 sample under illumination (Fig. S5 in the SI), suggesting that the separation and transfer efficiency of photoinduced electron-hole pairs was increased through an interfacial interaction between β -ZnMoO₄-180 and g-C₃N₄ particles in the composite. The proposed photocatalytic degradation process of the β -ZnMoO₄/g-C₃N₄ composite is illustrated in Fig. 9(c). The difference of chemical potential between the two semiconductor units results in band bending at the heterogeneous interface in the composite. This band bending induces a built-in electric field, which can drive the migration of photo-generated electrons and holes in opposite directions. Under illumination, photogenerated holes would form when electrons were excited from the VB to the CB of both β -ZnMoO₄ and g-C₃N₄. The photogenerated electrons in g-C₃N₄ could easily migrate to the β -ZnMoO₄ surface. The CB potential of β -ZnMoO₄ is more negative than the redox potential of the $\text{O}_2/\bullet\text{O}_2^-$ couple (-0.33 eV vs. NHE), which can produce $\bullet\text{O}_2^-$ radicals from dissolved O_2 . At the same time, the holes generated in the VB of β -ZnMoO₄ could migrate to g-C₃N₄. However, the VB potential of g-C₃N₄ is more negative than the redox potential of the $\bullet\text{OH}/\text{OH}^-$ couple (1.99 eV vs. NHE), thus it cannot lead to the production of $\bullet\text{OH}$ from the holes [13], which was also demonstrated in the photocatalytic experiments with radical scavengers (Fig. 8(b)). Therefore, the heterogeneous interface in the β -ZnMoO₄/g-C₃N₄ composite markedly promoted the separa-

Fig. 8. Inhibition effect of different radical scavengers on the photodegradation of SMZ by β -ZnMoO₄-180 (a) and β -ZnMoO₄-180/g-C₃N₄-2% (b).

Fig. 9. UV-vis diffuse reflectance spectra of β -ZnMoO₄ (a); Mott-Schottky plots for β -ZnMoO₄ (b); Energy levels of the β -ZnMoO₄ and g-C₃N₄ samples (c).

tion of photogenerated electron-hole pairs, thereby improving its SMZ photodegradation efficiency. For the β -ZnMoO₄-180/g-C₃N₄ samples, the in situ hydrothermal synthesis ensured favorable bonding between the g-C₃N₄ particles and β -ZnMoO₄-180 sheets. As a result, the highest degradation efficiency of SMZ was observed for the composite with 3% g-C₃N₄ (Fig. 6(c)). By contrast, for the samples prepared by the ultrasonic method, the bonding of the g-C₃N₄ particles on the surface of the β -ZnMoO₄-180 sheets may be not as strong as that of the samples prepared by the in situ hydrothermal method. Therefore, a larger g-C₃N₄ content of 8% was needed to achieve an evident enhancement effect of g-C₃N₄ on SMZ degradation for composites prepared by the ultrasonic method.

3.4. Degradation pathway of SMZ

The photodegradation of SMZ and the formation of several intermediates were studied by LC-MS analysis. Fig. 10(a) shows the total ion chromatogram obtained after 60 min of photodegradation by β -ZnMoO₄-180/g-C₃N₄. In this study, a molecular ion peak at a mass-to-charge (m/z) of 279 was observed at 5.265 min, which was attributed to SMZ. Seven products with different m/z ratios, as indicated by peak A to H in Fig. 10a, were identified and are labeled in Table S1. Fig. 10(b) reveals

that the TOC content of the solution decreased by 20% after 9 h of photocatalytic degradation, which indicated that SMZ was mineralized; that is, inorganic ions such as SO₄²⁻ and NO₃⁻ may be generated as the final degradation products. The LC-MS analysis results confirmed that SO₄²⁻ and NO₃⁻ were present in the solution with concentrations of 1.575 and 0.175 mg/L, respectively, after 6 h of photocatalytic degradation.

