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The enhanced photoactivity of nanosized Bi_2WO_6 catalyst for the degradation of 4-chlorophenol

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Abstract

Nanosized Bi_2WO_6 catalyst exhibited the enhanced photoactivity for the degradation of 4-chlorophenol (4-CP) under visible irradiation compared to the sample prepared by high-temperature solid reaction. The photoactivity of the catalyst was sensitive to pH variation of the suspension. Nanosized Bi_2WO_6 catalyst showed the highest activity at pH 7.2. The photodegradation of 4-CP by nanosized Bi_2WO_6 catalyst followed a pseudo-first-order reaction. After three recycling runs for the photodegradation of 4-CP, the activity of the catalyst did not show any significant loss, suggesting that the catalyst was stable under visible irradiation.

Keywords: A. Nanostructures; A. Semiconductors; D. Surface properties

1. Introduction

Development of visible-light-driven photocatalyst for the decomposition of the environmental pollutants has been urged from the viewpoint of utilizing solar energy [1]. Although TiO_2 doped by nitrogen could degrade 4-CP under visible irradiation [2], the doping of N atoms also serves as sites for electron–hole recombination, resulting in a low quantum yield [3].

In oxide semiconductors, the conduction band levels of small band-gap semiconductors are usually low because the deep valence bands are formed by O 2p. This is a major problem for developing visible-light-driven photocatalysis. To find a breakthrough, it is indispensable to control the valence band with orbitals of some elements instead of O 2p. Bismuth is a potential candidate for such a valence-band-control element [4]. Recently, a great deal of efforts have been devoted to developing the photocatalysts containing bismuth with high activities for environmental applications and/or water splitting, such as $BiVO_4$ [5], $CaBi_2O_4$ [6], $Bi_2Ti_2O_7$ [7] and $Bi_4Ti_3O_{12}$ [8].

Bi_2WO_6 has been found to possess interesting physical properties such as ferro-electric piezoelectricity, pyroelectricity, catalytic behavior and non-linear dielectric susceptibility [9]. Recently, Kudo and Hijii [10] have reported that Bi_2WO_6 catalyst prepared by the solid-state reaction from the mixtures of WO_3 and Bi_2O_3 showed the

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photocatalytic activity for O_2 evolution from an aqueous silver nitrate solution under visible-light irradiation. More recently, Zou and coworkers [11] reported that Bi_2WO_6 catalyst prepared by the same method showed not only the activity for photocatalytic O_2 evolution but also the activity of mineralizing both $CHCl_3$ and CH_3CHO contaminants under visible-light irradiation. Therefore, the photocatalyst with a strong oxidizing potential could be postulated. Bi_2WO_6 photocatalysts were often prepared by the solid-state reaction [10,11] and the size of the crystal was situated in the microsized scope. It has been reported that nanostructured photocatalysts usually presented enhanced photocatalytic activities due to their special morphologies, high surface areas and high efficiency of electron–hole separation [12]. Up to date, there is only a little information about the photochemical properties of nanosized Bi_2WO_6, thus, it is an urgent need to study this photocatalyst.

In a previous work [4,13], we have successfully synthesized Bi_2WO_6 nanoplates by a simple hydrothermal process. The as-prepared sample shows high activity for the rhodamine B photodegradation. We reported herein that the nanosized Bi_2WO_6 was more active for the 4-CP photodegradation compared to N-doped TiO_2 and, in particular, exhibited an unusually high activity compared to the sample prepared by the solid-state reaction. Furthermore, the material was stable under irradiation. To the best of our knowledge, the photodegradation of 4-CP by nanosized Bi_2WO_6 catalyst was first investigated. Our work indicated that nanosized Bi_2WO_6 could photodegrade colorless compound under visible-light irradiation.

2. Experimental

2.1. Sample preparation and characterization

Nanosized Bi_2WO_6 was prepared by the hydrothermal synthesis method [4,13]. For comparison, the sample prepared by a high-temperature solid-state reaction and $TiO_{2-x}N_x$ sample ($x = 0.0488$) were prepared according to the previous literatures [2,11]. The x value (nitrogen concentration) in $TiO_{2-x}N_x$ was measured by X-ray photoelectron spectroscopy (XPS). XPS analysis were performed on a PHI 5300 ESCA instrument using an Al Kα X-ray source.

X-ray diffraction (XRD) with Cu Kα radiation was measured using a Bruker D8 Advance X-ray diffractometer. UV–vis diffused reflectance (DR) spectra of the samples were measured with a Hitachi U-3010 spectrometer. The spectra were recorded in the range 200–700 nm.

2.2. Photoreactor and light source

The light source was a 500 W xenon lamp (Institute of Electric Light Source, Beijing) positioned inside a cylindrical reaction vessel. The system was cooled by wind, and maintained the room temperature. An appropriate cutoff filter was placed upside the vessel to ensure complete removal of the radiation below 400 nm. The average light intensity was 40 mW cm^{-2}.

2.3. Procedure and analyses

Aqueous suspensions of 4-CP (10 mg L^{-1}) and Bi_2WO_6 powder (50 mg L^{-1}) were placed in a vessel. Prior to irradiation, the suspensions were magnetically stirred in the dark for ca. 30 min to ensure the establishment of the equilibrium. The suspensions were kept under constant air-equilibrated conditions before and during the irradiation. At given time intervals, 3 mL of aliquots were sampled, and centrifugated to remove the particles. The filtrates were analyzed by recording the variations of the absorption band (224 nm) in UV–vis spectra of the suspension using a Hitachi U-3010 spectrometer (Japan). Total organic carbon (TOC) was measured with a Tekmar Dohrmann Apollo 9000 TOC analyzer. Cl^- ion was analyzed with a Shimadzu LC-10AS ion chromatograph.

3. Results

3.1. Characterizations of the catalyst

The sheet-shaped crystal could be observed for the sample prepared by the hydrothermal process [4]. The sizes of crystals were not uniform and distributed in the scope of 50–200 nm. The large surface area was therefore expected.