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A nanocrystalline oxygen-deficient bismuth oxide as an efficient adsorbent for effective visible-light-driven photocatalytic performance toward organic pollutant degradation

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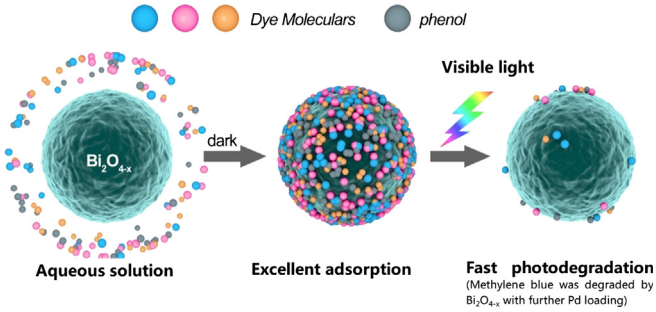
GRAPHICAL ABSTRACT

A binary oxygen-deficient Bi_2O_{4-x} was demonstrated as a new class of excellent visible-light-driven photocatalyst with remarkable initial adsorption capacity toward organic pollutants.



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ABSTRACT

In this work, a simple binary oxygen-deficient Bi_2O_{4-x} oxide was prepared, and its crystal structure, optical property, band structure and electronic structure were systematically investigated. Plane-wave-based density functional theory (DFT) calculations were also carried out to determine that Bi_2O_{4-x} is a typical indirect-gap semiconductor with the bandgap of 1.1 eV. Bi_2O_{4-x} adsorbed ca. 99% of rhodamine B and methyl orange, ca. 95% of methylene blue and ca. 80% of phenol in the dark within initial 30 min. The interaction of the oxygen-deficient structure-induced hydroxyls with pollutant molecules is responsible for the excellent adsorption capacity. Due to its excellent adsorption capacity, Bi_2O_{4-x} showed much higher photocatalytic degradation activity toward these pollutants (except for methylene blue) under visible light irradiation than the well-studied Bi_2O_4, Bi_2O_3 and P25, which had poor or negligible adsorption capacity toward the pollutants. Methylene blue was degraded by Bi_2O_{4-x} with further Pd loading. The photocatalytic mechanism of the oxygen-deficient Bi_2O_{4-x} were explored. The scavenging test results showed that direct h^+ oxidation contributes to the high photocatalytic activity of the oxygen-deficient Bi_2O_{4-x}. This study highlights the potential of developing Bi_2O_{4-x}-based materials as a new class with both excellent adsorption capacity and highly efficient photocatalytic activity toward versatile pollutants.

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1. Introduction

The removal of organic pollutants from the wastewater is one of the most important issues for environmental remediation. Among the various available water treatment methods, adsorption [1–3] and photocatalytic degradation based on nanoscience and nanotechnology [4–6] are respectively the most reliable and the most promising techniques for organic pollutant removal. However, the use of conventional adsorbents is usually limited because of their high production cost and significant drawbacks of the expensive and time-consuming regeneration process [7,8]. On the other hand, photocatalytic degradation used in and of itself is also unsatisfactory for wastewater treatment due to expensive photocatalyst preparation and low photocatalytic efficiency. Considering these problems, we wonder whether there exists a multifunctional nanomaterial that has both strong adsorption and photocatalytic capabilities toward organic pollutants. This nanomaterial can solve the problem of regeneration of traditional adsorbents by its own photocatalytic degradation of the adsorbed pollutants while promoting photocatalytic efficiency through its strong adsorption capability [9]. The development of such a multifunctional nanomaterial is imperative, challenging, and the goal of this study.

Among the various metal oxide semiconductors, bismuth oxide has attracted broad interest for a wide range of applications in catalysis, microelectronics, sensors, and optical coatings due to its outstanding physical and chemical properties [10,11]. As a photocatalyst, the hybridized O2p and Bi6s^2 valence bands in the Bi^{3+}-containing oxide lead to a narrower band gap relative to that of TiO_2, resulting in a more substantial utilization of the solar spectrum [12]. On the other hand, it is known that in oxides, in addition to its trivalent state, bismuth also exists in the pentavalent state, and the empty 6 s orbital of Bi^{5+} also supports the high visible-light photocatalytic activity for Bi^{5+}-containing compounds [13]. However, simple bismuth oxides with mixed-valent states have rarely been reported. Accor ding to the literature, most studies have focused on the preparation of these mixed-valent Bi-oxides. For example, in 1995, Kumada et al. [14,15] prepared monoclinic dibismuth tetraoxide (m-Bi_2O_4) mixed-valent bismuth oxide with the structure analogous to the β-Sb_2O_4-type structure. Begemann et al. [16] prepared cubic Bi_2O_{4-x} for the first time via the thermal decomposition of $HBiO_3{\cdot}nH_2O$ and amorphous Bi_2O_5 under high oxygen pressures. Prakash et al. [17] further synthesized the cubic Bi_2O_{4-x} by oxidative precipitation using $K_2S_2O_8$ as the oxidant and suggested that its cubic fluorite related structures are stabilized by some amount of Bi(V). Unfortunately, the electronic structure details or the applications of these oxides were not reported. Recently, Hameed et al. reported the use of the UV irradiation-induced surface Bi_2O_{4-x} decorated Bi_2O_3 nanocomposite for the degradation and mineralization of organic pollutants [18,19] under complete spectrum and visible region of sunlight. In our previous study, based on understanding the self-oxidation feature of Bi_2O_3 under UV light irradiation, we found that the formation of the Bi_2O_{4-x} surface active species on the Bi_2O_3 sample could be accelerated using an H_2O_2 treatment [20]. Although the surface-decorated Bi_2O_{4-x} has been known as the active visible light responsive species from the above-described studies, more detailed information regarding the electronic structure, band structure and intrinsic photocatalytic activity, all of which are very important factors for the photocatalytic performance, has not yet been systematically obtained for the Bi_2O_{4-x} species. On the other hand, the mixed-valent state in an oxide may also induce structural defects that are believed to be highly related to the oxide surface chemistry. To date, there have been a number of reports related to the defect studies of zinc oxide, titanium oxide and cerium oxide [21–23]. However, to the best of our knowledge, such studies focusing specifically on extending the adsorption property for applications have not been performed for bismuth oxides with a mixed-valent state.