A number of studies have determined that degradation of sulfonamides occurs through cleavage at various positions [43], as shown in Fig. 11. In this study, compound *d* (m/z = 215) was observed, which is most likely a product of -SO₂- extrusion (cleavage at the γ and δ positions in Fig. 11). Several possible pathways for the formation of extrusion products with m/z = 215 have been proposed [33,44,45]. Subsequently, the h⁺ and •O₂⁻ attacked the carbon-nitrogen bond between the benzene and pyrimidine rings in compound *d*, resulting in two products, *a* and *c* (Fig. 11), as also identified by Guo *et al.* [44]. The product with m/z = 265 identified at 1.245 min (compound *b*) and that with m/z = 239 identified at 2.326 min (compound *e*) correspond to products of amino group extrusion (cleavage at position β) or methyl group extrusion. Another pathway involves the benzene and pyrimidine rings of SMZ being attacked by reactive oxygen species to cause hydroxylation, which has been reported in other studies [33]. Moreover, the continuous

Fig. 10. TIC of SMZ after photodegradation for 1.5 h (a). Decrease of TOC in the solution during SMZ photodegradation (b). The initial concentration of SMZ was 10 mg/L. β -ZnMoO₄-180/g-C₃N₄-3% was used as the catalyst.

Fig. 11. Proposed pathways for SMZ photodegradation by the β -ZnMoO₄-180/g-C₃N₄-3% composite.

attack of the hydroxylated SMZ by reactive species results in the loss of an amino or methyl group, corresponding to the product with $m/z = 283$ (compound **f**). Intermediate **f** might also be formed by the hydroxylation of compound **b** with $\cdot\text{OH}$. Subsequently, these intermediates may decompose into smaller molecules, ending up as environmentally benign compounds, such as SO_4^{2-} and NO_3^- , which were detected by ion chromatography.

4. Conclusions

In summary, β -ZnMoO₄ catalysts with different morphologies were synthesized via the hydrothermal method. Both the in situ hydrothermal and ultrasonic methods were used to fabricate g-C₃N₄-modified β -ZnMoO₄ composites. Our results indicated that β -ZnMoO₄ microparticles with a unique microstructure were good platforms for the introduction of visible-light-responsive g-C₃N₄. The pristine β -ZnMoO₄-280 sample obtained showed higher photocatalytic activity than β -ZnMoO₄-180. In the case of β -ZnMoO₄-180/g-C₃N₄ composites, the surface-modified samples all showed enhanced photocatalytic activity relative to that of the pristine β -ZnMoO₄-180 sample. By contrast, the structural incorporation of g-C₃N₄ into β -ZnMoO₄ crystals prepared at 280 °C lowered their crystallinity, thereby deteriorating the performance of these composite catalysts. Study of the photocatalytic mechanism of the compo-

sites revealed that h^+ and $\cdot\text{O}_2^-$ were the dominant oxidative species in the SMZ photodegradation process. The enhanced photocatalytic performance of the composites was attributed to the higher separation efficiency of the photogenerated electron-hole pairs at their heterogeneous interfaces. Compared with the ultrasonic method, the hydrothermal synthesis at 180 °C resulted in a more favorable interaction between g-C₃N₄ and β -ZnMoO₄, and the optimal g-C₃N₄ content was 3%. SMZ was effectively photodegraded by the β -ZnMoO₄/g-C₃N₄ composites, and the degradation mechanism involved the extrusion of $-\text{SO}_2-$ and amino groups. This work highlights the importance of selecting an appropriate method to prepare composite photocatalytic materials based on g-C₃N₄. The abundant molybdenum resources in China may be used to prepare catalytic materials for various applications in environmental and energy fields.

References

- [1] L. Huang, W. Zhang, J. W. Xiang, H. H. Xu, G. L. Li, Y. H. Huang, *Sci. Rep.*, **2016**, 6, 31465.
- [2] Z. Q. Zhang, H. D. Zhang, X. Y. Zhang, D. Y. Yu, Y. Ji, Q. S. Sun, Y. Wang, X. Y. Liu, *J. Mater. Chem. A*, **2016**, 4, 18578–18584.
- [3] A. V. Veresnikova, B. K. Lubsandorzhiev, I. R. Barabanov, P. Grabmayr, D. Greiner, J. Jochum, M. Knapp, C. Osswald, R. V. Poleshuk, F. Ritter, B. A. M. Shaibonov, Y. E. Vyatchin, G. Meierhofer, *Nucl. Instrum. Methods in Phys. Res., Sect. A*, **2009**, 603, 529–531.

