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Efficient decomposition of organic compounds and reaction mechanism with BiOI photocatalyst under visible light irradiation

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ABSTRACT

BiOI photocatalyst was synthesized by a precipitation–filtration process and consequent hydrothermal treatment. The as-prepared BiOI exhibits efficient photocatalytic activity on the decomposition of widely used model pollutants, methyl orange (MO) and phenol, under visible light irradiation. Even under the illumination of a compact fluorescent lamp, the obtained BiOI also exhibits high photocatalytic activity. The possible photodegradation mechanism was studied by the examination of active species $HO^\bullet$, h_{vb}^+, or $O_2^{-\bullet}$ anions through adding scavengers such as *tert*-butanol (*t*-BuOH), I^- anion, bromate anion and benzoquinone (BQ). The results show that photodegradation of MO molecules is attributed to the action of h_{vb}^+ via direct hole oxidation process and the oxidation action of the generated $O_2^{-\bullet}$ radicals. Dissolved oxygen play an important role in photocatalytic reaction, which could trap the photogenerated electrons to reduce the recombination of h_{vb}^+ and e_{cb}^- and also function as a precursor of main oxidant $O_2^{-\bullet}$. Hydroxyl radical was verified to be inappreciable for the decomposition of MO.

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1. Introduction

Nowadays, two of the most urgent issues facing modern society are the depletion of energy resources and the deterioration of the natural environment. Semiconductor-based photocatalysis is attracting extensive interest as a kind of "green" technology to alleviate both the problems by splitting water for green energy hydrogen production and degrading toxic pollutants [1,2]. However, the widely used photocatalyst TiO_2 is only active in the UV range [3], so developing more efficient visible-light-driven photocatalysts is indispensable. Although dye sensitization or doping of other elements makes the utilization of visible light possible [4–7], stable and efficient dyes are rare while dopants act usually as a recombination centers for the photogenerated electrons and holes. Therefore, many researchers focus their efforts on the design and development of new single-phase effective photocatalysts under visible light irradiation.

Recently, the Bi-based layered structure compounds, including Aurivillius family [8–10], Sillén family [11–13] and Aurivillius–Sillén intergrows [14], have been extensively investigated as visible-light-driven photocatalysts due to their unique layered structure and high activity. It is believed that the formed internal electric fields between the slabs are beneficial to inducing the efficient separation of photogenerated electron-hole pairs and then improving the photocatalytic activity of the catalysts [15]. BiOI, belonging to the Sillén family expressed by $[M_2O_2][I_m]$ ($m = 2$), has drawn increasing attention for the application as photocatalyst owing to its small band gap (1.77–1.92 eV) and strong absorption in visible-light region. Up to now, different morphologies of BiOI, such as 3D hierarchical structures [16–18], nanosheets [19,20] and nanolamellas [21] have been fabricated successfully by a variety of methods, and various model pollutants, including methyl orange (MO), methylene blue (MB), rhodamine (RhB), sodium pentachlorophenol (PCP-Na) and phenol, have been used to evaluate their photocatalytic activity. Among them, Lei et al. fabricated BiOI with 3D flower-like hierarchical structure and investigated its formation process and photocatalytic activity on the degradation of organic dye pollutants [17]. Xiao et al. obtained more uniform 3D BiOI microspheres in ethanol–water mixed solvent and studied its self-assembled mechanism and visible light photocatalytic activity for the degradation and mineralization of phenol [18]. Although many investigations have been performed on the preparation and photocatalytic activity of BiOI, only Chang's group [20] investigated the photocatalytic mechanism of BiOI nanosheets and systematic research on photodegradation mechanism of BiOI is lack. In addition, considering the future practical application it is still in need of studies on enhancing the photocatalytic activity of BiOI.

In the filed of photocatalysis, it is generally accepted that the photodegradation of dyes and organic pollutants has been proceeded via photocatalytic oxidation (PCO) process. The primary reactive species (RS) involved in PCO process include RS_{ads} on surface of photocatalyst (h^+, $^\bullet OH_{ads}$) and RS_{free} in solution ($O_2^{-\bullet}$, $^\bullet OH_{free}$, H_2O_2). However, so far, whether photoreaction occurs on

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the catalyst surface or in the solution has long been continuous controversy, and the behaviors of different active species in the various stages of photocatalysis are not clear. It is also the case for the photocatalysis of BiOI.

In the present work, we synthesized BiOI photocatalyst with highly enhanced photocatalytic activity by a precipitation–filtration process and consequent hydrothermal treatment. Phenol and MO were chosen as model pollutants to evaluate the photocatalytic performance of the BiOI samples. Various free radical scavengers were introduced to the photocatalytic reaction system to explore the behaviors of different reactive species and the reaction mechanism underlying.

2. Experimental

2.1. Sample preparation

All the reagents were of AR grade and were used without further purification. In a typical synthesis, 5 mmol $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 10 mL 3 mol L^{-1} HNO_3. 2 mol L^{-1} NaOH solution was added dropwise to adjust the pH value of the solution to 3.0 under vigorous stirring. The mixture was stirred for 0.5 h at room temperature in air. The resulting precursor precipitates were filtrated and washed with deionized water thoroughly, and then transferred to a 100 mL Teflon-lined autoclave together with 10 mmol KI. The deionized water was added up to 70% of the total volume. After being further stirred for 0.5 h, the autoclave was sealed in a stainless steel tank and heated at 160 °C for 12 h under autogenously pressure, and then air cooled to room temperature. The resulting precipitates were filtrated and washed with ethanol and deionized water thoroughly and dried at 80 °C in air.

