



Efficient photodegradation of chlorophenols by BiOBr/NaBiO₃ heterojunctioned composites under visible light



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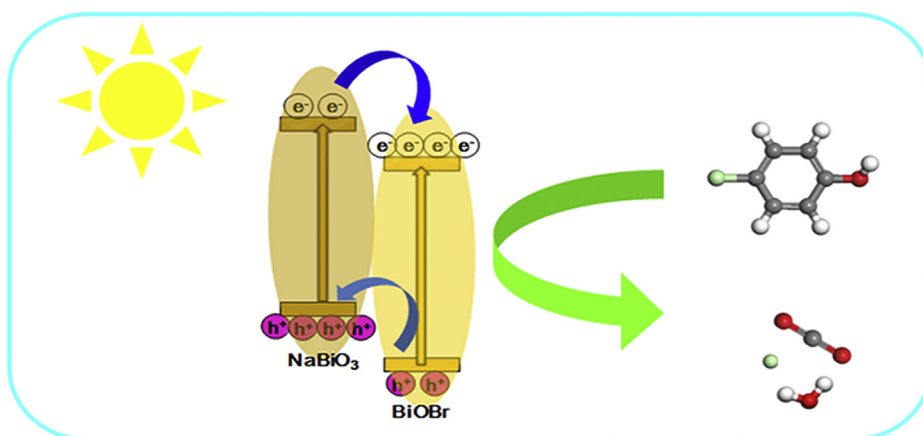
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HIGHLIGHTS

- BiOBr/NaBiO₃ heterojunctions synthesized by corrosion of NaBiO₃ with HBr.
- Intimately contacted interfaces due to commensurate planes of BiOBr and NaBiO₃.
- 9% BiOBr/NaBiO₃ exhibits superior degradation efficiency of chlorinated compounds.
- Activity optimized by oxidation ability of holes and charge separation efficiency.

GRAPHICAL ABSTRACT



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ABSTRACT

Forming heterojunctioned composites is an effective way to develop visible-light-driven photocatalysts. A series of BiOBr/NaBiO₃ composites were synthesized by surface transformation of NaBiO₃ with hydrobromic acid. Commensurate planes of BiOBr and NaBiO₃ enabled the formation of a closely bound interface. Composites with <20 wt.% BiOBr exhibited excellent photocatalytic activity towards the degradation of chlorophenols under low intensity visible light ($\lambda > 400$ nm). The best photocatalyst was 9% BiOBr/NaBiO₃ with a quantum yield of 0.365. No photocorrosion was observed after three cycles. Using radical scavengers and inert atmosphere, holes, superoxide and hydroxyl radicals were found to be involved in the photoactivity of the BiOBr/NaBiO₃ composite. Hydroxylated and open-ring diacid molecules were identified as intermediates in the mineralization of 4-chlorophenol.

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1. Introduction

Chlorophenols are widely used as biocides and pesticides. Specifically, 4-chlorophenol has been used as a disinfectant at home, in hospital and farms [1], as well as an antiseptic in root canal

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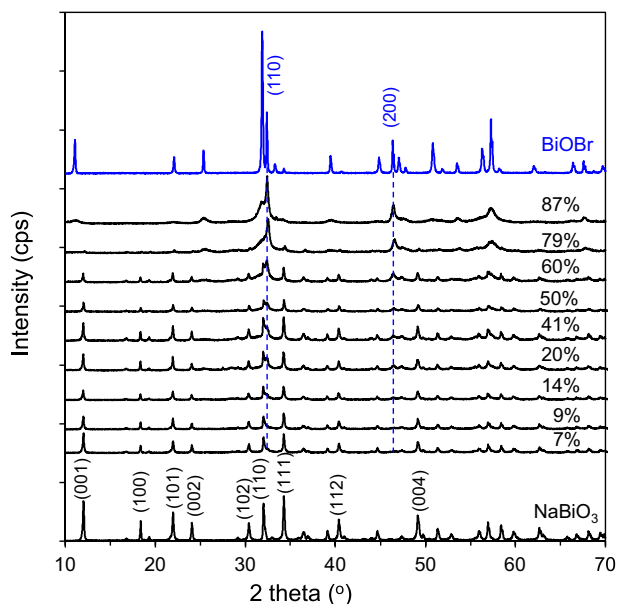


Fig. 1. XRD patterns of NaBiO₃, BiOBr and their composites.

treatment [2]. Most of the chlorophenols released into the environment go into water, and can cause severe effects on the liver and the immune system of human body. Furthermore, chlorophenols (such as 2, 4, 6-trichlorophenol) are possibly carcinogenic. Therefore, it is of utmost importance to mineralize the chlorophenols in water to harmless products. Photocatalytic degradation of these compounds is an option that has drawn the attention of many researchers.