Graphical Abstract

Chin. J. Catal., 2017, 38: 2009–2020 doi: 10.1016/S1872-2067(17)62935-8

Photocatalytic degradation of sulfamethazine by graphitic carbon nitride-modified zinc molybdate: Effects of synthesis method on performance, degradation kinetics, and mechanismJing Zhang, Xuhui Mao *, Wei Xiao, Yanfeng Zhuang *
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$\beta\text{-ZnMoO}_4/\text{C}_3\text{N}_4$ composites were successfully synthesized via different methods. Surface modification of $\beta\text{-ZnMoO}_4$ with C_3N_4 resulted in enhanced photocatalytic activity, and this observation is attributed to the higher separation efficiency of photogenerated electron-hole pairs.

- [4] V. B. Mikhailik, H. Kraus, V. Kapustyanyk, M. Panasyuk, Y. Prots, V. Tsybul'skyi, L. Vasylechko, *J. Phys.*, **2008**, 20, 365219.
- [5] Y. Liang, P. Liu, H. B. Li, G. W. Yang, *Cryst. Growth Des.*, **2012**, 12, 4487–4493.
- [6] M. Grzywa, W. Łasocha, W. Surga, *J. Solid State Chemistry*, **2007**, 180, 1590–1594.
- [7] G. K. Zhang, S. J. Yu, Y. R. Yang, W. Jiang, S. M. Zhang, B. B. Huang, *J. Cryst. Growth*, **2010**, 312, 1866–1874.
- [8] Y. R. Jiang, W. W. Lee, K. T. Chen, M. C. Wang, K. H. Chang, C. C. Chen, *J. Taiwan Inst. Chem. Eng.*, **2014**, 45, 207–218.
- [9] Y. Keereeta, T. Thongtem, S. Thongtem, *Superlattices Microstruct.*, **2014**, 69, 253–264.
- [10] M. Ramezani, S. M. Hosseinpour-Mashkani, A. Sobhani-Nasab, H. Ghasemi Estarki, *J. Mater. Sci.*, **2015**, 26, 7588–7594.
- [11] Q. D. Zeng, J. M. Liu, K. Z. Qin, H. R. Fan, S. X. Chu, Y. B. Wang, L. L. Zhou, *Int. Geol. Rev.*, **2013**, 55, 1311–1358.
- [12] S. W. Cao, J. X. Low, J. G. Yu, M. Jaroniec, *Adv. Mater.*, **2015**, 27, 2150–2176.
- [13] S. W. Zhang, J. X. Li, M. Y. Zeng, G. X. Zhao, J. Z. Xu, W. P. Hu, X. K. Wang, *ACS Appl. Mater. Interfaces*, **2013**, 5, 12735–12743.
- [14] S. W. Liu, F. Chen, S. T. Li, X. X. Peng, Y. Xiong, *Appl. Catal., B*, **2017**, 211, 1–10.
- [15] S. L. Ma, S. H. Zhan, Y. N. Jia, Q. Shi, Q. X. Zhou, *Appl. Catal., B*, **2016**, 186, 77–87.
- [16] M. X. Ji, J. Di, Y. P. Ge, J. X. Xia, H. M. Li, *Appl. Surf. Sci.*, **2017**, 413, 372–380.
- [17] Y. J. Wang, Z. X. Wang, S. Muhammad, J. He, *CrystEngComm*, **2012**, 14, 5065–5070.
- [18] G. C. Bi, J. Q. Wen, X. Li, W. Liu, J. Xie, Y. P. Fang, W. W. Zhang, *RSC Adv.*, **2016**, 6, 31497–31506.
- [19] G. Z. Liao, S. Chen, X. Quan, H. T. Yu, H. M. Zhao, *J. Mater. Chem.*, **2012**, 22, 2721–2726.
- [20] D. L. Jiang, L. L. Chen, J. J. Zhu, M. Chen, W. D. Shi, J. M. Xie, *J. Chem. Soc., Dalton Trans.*, **2013**, 42, 15726–15734.
- [21] J. Xu, G. X. Wang, J. J. Fan, B. S. Liu, S. M. Cao, J. G. Yu, *J. Power Sources*, **2015**, 274, 77–84.
- [22] L. Pi, R. Jiang, W. C. Zhou, H. Zhu, W. Xiao, D. H. Wang, X. H. Mao, *Appl. Surf. Sci.*, **2015**, 358, 231–239.
- [23] Y. Z. Hong, C. S. Li, G. Y. Zhang, Y. D. Meng, B. X. Yin, Y. Zhao, W. D. Shi, *Chem. Eng. J.*, **2016**, 299, 74–84.
- [24] X. J. Bai, L. Wang, Y. J. Wang, W. Q. Yao, Y. F. Zhu, *Appl. Catal., B*, **2014**, 152, 262–270.
- [25] M. S. Akple, J. X. Low, S. Wageh, A. A. Al-Ghamdi, J. G. Yu, J. Zhang, *Appl. Surf. Sci.*, **2015**, 358, 196–203.
- [26] L. F. Cui, X. Ding, Y. G. Wang, H. C. Shi, L. H. Huang, Y. H. Zuo, S. F. Kang, *Appl. Surf. Sci.*, **2017**, 391, 202–210.
- [27] Q. Hao, S. M. Hao, X. X. Niu, X. Li, D. M. Chen, H. Ding, *Chin. J. Catal.*, **2017**, 38, 278–286.
- [28] J. Li, M. Zhang, Q. Y. Li, J. J. Yang, *Appl. Surf. Sci.*, **2017**, 391, 184–193.
- [29] J. G. Yu, S. H. Wang, B. Cheng, Z. Lin, F. Huang, *Catal. Sci. Technol.*, **2013**, 3, 1782–1789.
- [30] D. D. Tang, G. K. Zhang, *Appl. Surf. Sci.*, **2017**, 391, 415–422.
- [31] C. Han, Y. D. Wang, Y. P. Lei, B. Wang, N. Wu, Q. Shi, Q. Li, *Nano Res.*, **2015**, 8, 1199–1209.
- [32] S. Fukahori, T. Fujiwara, *J. Environ. Manage.*, **2015**, 157, 103–110.
- [33] S. Rafqah, Z. S. Seddigi, S. A. Ahmed, E. Danish, M. Sarakha, *J. Mass Spectrom.*, **2015**, 50, 298–307.
- [34] X. F. Li, J. Zhang, L. H. Shen, Y. M. Ma, W. W. Lei, Q. L. Cui, G. T. Zou, *Appl. Phys. A*, **2008**, 94, 387–392.

