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Sonochemical synthesis and characterization of BiOI nanoplates for using as visible-light-driven photocatalyst

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ABSTRACT

BiOI nanoplates were successfully synthesized by a simple sonochemical method. X-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and X-ray photoelectron spectroscopy (XPS) revealed the presence of pure tetragonal BiOI nanoplates in the solutions with the pH of 8–12. The photocatalytic activities of the BiOI nanoplates were evaluated through the degradation of rhodamine B (RhB) under xenon visible-light irradiation. Obviously, the pH of precursor solutions played an important role in the photocatalytic activities. In this research, the BiOI nanoplates synthesized in the solution with the pH of 12 showed the highest efficiency of 81.19% within 180 min.

1. Introduction

In recent years, semiconducting photocatalysts can play an important role in degradation of environmental contamination by active radicals and creating nontoxic CO_2 and H_2O under solar radiation [1,2]. In particular, TiO_2 has been the most widely investigated photocatalyst for degradation of some refractory organic pollutants [2,3]. Moreover, TiO_2 can absorb photon only in the UV region (<4% of solar radiation) because it has a band gap of 3.2 eV [2–4]. BiOI with a narrow band gap of 1.7–1.9 eV is considered to be one of the most prospective photocatalyst due to its good photocatalytic activity under visible light irradiation (~48% of solar radiation) [1,4,5] to degrade p-chloroaniline [1], rhodamine B [2,6], 2,2-bis(4-hydroxyphenyl)propane [4], methylene blue [6], methyl orange [6], 3,4,5-trihydroxybenzoic acid [7], etc. BiOI is a layered structure material consisting of positive $[Bi_2O_2]^{2+}$ and negative halide anionic slabs parallel to the (0 0 1) facet, connected through internal static electric field [1,2]. The unique layered structure has the benefit to separate photogenerated exitons along the [0 0 1] direction [1,2].

According to our knowledge, this is the first report on the synthesis of BiOI by sonochemical method. The effect of solution pH on phase, morphology and photocatalytic property of BiOI was studied and discussed in order to relate with the degradation of rhodamine B (RhB) under visible light irradiation.

2. Experiment

In this research, each 0.005 mol of $Bi(NO_3)_3{\cdot}6H_2O$ and NaI was dissolved in 100 ml deionized water under vigorous stirring till complete dissolution. Subsequently, 3 M NaOH solution was slowly added to these solutions until reaching the pH of 2–12. These solutions were processed in 35 kHz ultrasonic bath at 80 °C for 5 h. The as-synthesized precipitates were collected and dried for further characterization.

Crystallinity and crystalline phase of the synthesized nanostructures were characterized by an X-ray diffractometer (XRD, Philips X'Pert MPD) with Cu-K_α radiation in the range of 15°–60°. The morphology was recorded on a transmission electron microscope (JEOL JEM-2010 TEM) at an acceleration voltage of 200 kV. The products were carried out by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos Analytical Ltd.) with a monochromatic source of X-rays (Al K_α photon energy of 1486.6 eV). All the as-obtained spectra were calibrated w.r.t. the C 1 s peak at 285.1 eV.

The reaction was carried out by dispersing each 200 mg catalyst in 200 ml of 1×10^{-5} M RhB aqueous solutions. The suspensions were kept in the dark for 30 min under magnetic stirring before visible light illumination from a Xe lamp. At a given time interval, each 5 ml solution was collected and centrifuged. The residual con-

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centration of RhB was measured at 553 nm using a UV–visible spectrophotometer (Perkin Elmer Lambda 25).

3. Results and discussion

Fig. 1a shows XRD patterns of BiOI synthesized in the solutions with different pH values by sonochemical method. XRD patterns of the as-synthesized products at the pH of 2, 4 and 6 were specified as major phase of tetragonal BiOI corresponding to the database of JCPDS No. 10-0445 [8] mixed with minor unknown phase. Upon further increasing the pH to 8, 10 and 12, all the diffraction peaks of samples can be indexed as the pure tetragonal BiOI phase with cell parameters of a = 3.9940 Å, b = 3.9940 Å and c = 9.1490 Å (JCPDS No. 10-0445) [8]. Furthermore, the diffraction peaks of the as-prepared BiOI are sharp and intense, indicating the presence of single phase of BiOI products with high-ordered atomic arrangement. No characteristic peaks of impurity were detected by XRD, certifying that the BiOI products can be synthesized by a one-step sonochemical method in the alkaline solutions with the pH of 8–12.

The surface component and chemical state of BiOI at the pH of 12 were investigated by XPS. The XPS spectra of Bi 4f (Fig. 1b) shows two binding energy peaks at 159.18 and 164.49 eV which are attributed to the Bi $4f_{7/2}$ and Bi $4f_{5/2}$, respectively [1,6,7]. They certified that Bi^{3+} species belong to BiOI [1,6,7]. The main binding energy of O 1 s (Fig. 1c) was detected at 530.03 eV, corresponding to the lattice oxygen of Bi–O bond in BiOI sample [1,6]. Other binding energies of O 1 s peaks are in accordance with oxygen of adsorbed moisture, hydroxyl group and C—O contaminant on surface of sample [1,7,9]. The XPS spectra of I 3d (Fig. 1d) show binding energy peaks at 619.12 and 630.66 eV belonged to the I $3d_{5/2}$ and I $3d_{3/2}$ states, certifying the existence of I^- in BiOI [1,6,7].

