Preparation of Sepiolite-Flower-like BiOCl Nanocomposites and Their Photocatalytic Performance Postprint

Authors: He Mingyi, Zhang Huan, Dai Yatang, Wang Wei, Luo Hongmei, Wang Tilong, Hu Xiaoping

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Abstract

BiOCl-sepiolite composite materials were prepared by loading BiOCl onto sepiolite via a hydrolysis precipitation method, and the effects of temperature, pH value, and Bi(NO3)3 dosage on the material morphology were investigated; using Rhodamine B as the target pollutant, the photocatalytic performance of the materials was explored. The results demonstrated that controlling temperature, pH value, and Bi(NO3)3 dosage enables the preparation of flower-like spherical BiOCl loaded materials. The BiOCl spheres were assembled from BiOCl nanosheets and uniformly dispersed within the sepiolite; the BiOCl spheres exhibited a 14.29%-16.67% improvement in photocatalytic efficiency compared to pure BiOCl, and possessed excellent cycling stability.

Full Text

Preamble

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Preparation and Photocatalytic Activity of Sepiolite/Flower-Like BiOCl Nanocomposites

HE Mingyi, ZHANG Huan, DAI Yatang, WANG Wei, LUO Hongmei, WANG Tilong, HU Xiaoping
School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang 621010, China

Abstract
Sepiolite/flower-like BiOCl nanocomposites were successfully prepared via a hydrolysis precipitation method, and the influence of temperature, pH, and

$Bi(NO_3)_3$ concentration on the morphology of the materials was investigated. Using rhodamine B as a target pollutant, the photocatalytic performance of the composites was evaluated. The results demonstrate that controlling temperature, pH, and $Bi(NO_3)_3$ dosage yields sepiolite-supported materials with flower-like BiOCl morphology. The BiOCl microspheres, assembled from BiOCl nanosheets, are uniformly dispersed throughout the sepiolite matrix. The composite material exhibits a photocatalytic efficiency 14.29%-16.67% higher than that of pure BiOCl, along with excellent cycling stability.

Keywords inorganic nonmetallic materials, BiOCl, sepiolite, photocatalysis, flower-like
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Corresponding author: ZHANG Huan, Tel: (0816)2419630, E-mail: zhanghuan348@126.com

Introduction

Environmental pollution has become a critical challenge facing modern society, driving research toward simple and effective remediation methods. Semiconductor photocatalytic oxidation technology, which can decompose pollutants under ambient conditions using light energy, has attracted considerable interest from researchers [1]. Recent photocatalysis research has focused on two main areas: modification of traditional photocatalysts (such as TiO_2, CdS, ZrO_2, ZnO) and exploration of novel photocatalytic materials. In 2006, Zhang et al. [2] first reported that BiOCl exhibits higher catalytic efficiency than TiO_2, while offering advantages of low cost, facile preparation, structural stability, and non-toxicity [3]. Consequently, numerous studies have investigated BiOCl in greater depth [4-9]. Current research primarily concentrates on the preparation and modification of BiOCl with special morphologies, as suitable support materials significantly influence catalytic efficiency. Traditional supports include sepiolite, diatomite, bentonite, kaolinite, expanded vermiculite, and wollastonite. Among these, sepiolite is a fibrous clay mineral with high specific surface energy that can adsorb or accommodate various catalyst species, demonstrating superior adsorption capacity [10]. For instance, TiO_2 supported on sepiolite shows substantially enhanced photocatalytic performance [11-12], ZnO-sepiolite composites exhibit improved photocatalytic activity [13], and H-Fe-S photocatalysts synthesized using sepiolite demonstrate high efficiency [14].

In this work, we prepared sepiolite/flower-like BiOCl composite photocatalysts using $Bi(NO_3)_3$ as the bismuth source, concentrated HCl as the chlorine source, and ammonia water to control pH during hydrolytic precipitation. The influence of sepiolite on BiOCl morphology was investigated, and the effects of temperature, pH, and $Bi(NO_3)_3$ dosage on the material morphology were systematically

explored.

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1. Experimental Methods

1.1 Materials and Preparation

The raw materials included sepiolite, ammonia water (36–38%), $Bi(NO_3)_3 \cdot 5H_2O$ (analytical grade), HNO_3 (65–68%), and concentrated HCl (36–38%).

Sepiolite purification was performed by mixing raw sepiolite ore with water at a solid-to-liquid mass ratio of 1:50, stirring for 12 h, then settling for 12 h. After removing the supernatant and precipitates, the intermediate product was treated with 1 mol/L HCl for 12 h, filtered, and washed. The filter cake was dried at 60 °C for 12 h to obtain purified sepiolite.

For composite synthesis, 2 g of purified sepiolite was dispersed in 100 mL distilled water at 30 °C in a flask, followed by addition of 6 mL concentrated HCl and mechanical stirring for 30 min. Subsequently, 30 mL of 0.2 mol/L $Bi(NO_3)_3$ solution was added and stirred for 30 min. Ammonia water was then added dropwise at constant rate using a peristaltic pump to adjust the pH to 2, and the reaction continued for 0.5 h. The product was filtered, washed, dried at 60 °C for 12 h, and ground to obtain the sepiolite-BiOCl composite.