- [35] S. C. Yan, Z. S. Li, Z. G. Zou, *Langmuir*, **2009**, 25, 10397–10401.
- [36] D. C. Agarwal, D. K. Avasthi, S. Varma, F. Kremer, M. C. Ridgway, D. Kabiraj, *J. Appl. Phys.*, **2014**, 115, 163506.
- [37] M. Cerna, C. Guillard, E. Puzenat, M. Vesely, P. Dzik, *Int. J. Chem. Environ. Eng.*, **2011**, 2, 255–260.
- [38] P. Y. Dong, Y. H. Wang, B. Liu, L. N. Guo, Y. J. Huang, S. Yin, *Appl. Surf. Sci.*, **2012**, 258, 7052–7058.
- [39] T. Z. Liu, Y. Y. Li, H. Zhang, M. Wang, X. Y. Fei, S. W. Duo, Y. Chen, J. Pan, W. Wang, *Appl. Surf. Sci.*, **2015**, 357, 516–529.
- [40] L. S. Cavalcante, J. C. Sczancoski, M. Siu Li, E. Longo, J. A. Varela, *Colloids Surf., A*, **2012**, 396, 346–351.
- [41] S. Emin, M. de Respinis, T. Mavrič, B. Dam, M. Valant, W. A. Smith, *Appl. Catal., A*, **2016**, 523, 130–138.
- [42] B. C. Zhu, P. F. Xia, Y. Li, W. K. Ho, J. G. Yu, *Appl. Surf. Sci.*, **2017**, 391, 175–183.
- [43] Y. K. Liu, J. L. Wang, *J. Hazard. Mater.*, **2013**, 250–251, 99–105.
- [44] C. S. Guo, J. Xu, S. F. Wang, Y. Zhang, Y. He, X. F. Li, *Catal. Sci. Technol.*, **2013**, 3, 1603–1611.
- [45] M. Perisa, S. Babic, I. Skoric, T. Fromel, T. C. P. Knepper, *Environ. Sci. Pollut. Res.*, **2013**, 20, 8934–8946.