TEM images and SAED patterns were used to specify the morphology and growth direction of the as-prepared BiOI as the results shown in Fig. 2. Clearly, the TEM images of all samples were composed of nanoplate-like particles. Their surfaces are very smooth and even. Their SAED patterns appeared as bright spots of electron diffraction, indicating the single crystalline BiOI nanoplates with high crystallinity. They can be indexed to the (1 1 0), (2 0 0) and (1 −1 0) planes with electron beam along the [0 0 −1] direction. They were suggested that the BiOI nanoplates were composed of ±(0 0 1) top and bottom and ±(1 1 0) edge surfaces.

Fig. 3a shows the temporal absorption spectral change of RhB solution caused by the as-prepared BiOI at the pH of 12 under visible light irradiation. Obviously, the primary absorption peak of RhB was at 553 nm wavelength. The starting red-pink solution gradually became paler into colorless and transparent one within 180 min, suggesting that RhB molecules were completely decomposed. At the same time, a spectral blue-shift can be ascribed to the de-ethylation process due to RhB dye photodegradation [4,10,11]. Fig. 3b shows the photocatalytic degradation efficiency of RhB by three different photocatalysts under visible light irradiation within 180 min. The photocatalytic degradation efficiencies of RhB degradation were 64.21%, 73.31% and 81.19% for BiOI synthesized in the solutions with the pH of 8, 10 and 12, respectively. Interestingly, the highest photocatalytic performance of BiOI synthesized at the pH of 12 is 1.26 and 1.11 times of the performance of BiOI synthesized at the pH of 8 and 10, respectively.

To have a better understanding of the reaction kinetics of RhB degradation, the experimental data were fitted to pseudo-first-order simplification of Langmuir–Hinshelwood kinetics, which is well established for photocatalysis at low initial pollutant concentration. The relevant equation is shown as follows.

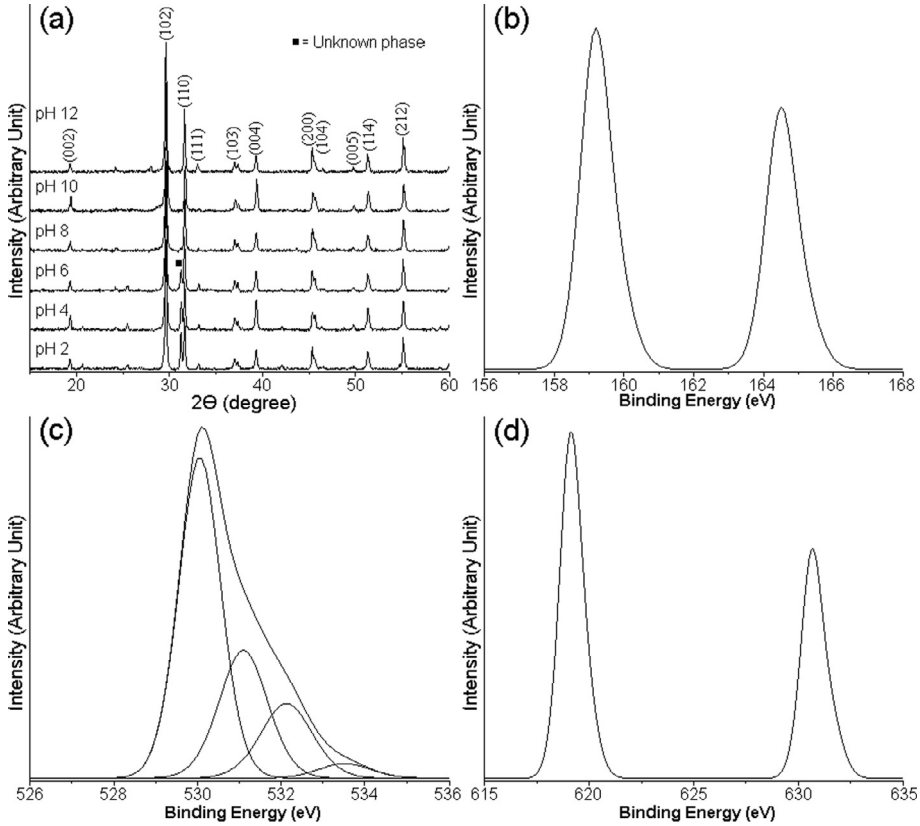

Fig. 1. (a) XRD patterns of BiOI synthesized by sonochemical method at the pH of 2, 4, 6, 8, 10 and 12. XPS spectra of (b) Bi 4f, (c) O 1 s and (d) I 3d of BiOI synthesized by sonochemical method at the pH of 12.