1.2 Characterization

X-ray diffraction (XRD) analysis was performed using an X' Cert PRO diffractometer with Cu Kα radiation (40 kV, 40 mA). Morphology was examined using an Ultra 55 field-emission scanning electron microscope and a TM-1000 scanning electron microscope.

1.3 Photocatalytic Activity Test

Photocatalytic performance was evaluated using a 400 W high-pressure mercury lamp (λ = 365 nm) as the UV source and rhodamine B solution as the target pollutant. A quantity of photocatalyst containing 10 mg of BiOCl was added to 100 mL of rhodamine B solution (10 mg/L) in a 500 mL beaker under magnetic stirring. The lamp was positioned 15 cm above the solution surface. After stirring in the dark for 0.5 h to establish adsorption equilibrium, the UV lamp was turned on. At designated intervals, reaction solutions were centrifuged (4000 r/min for 15 min) and the supernatant was analyzed using a UV-Vis spectrophotometer.

According to the Lambert-Beer law, absorbance is linearly proportional to concentration. The photocatalytic degradation rate of rhodamine B was calculated using the following equation:

$$\text{Degradation rate} = \frac{A_0 - A_t}{A_0} \times 100\%$$

where A_0 is the initial absorbance and A_t is the absorbance at reaction time t. This relationship was used to evaluate the photocatalytic efficiency of the materials.

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2. Results and Discussion

2.1 Sample Composition

[Figure 1: see original paper] presents the XRD patterns of the prepared samples. The sepiolite pattern corresponds to purified sepiolite, exhibiting its characteristic diffraction peaks. The BiOCl pattern shows that all diffraction peaks match the tetragonal phase of BiOCl (JCPDS: 06-0249), indicating high crystallinity and well-developed structure. The sepiolite-BiOCl composite pattern displays BiOCl peaks at 2 = 25.86°, 32.46°, 33.40°, 34.72°, 36.48°, 40.84°, 48.30°, 49.68°, 55.04°, and 58.56°, corresponding to the (110), (110), (102), (111), (003), (112), (201), (113), (104), and (212) crystal planes, respectively. Additional peaks at 9.49°, 10.46°, 19.02°, and 27.10° correspond to sepiolite. The overlapping peaks of BiOCl at 11.92° and 24.10° with sepiolite peaks at 12.20° and 24.46° result in merged peaks at 11.03° and 24.46°. These results confirm that the composite consists of sepiolite and BiOCl.

2.2 Effect of Process Conditions on Composite Morphology

2.2.1 Effect of pH To investigate pH effects, sepiolite-BiOCl composites were prepared at pH values of 2, 4.5, 7, and 9.5 while keeping other parameters constant. [Figure 2: see original paper] shows SEM images of the resulting materials. At pH = 2, BiOCl microspheres were uniformly dispersed throughout the sepiolite matrix. As pH increased, BiOCl could not form regular spheres; instead, irregular BiOCl nanosheets were randomly distributed in the sepiolite.

The presence of sepiolite fibers divides the solution into numerous isolated microdomains. In solution, Bi^{3+} possesses three vacant bonding orbitals and a lone pair of electrons, enabling coordination with oxygen atoms to form Bi_2O_2 layers that are interconnected via interlayer Cl^- ions, resulting in layered BiOCl structures [2]. At low pH, the Bi_2O_2 structure forms, creating BiOCl nuclei. With increasing time, more Bi^{3+} hydrolyzes and slowly develops into spherical BiOCl. At high pH, spontaneous hydrolysis yields only sheet-like BiOCl [15, 16], whereas low pH restricts Bi^{3+} hydrolysis. Therefore, pH = 2 is optimal for forming sepiolite-supported BiOCl with unique morphologies.

2.2.2 Effect of Temperature To examine temperature effects, sepiolite-BiOCl composites were prepared at 0 °C, 10 °C, 20 °C, 30 °C, 40 °C, and

50 °C. [Figure 3: see original paper] presents SEM images of these materials. At 10 °C, 40 °C, and 50 °C, sheet-like BiOCl was randomly dispersed in sepiolite. At 0 °C, only a few irregular BiOCl spheres formed, with most being disordered sheets. Between 20 °C and 30 °C, sheet-like BiOCl assembled into spherical structures. At 20 °C, the BiOCl spheres had diameters of ~8 m, while at 30 °C they were ~2 m and uniformly distributed.

According to the Arrhenius equation, reaction rate increases with temperature. At low temperatures, reduced reaction rates and particle activity decrease the number of effective reacting species. Additionally, the weak Bi-O bonds in Bi_2O_2 layers and the weak interaction between Bi_2O_2 and Cl^- ions hinder BiOCl nucleation, limiting flower-like sphere formation. Excessively high temperatures cause excessive particle motion and reaction rates, which are also unfavorable for forming flower-like structures. At 30 °C, the reaction rate is optimal for producing flower-like BiOCl.