For the purpose of comparison, BiOI powders were also prepared by a chemical precipitation reaction following the previous study [22], the product was named as PR-BiOI.

2.2. Characterization

The X-ray diffraction (XRD) patterns of the samples were measured on an X'Pert PRO X-ray powder diffractometer with Cu-Kα radiation (λ = 1.5418 Å). The morphology of the samples was investigated by scanning electron microscopy (SEM, Zeiss EVO LS-15), transmission electron microscopy (TEM, Tecnai G^2 20 S-TWIN) and high resolution transmission electron microscopy (HRTEM, JEOL JEM-2100). UV–vis diffuse reflectance spectra (DRS) were obtained using a UV–vis spectrometer (Shimadzu U-3010) by using $BaSO_4$ as a reference. Nitrogen adsorption–desorption isotherms were collected on a NOVA 1000e surface area and porosity analyzer (Quantachrome, USA) at 77 K after the sample had been degassed in the flow of N_2 at 150 °C for 1.5 h. The BET surface area was estimated using desorption data.

2.3. Photocatalytic activity test

The photocatalytic performance of the as-prepared samples was characterized by decomposing methyl orange (MO) or phenol under visible light irradiation at room temperature. A 500 W Xe-illuminator was used as a light source, 2 mol L^{-1} $NaNO_2$ solution to eliminate UV light (cutoff $\lambda < 400$ nm) [1]. The photodegradation experiments were carried out with the samples (500 mg) suspended in MO or phenol aqueous solution (500 mL, 10 mg L^{-1} and 20 mg L^{-1}, respectively) with constant stirring. Prior to the irradiation, the suspensions were magnetically stirred in the dark for 1 h to establish the adsorption/desorption equilibrium. At the given time intervals, about 5 mL of the suspension was taken for analysis after centrifugation. The concentration of MO was detected by measuring the absorption intensity at a wavelength of 464 nm. The absorption intensity was converted to the MO concentration referring to a standard curve which showed a linear relationship between the concentration and the absorption intensity. The concentration of phenol was estimated by measuring the absorption at a wavelength of 510 nm using the colorimetric method of 4-aminoantipyrine [23].

To investigate the possibility of practical application, a U-type compact fluorescent lamp (Philips Genie energy saving lamp, 23 W) was also selected as a light source for the degradation of MO.

In experiments requiring scavengers, the calculated amount of scavengers was introduced into the MO solution before the addition of the catalyst. For experiments with purging nitrogen gas, the flow rate of nitrogen gas was controlled at 0.4 L min^{-1}. Before the experiments, nitrogen gas was purged for 30 min to give the desired oxygen level.

Terephthalic acid, which reacts readily with $OH^{\bullet}$ to produce a highly fluorescent product, 2-hydroxyterephthalic acid, was employed as a probe molecule to detect the formed hydroxyl radicals ($OH^{\bullet}$) [24]. The fluorescence intensity around 425 nm, which can be ascribed to the characteristic of 2-hydroxyterephthalic acid, is proportional to the amount of hydroxyl radicals formed in solution. The detection experiment process is similar to the photodegradation experiment, with the exception of a basic terephthalic acid solution instead of MO or phenol suspension. The concentration of terephthalic acid was set at 5×10^{-4} mol L^{-1} in a dilute NaOH (2×10^{-3} mol L^{-1}) solution. The sampling was carried out every 15 min, and the withdrawn solution was measured on a Hitachi F-4500 fluorescence spectrophotometer after centrifugation. The excitation wavelength used was 315 nm.

3. Results and discussion

3.1. Characterizations of the BiOI samples

The morphology and microstructure of the BiOI samples was revealed by the SEM and TEM images (Fig. 1). The as-prepared samples have a 3D hierarchical structures constructed by nanoplates (Fig. 1a), the size of which can be estimated to be about 250–500 nm by the TEM investigation as shown in Fig. 1b. The as-prepared photocatalysts possess 3D hierarchical architectures, which will be beneficial to the separation of electron–holes and therefore improving the photocatalytic activity. In addition, the photocatalysts with hierarchical structures are more easily separated and recycled from the practical point of view [25].

Fig. 2 presents the XRD patterns of the BiOI samples before and after photocatalytic reaction. The as-prepared BiOI is well crystallized in a single phase, all of the diffraction peaks can be indexed to the tetragonal phase BiOI (space group P4/nmm, JCPDS 10-0445). No other impurities can be detected. The intense and narrow diffraction peaks reveal the good crystallinity of the BiOI samples. The standard intensity of the (1 1 0) peak is much weaker than that of the (1 0 2) peak, which could be expressed as $I(1\,1\,0)/I(1\,0\,2) = 0.55$. In our case, the intensity of the (1 1 0) peak is close to that of (1 0 2) peak, the value of $I(1\,1\,0)/I(1\,0\,2)$ was increased to 0.98. The related high-resolution TEM (HRTEM) images of a single nanoplate from as-prepared BiOI sample are shown in Fig. 1c and d, which display clearly resolved crystalline domain with a uniform interplanar spacing of 0.282 nm, corresponding well to the (1 1 0) plane of the tetragonal phase BiOI (JCPDS 10-0445). It indicates that the BiOI anisotropic grew along the (1 1 0) plane, which is in good agreement with the results of XRD.

The UV–vis diffuse reflectance spectrum of the as-synthesized BiOI samples is shown in Fig. 3. The absorption edge of the samples extends nearly to the whole spectra of visible light, ranging from 200 nm to 600 nm. The obvious absorption edge is located at about

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