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Synthesis of BiOCl/TiO_2–zeolite composite with enhanced visible light photoactivity

Guangxin Zhang, Zhiming Sun*, Xiaolong Hu, Ankang Song, Shuilin Zheng*

School of Chemical and Environmental Engineering, China University of Mining & Technology (Beijing), Beijing 100083, PR China

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ABSTRACT

The BiOCl/TiO_2–zeolite composite was synthesized via a hydrolysis–precipitation method. The prepared samples were characterized by X-ray diffraction, thermogravimetric analysis, N_2 adsorption–desorption, scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, UV–vis diffused reflectance spectroscopy and photoluminescence. Using liquid rhodamine B and gaseous formaldehyde as the target pollutants, the visible light photoactivity of as received BiOCl/TiO_2–zeolite composites was evaluated. Compared with bare BiOCl and TiO_2, the composites exhibited considerably enhanced photoactivity for rhodamine B and gaseous formaldehyde. The enhancement should be attributed to the higher adsorption ability and the formation of effective BiOCl/TiO_2 heterojunction in BiOCl/TiO_2–zeolite composite. The influence of calcination temperatures on the photocatalytic performance of BiOCl/TiO_2–zeolite composite was also investigated. The optimal calcination temperature is identified as 400 °C for liquid RhB decoloration due to the highest RhB adsorption capacity of composite. However, the composite calcined at 600 °C displayed the best gaseous formaldehyde degradation because of the high crystallinity of TiO_2 and abundant (001) facets of BiOCl. This result further indicated that the enhanced photoactivity of BiOCl/TiO_2–zeolite composite should be attributed to the coexistence of higher surface area and proper crystallinity. The BiOCl/TiO_2–zeolite composite has broad application foreground in pollutants purification.

1. Introduction

Photocatalysis has gained increasing attention for decades due to its many advantages [1–3]. Characteristics such as sustainability, low-cost and practicability make it superior to other contamination remediation approaches. Most of the pollutants can be degraded by photocatalyst under mild conditions [4–6]. Formaldehyde, the major indoor pollutant, can be released from wooden furniture, decoration materials and textiles continually [7,8]. People who dwell overlong in an indoor environment where the concentration of formaldehyde exceeds safety standard are susceptible to the disease of respiratory and nervous system [9]. Therefore, the purification of indoor formaldehyde has become a looming problem in the past decades. Besides, the treatment of dyestuff wastewater is also an important and difficult problem [5,10]. Among the contamination remediation techniques, photocatalysis seems to be one of the most effective methods for completely eliminating pollutants.

Titanium dioxide (TiO_2) is a promising photocatalyst that has many advantages including strong oxidation, non-toxic and excellent chemical stability properties [11,12]. Because of the weak visible light response of TiO_2, various methods (element doping [13], noble metal deposition [14], sensitization [15], coupled semiconductor [16] and supported semiconductors [17–18]) have been used for enhancing its visible light photocatalytic activity. Among these methods, the construction of heterojunction is an effective modification way. Many heterostructures such as g-C_3N_4/TiO_2 [19,20], CdS/TiO_2 [21], Bi_2O_3/TiO_2 [22,23], BiOI/TiO_2 [24,25] and BiOBr/TiO_2 [26,27] has been developed over the past few years. Bismuth oxychloride (BiOCl) has anisotropic layered structure with an internal electric field, which is beneficial to enhance the separation of electrons–holes pairs [28]. BiOCl/TiO_2 has been proved strong visible light response by several literatures. Li et al. [29] reported BiOCl/TiO_2 hierarchical composite with superior visible-light response, enhanced photoactivity and photostability for decomposing rhodamine B. Choi et al. [24] prepared TiO_2/BiOCl hybrid microspheres for single, mixed dyes and natural dyes treatment under visible light irradiation. Even though TiO_2 and modified TiO_2 have excellent photocatalytic performance, the widespread use of TiO_2 nano-material has been restricted by its weak adsorption ability and high aggregation tendency [30]. Therefore, many kinds of supports have been used for dispersing nanoparticles. Porous minerals [31–33], carbon materials [34,35], fibrous materials [36,37] and

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* Corresponding authors.
E-mail addresses: zhimingsun@cumtb.edu.cn (Z. Sun), shuilinzheng8@gmail.com (S. Zheng).

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Table 1.
Chemical compositions of zeolite (wt %).

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	L.O.I.[a]
Zeolite	84.61	2.21	0.07	0.41	0.17	0.01	10.34

[a] Loss on ignition.

glass materials [38] have been applied for the preparation of the TiO_2-immobilized composite. Jansson et al. [39] reported zeolite–TiO_2 hybrid composites for formaldehyde degradation. Portela et al. [32] prepared natural silicate–TiO_2 hybrids for photocatalytic oxidation of formaldehyde using sepiolite, bentonite, mordenite and kaolinite as support, respectively. It is regrettable that these reported materials only have photoactivity under UV light irradiation. Therefore, photocatalysts with visible light response should be prepared and used for pollutants degradation under visible light irradiation.

As far as we know, few papers paid attention to the degradation of formaldehyde under visible light irradiation. Furthermore, the effect of calcination temperatures on the photocatalytic performance of BiOCl/TiO_2 has not been reported hitherto. Natural zeolite is a common porous mineral with high specific surface area and pore volume. In this work, BiOCl/TiO_2–zeolite composites with different calcination temperatures were synthesized through a hydrolysis–precipitation method. The influence of calcination temperatures on the physicochemical property and photocatalytic activity of the composite was also discussed.