2.2.3 Effect of $Bi(NO_3)_3$ Concentration To study the effect of $Bi(NO_3)_3$ amount, composites were prepared using 10 mL, 20 mL, 30 mL, 40 mL, and 50 mL of 0.2 mol/L $Bi(NO_3)_3$ solution while maintaining other parameters constant. [Figure 4: see original paper] shows SEM images of these materials. With small amounts of $Bi(NO_3)_3$, dispersed BiOCl sheets formed. At 20 mL, a few spheres began to appear. At 40 mL, numerous spheres formed but with non-uniform sizes and some residual sheet-like structures. When $Bi(NO_3)_3$ exceeded 40 mL, spherical BiOCl could not form. At 30 mL of $Bi(NO_3)_3$, uniformly sized BiOCl spheres were obtained.

For a general reaction aA + bB → gG + dD, the reaction rate is given by $u = kc(A)^a c(B)^b$, where $c(A)$ and $c(B)$ are concentrations. This relationship explains the morphology dependence: at low concentrations, insufficient Bi^{3+} is available for hydrolysis within the sepiolite microdomains, preventing sphere formation. Conversely, excessively high Bi^{3+} concentration leads to overly rapid reaction rates, generating numerous sheet-like BiOCl crystals in a short time rather than flower-like spheres.

In summary, the optimal conditions for preparing sepiolite-supported flower-like BiOCl are: 2 g sepiolite, reaction temperature 30 °C, 30 mL of $Bi(NO_3)_3$ solution, and pH = 2.

[Figure 5: see original paper] shows SEM images of pure BiOCl, sepiolite, and sepiolite-BiOCl composites. Pure BiOCl prepared by hydrolytic precipitation exhibits irregular sheet-like structures with disordered arrangement. Sepiolite consists of aggregated irregular fibers. In the composite, numerous flower-like BiOCl microspheres are uniformly dispersed among the sepiolite fibers. [Figure 5: see original paper]d (a high-magnification image) reveals that the BiOCl spheres are assembled from BiOCl nanosheets, with sphere diameters of approximately 2 mm. This morphology likely arises because the fibrous sepiolite structure creates isolated microdomains with favorable pH, appropriate Bi^{3+} concen-

tration, and suitable temperature for independent BiOCl growth. Within these domains, Bi^{3+} hydrolyzes to form Bi_2O_2 structures that develop into BiOCl nuclei, which then grow radially over time to form spherical structures.

2.3 Photocatalytic Performance

Photocatalytic experiments were conducted using pure BiOCl and the optimal sepiolite-flower-like BiOCl composite. [Figure 6: see original paper]a and b show UV-Vis absorption spectra of rhodamine B solutions during photocatalytic degradation, while [Figure 6: see original paper]c plots the concentration versus time. Negative time values represent the period before photocatalysis; the change from -1 min to 0 min indicates the adsorption equilibrium process. Both materials show similar adsorption capacity for rhodamine B. lists the absorbance and concentration of rhodamine B solution after adsorption equilibrium. Pure BiOCl yields an equilibrium concentration of 8.79 mg/L, while the sepiolite-BiOCl composite gives 8.75 mg/L—a negligible difference of 0.04 mg/L—indicating that sepiolite contributes minimal adsorption under these conditions.

The "Rh-B Blank" curve in [Figure 6: see original paper]c shows negligible concentration change for rhodamine B under UV light without catalyst, while the "sepiolite" curve demonstrates that sepiolite alone has no photocatalytic activity. Pure BiOCl requires 6–7 min for complete degradation, whereas sepiolite-BiOCl achieves complete degradation in 5–6 min, representing a 14.29%–16.67% improvement in photocatalytic efficiency.

The enhanced performance of sepiolite-flower-like BiOCl arises from its unique structure. Without sepiolite, BiOCl nanosheets aggregate randomly, limiting dispersion, contact with rhodamine B, and light absorption. In the composite, sepiolite induces formation of uniformly dispersed, size-consistent BiOCl microspheres assembled from nanosheets. This regular architecture significantly increases the photocatalytic reaction surface area and facilitates efficient contact with the pollutant solution, thereby enhancing photocatalytic activity.

Stability was evaluated through recycling experiments. [Figure 7: see original paper] shows rhodamine B concentration versus time for three cycles. In the second and third cycles, sepiolite-BiOCl still achieves complete degradation within 6 min, while pure BiOCl requires 7 min, confirming the excellent stability of the composite.

Conclusions

1. Sepiolite-flower-like BiOCl composite photocatalysts were successfully prepared at 30 °C using 30 mL of $Bi(NO_3)_3$ solution with pH adjusted to 2 via ammonia addition. The BiOCl formed uniform microspheres dispersed in the sepiolite matrix.

2. Using rhodamine B as a target pollutant, sepiolite-flower-like BiOCl demonstrated superior photocatalytic efficiency compared to pure BiOCl, with the sepiolite support improving photocatalytic performance by 14.29%–16.67%.

3. After three catalytic cycles, the photocatalytic activity of sepiolite-flower-like BiOCl remained essentially unchanged, indicating high cycling stability.

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16. (Reference incomplete in original)

Note: Figure translations are in progress. See original paper for figures.