g-C₃N₄修饰β-ZnMoO₄光催化降解磺胺二甲嘧啶：合成方法的影响、降解动力学及机理

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摘要: 在过去几十年中, 钼酸盐在功能材料领域的应用备受关注。例如, 半导体材料二价金属钼酸盐MMoO₄ (M = Ca, Mg, Zn)在发光、催化、电容器、闪烁探测器等方面已有良好的应用。研究表明, 钼酸锌在紫外或可见光照射下能够有效降解甲基橙、维多利亚蓝、苯酚等污染物。中国拥有丰富的钼资源, 目前钼主要用于生产高强度钢。制备钼基高效除污除材料可作为钼资源的另一种高附加值利用模式。氮化碳(g-C₃N₄)作为一种低成本的光活性改性剂, 可提高半导体材料的光催化性能。迄今为止, 基于氮化碳复合材料的制备方法包括: 原位水热合成、超声波复合、一步升温合成和沉淀法等。然而, 很少讨论合成方法对复合材料性能的影响。本文以β-ZnMoO₄为主体材料, g-C₃N₄为修饰材料, 首次制备了两者复合的新型光催化剂。采用不同的方法和条件制备了β-ZnMoO₄和β-ZnMoO₄/C₃N₄复合材料, 探讨了合成方法对复合材料光催化性能的影响, 并进一步研究了材料光催化降解磺胺二甲嘧啶的动力学和降解途径。

以钼酸钠和硝酸锌为原料, 在不同温度和时间条件下, 采用水热法合成得到了两种不同形貌的β-ZnMoO₄材料。光催化降解实验结果显示, 水热合成条件对催化剂的光催化活性影响很大, 280 °C水热条件下维持24 h, 得到表面光滑的不规则微米颗粒(β-ZnMoO₄-280), 其光催化活性高于180 °C条件下获得的片状形貌的钼酸锌材料(β-ZnMoO₄-180)。β-ZnMoO₄/C₃N₄复合材料通过原位水热法和超声法合成, 结果显示, 原位水热合成条件下获得的β-ZnMoO₄-180/C₃N₄光催化剂对磺胺二甲嘧啶表现出显著增强的降解能力。相比之下, 在280 °C水热条件下, C₃N₄颗粒发生逐步分解, 且反应开始时C₃N₄颗粒会扰乱β-ZnMoO₄-280晶体生长的连续性, 使复合材料性能下降。对于超声法合成的β-ZnMoO₄/C₃N₄材料, 两种β-ZnMoO₄/C₃N₄复合材料的光催化活性均提高, 但提高程度不及水热法180 °C条件下制备的材料。结果表明, 对于光催化复合材料的制备, 要选择适当的合成方法, 才能得到高性能复合光催化材料, 本文采用180 °C的水热合成条件, 添加3% g-C₃N₄, 可得到性能最佳的β-ZnMoO₄-180/C₃N₄复合光催化剂。

添加自由基抑制剂的光催化降解实验结果表明, 超氧负离子(•O₂⁻)和空穴(h⁺)在降解中起主导作用。β-ZnMoO₄/C₃N₄复合材料光催化活性的增强归因于C₃N₄与β-ZnMoO₄之间形成异质结, 该异质结提高了光生电子-空穴对的分离效率。通过液相-质谱联用手段, 测定了磺胺二甲嘧啶降解的中间产物, 结果表明, 污染物的光催化降解途径主要包括脱氨基和脱甲基过程。

关键词: 钼酸锌; 石墨相氮化碳; 光催化; 磺胺二甲嘧啶; 水处理

收稿日期: 2017-09-11. 接受日期: 2017-10-19. 出版日期: 2017-12-05.

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基金来源: 国家自然科学基金(51778505); 湖北省技术创新重大专项(2016ACA162); 湖北省自然科学基金创新团队项目(2015CFA017).

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