2. Experimental

2.1. Preparation of BiOCl/TiO_2–zeolite composite

The zeolite (Guangxi, China) was used as support for the preparation of BiOCl/TiO_2–zeolite composite. The zeolite used in the work was acid leaching zeolite prepared according to the previous literature [40]. Table 1 shows the main chemical compositions of zeolite. Firstly, 5 g of zeolite powders were mixed with 28 mL of $TiOSO_4$ solution (1 M) followed by adjusting the pH of the suspension to 4.5 using diluted ammonia at room temperature. The loading amount of TiO_2 was 45 wt % (mass ratio of TiO_2 to zeolite). The white precipitates were filtrated and washed by distilled water. Subsequently, the above precipitates were mixed with nitric acid solution (100 mL, 1 M) of $Bi(NO_3)_3{\cdot}5H_2O$ (5.1 g) under vigorous stirring. Solution containing 1.2 g of KCl (1:1.5, molar ratio of Bi to Cl) was dropwise added into the solution. The pH of the solution was adjusted to 6 using diluted ammonia. The loading amount of BiOCl was 55 wt% (mass ratio of BiOCl to zeolite). The precipitates were filtrated and dried afterward. Finally, dried powders were calcinated at 400 °C, 500 °C, 600 °C and 700 °C for 2 h in air. The samples were labeled as BT-Z-X, where X represented the calcination temperature. Pure BiOCl and TiO_2 were also prepared through the same method except that zeolite was not added. All chemicals were analytical grade and deionized water was used throughout this study.

2.2. Characterization

The XRD patterns were recorded on a Bruker D8 ADVANCE X-ray diffractometer operating at 40 mA and 40 kV using Cu Kα radiation. TG-DSC analysis was performed on a METTLER TGA/DSC 1 SF/1382 thermal gravimetric analyzer under air atmosphere with a heating rate of 10 °C/min. Nitrogen adsorption–desorption was measured using JW-BK nitrogen adsorption apparatus. SEM images were collected on a Hitachi SU8010 field-emission scanning electron microscopy. TEM were recorded on the Tecnai G2 F20 FE-TEM operating at 200 kV. XPS were recorded on a Thermo Escalab 250Xi spectrometer, using Al Kα radiation. The peak positions of the elements were calibrated by the C1s binding energy. FTIR spectra of samples were recorded by Nicolet 6700. UV–vis absorption spectroscopy was conducted on a UV-9000S UV–vis spectrophotometer (Metash) using an integrating sphere accessory. A Hitachi F-7000 spectrometer was used to obtain the photoluminescence spectra with excitation wavelength of 240 nm.

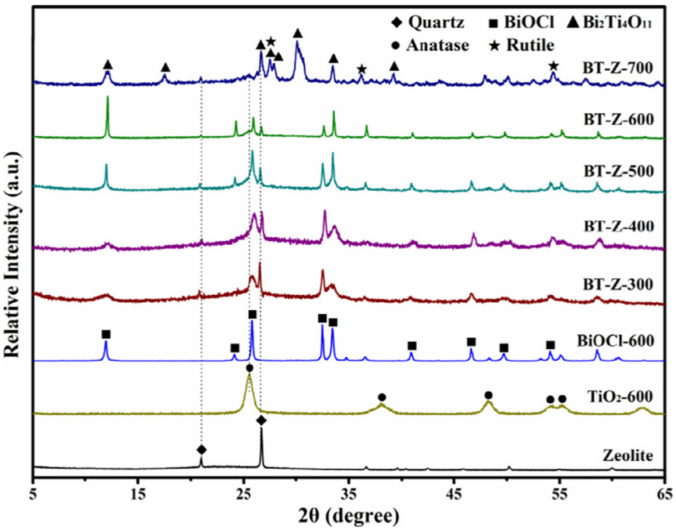

Fig. 1. XRD patterns of the zeolite, TiO_2, BiOCl and BT-Z-X.

2.3. Photocatalytic activity

The photocatalytic degradation for RhB was evaluated by a photoreactor. The visible light was provided by a 500 W Xenon lamp with a 400 nm UV cut-off filter. Typically, 0.1 g of samples was mixed with 100 mL RhB solution (10 mg/L). After reacting a while, the suspension was collected and centrifuged (8000 rpm). The absorbance of RhB solution (λ_{max} = 554 nm) was measured on an UV–vis spectrophotometer. The degradation efficiency was calculated by the change in absorbance. The photocatalytic activities of BiOCl/TiO_2–zeolite were evaluated in a photoreactor as described in the literature [33]. The photocatalysts were prepared by dispersing 1.0 g of samples on the glass plate using water, and then dried at room temperature. Glass coated with sample was placed in the photoreactor. Formaldehyde was injected into the photoreactor in gas form. The initial concentration of formaldehyde was 0.85 mg/m^3. The visible light was provided by two fluorescent lamps (14 W per lamp). Electric fan was used for making the flow of formaldehyde gas. The concentration of HCHO was measured according to the spectrophotometric method (China National Standard GB/T 18,204.26-2000).

3. Results and discussion

3.1. Phase analysis

The phase compositions of the samples were evaluated by XRD analysis. The results are showed in Fig. 1. The XRD peaks of TiO_2-600 at 25.3°, 37.8°, 48.0°, 53.9° and 55.1° are characteristic of anatase TiO_2 (JCPDS 21-1272). The BiOCl-600 shows peaks at 12.0°, 24.1°, 25.9°, 32.5° and 33.4°, corresponding to (001), (002), (101), (110) and (102) planes of BiOCl (JCPDS 06-0249), respectively. Obviously, samples BT-Z-X (X = 300, 400, 500 and 600) have the similar XRD patterns. The difference is that the peak intensity of TiO_2 and BiOCl of BT-Z-X changed with the increase of calcination temperature. As temperature rises, peaks of both TiO_2 and

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