In this study, we systematically compared the physical and chemical properties, such as the crystal structure, optical properties, band structure and electronic structure, of the Bi_2O_{4-x}, Bi_2O_4 and Bi_2O_3 oxides and investigated their potential applications in adsorption and visible-light-sensitive photocatalysis for the removal and degradation of a broad range of pollutants, including cationic and anionic dyes and even recalcitrant phenols. Remarkable dark adsorption of the three selected dye molecules (rhodamine B (RhB), methyl orange (MO) and methylene blue (MB)) and of phenol molecules was demonstrated for the first time for the oxygen-deficient Bi_2O_{4-x}. Bi_2O_{4-x} was different from the other materials for which the ionic molecules adsorption ability depended on their isoelectric point. The oxygen-deficient Bi_2O_{4-x} was further found to have excellent visible-light-sensitive photocatalytic activity toward these organic pollutants compared to Bi_2O_3, Bi_2O_4 and commercial TiO_2 (P25). In addition to the use of pure bismuth-based materials, improved photocatalytic performance can be achieved by metal modification [24] and coupling to other semiconductors [25]. In this study, the photocatalytic activity for the degradation of methylene blue was further enhanced by Pd loading on the Bi_2O_{4-x}. The adsorption capacity and degradation mechanism of the organic pollutants were also explored. Based on these results, the oxygen-deficient Bi_2O_{4-x} is demonstrated to be a promising alternative for wastewater treatment.

2. Experimental section

2.1. Materials

The raw materials of bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$), sodium bismuthate dehydrate ($NaBiO_3{\cdot}2H_2O$), sodium persulfate ($Na_2S_2O_8$), sodium hydroxide (NaOH), ammonium nitrate (NH_4NO_3), nitric acid (HNO_3), palladium chloride ($PdCl_2$), methylene blue (MB), methyl orange (MO) and rhodamine B (RhB) and phenol were purchased from Wako Pure Chemicals Ind., Ltd., Japan and were used directly without further purification. Isopropanol (IPA) and triethanolamine (TEA) were purchased from Sigma-Aldrich and were used without further purification. Distilled water was used as the solvent in this study.

2.2. Preparation of Bi_2O_{4-x}, Bi_2O_3 and Bi_2O_4

The preparation of Bi_2O_{4-x} is the same as in previous reports [17]. In a typical process, to avoid heat generation, NaOH (22 g, 550 mmol) was slowly dissolved in 500 ml of distilled water in a beaker. The alkali solution was then heated on a hot plate under constant stirring using a magnetic rotor (250 rpm). During the heating, a $Bi(NO_3)_3{\cdot}5H_2O$ suspension solution was prepared. Bi $(NO_3)_3{\cdot}5H_2O$ (10 g) was dissolved in 50 ml of distilled water with concentrated HNO_3 (1 ml) and ultrasonicated for 10 min. When the alkali solution temperature reached 95–100 °C, $Na_2S_2O_8$ (14.4 g) and the $Bi(NO_3)_3{\cdot}5H_2O$ milky suspension solution described above were added sequentially. A large amount of a brown precipitate was rapidly generated. The mixture solution was heated at 95–100 °C for 3 h under constant stirring (250 rpm). Then, the suspension was cooled to room temperature and centrifuged at 7000 rpm for 5 min. To avoid both its peptization and hydrolysis at neutral pH, the precipitate was washed several times with 1 wt% NH_4NO_3 solution to ensure the complete removal of the soluble ions. Finally, the brown precipitate was dried at 100 °C overnight for subsequent use. Bi_2O_3 was obtained from the calcination of Bi_2O_{4-x} carried out at 500 °C for 3 h.

Bi_2O_4 was synthesized via the hydrothermal method using $NaBiO_3$ and distilled water as the starting materials. In a typical