Whilst titania is a well-known photocatalyst [3–5], it requires the use of ultraviolet radiation due to its wide band gap. Hence, there is a strong impetus to develop photocatalysts that are visible-light active. In this respect, many bismuth-containing semiconductors have been reported to be efficient photocatalysts. These include compounds such as Bi₂O₃ [6–8], Bi₂S₃ [9,10], bismuth oxyhalides [11–15], BiVO₄ [16,17], Bi₂WO₆ [18–20] and CaBi₂O₄ [21]. The formation of heterojunctioned composites has been an area of active research in the development of visible light-driven photocatalysts. The vectorial transfer of electrons or holes from one semiconductor to the other reduces the intrinsic recombination rate, thereby increasing the probability of interfacial charge-transfer processes over that of a single phase material. Several bismuth(III)-containing composites, such as BiOCl/Bi₂O₃ [22], BiOBr/Bi₂O₃ [23], BiOBr/BiOCl [24,25], and Bi₇O₉I₃/α-Bi₅O₇I [26] have been recently reported. In comparison, there are fewer studies on Bi(V) compounds although NaBiO₃ has been reported to be a photocatalyst for the degradation of methylene blue [27], isopropanol [27], sodium pentachlorophenate [28], Rhodamine B (RhB) [29], 4-*tert*-octylphenol [30], and polycyclic aromatic hydrocarbons [31]. NaBiO₃ has a unique layered structure, where layers of BiO₆ octahedra are sandwiched in between NaO₆ octahedral layers (Fig. S1). The conduction band is composed of hybridized Na 3s, Bi 6s and O 2p orbitals (Fig. S2), in contrast to Bi₂O₃ where Bi 6p orbitals make the major contribution [21]. The strong dispersion of the conduction band suppresses the recombination of electron-hole pairs in NaBiO₃, and gives it a higher photocatalytic activity than Bi₂O₃. Heterojunctioned composites of NaBiO₃/BiOCl [32] and Bi₂O₃/NaBiO₃ [33] have been reported for the degradation of Rhodamine B (RhB) and malachite green dyes, respectively. A recent publication by Ji et al. [34] showed that a 40 mol% BiOBr/NaBiO₃ sample could degrade RhB efficiently although differences in dark adsorption were not taken into account.

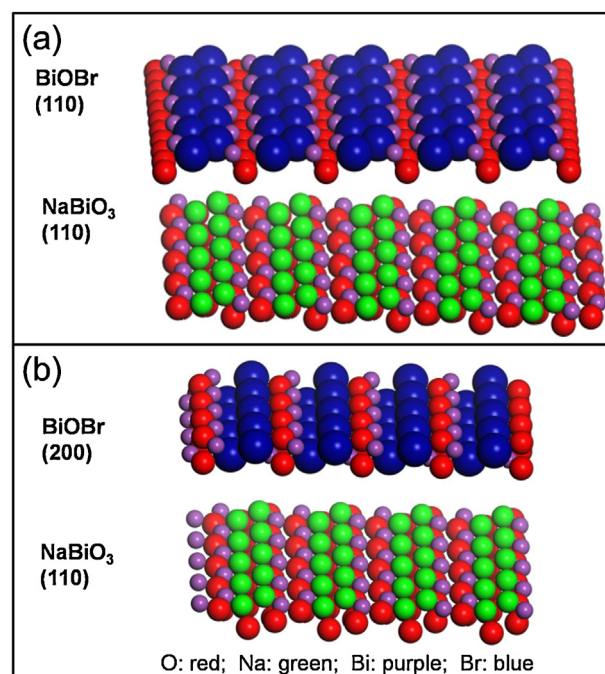


Fig. 2. Planes of BiOBr and NaBiO₃.

To the best of our knowledge, outside of dyes where photosensitization can be involved, the application of NaBiO₃ composites for photodegradation of non-colored pollutants has not been reported. We recently found that heterojunctioned Bi₇O₉I₃/α-Bi₅O₇I materials show excellent removal efficiency for alkyl phenols [26]. However, they displayed poor activity for chlorophenols, thus prompting our investigation into BiOBr/NaBiO₃ composites for this group of compounds. To ensure a tight interface between the components, NaBiO₃ was treated with hydrobromic acid to form a BiOBr overlayer. The extent of the overlayer coverage was varied by using different amounts of hydrobromic acid.

2. Experimental

2.1. Sample preparation

All the reagents were of analytical grade and were used without further purification. The BiOBr/NaBiO₃ heterojunctions were prepared by an etching reaction of NaBiO₃ with hydrobromic acid. 1.4 g (5 mmol) of sodium bismuthate (Merck) was dispersed in a mixture of 20 ml absolute ethanol and 10 ml deionized water. Defined amounts of 33% hydrobromic acid containing from 0.9 to 30 mmol of HBr in acetic acid was then added. After stirring for an hour, the solid was recovered by centrifugation, washed with absolute ethanol and dried at 80 °C overnight in an oven. The samples are labeled as x% BiOBr/NaBiO₃, where x% denotes the weight percentage of BiOBr in the heterojunctioned samples.

2.2. Characterization

Powder X-ray diffraction patterns were measured using a Siemens D5005 diffractometer (Cu anode) for 2θ from 10 to 70° using a step size of 0.02° s⁻¹ and a dwell time of 1 s per step. The elemental composition of the samples was determined using inductively coupled plasma-atomic emission spectroscopy (Thermo Jarrell Ash Duo Iris). Nitrogen adsorption and desorption isotherms were measured at -196 °C using a TriStar 3000 v5.02 (Micromeritics) porosimeter and the surface area was calculated using the Brunauer–Emmett–Teller (BET) equation. Scanning

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