Synthesis of Indium Borate and Its Application in Photodegradation of 4-Chlorophenol

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ABSTRACT: Indium borate has been prepared by a sol–gel method. The structure, morphology, and photophysics of the resultant photocatalysts have been studied via the techniques of X-ray diffraction (XRD), transmission electron microscopy (TEM), and diffuse reflectance UV–visible light spectroscopy. These photocatalysts have been used to photodegrade 4-chlorophenol. The photocatalytic activity depends on the annealing temperature during preparation. It is found that borates can exhibit a high photodegradation activity under UV-light irradiation, for which the efficiency can be higher than that of as-prepared TiO2. This is explained according to the results of fluorescence spectra and valence band X-ray photoelectron spectroscopy (XPS). It is confirmed by the results of time-resolved photoluminescence decay spectra; i.e., the lifetime of electrons and holes involved in the radiative process can be longer for the borates than that for TiO2. This implies that indium borate can be a promising photocatalyst for future applications in treatment of environment contaminants.

INTRODUCTION

The 4-chlorophenol (4-CP), a hazardous waste and toxic pollutant, has been widely used in many fields such as pharmacy and dyes over the past few decades. It shows high toxicity and strong irritant on the organisms. Since it is difficult to purify the wastewater contaminated by 4-CP, it is critical to develop an efficient method to degrade it. Compared to conventional treatment processes, a promising approach is to employ a photocatalyst to oxidize it at room temperature using clean solar energy.1,2 Many photocatalysts have been designed and prepared to achieve this. Among them, TiO2 is the most widely studied one due to its nontoxicity and high photostability.3 However, so far, the photocatalytic efficiency for all of these catalysts is still relatively low, which keeps them away from practical applications. Hence, it is important to develop new photocatalysts to degrade 4-CP with a high efficiency.4

Indium borate (InBO3) is an optoelectronic material with a good chemical stability,4–6 which is often used as the host of luminescence materials. It is a wide-gap semiconductor, which makes it with a lower recombination rate of photoproduced charge carriers. Moreover, the holes photogenerated in it can be involved in decomposing organic molecules since the potential of its valence band is positive enough (vs SHE). However, so far, only few reports about InBO3 as a photocatalyst have been reported. One example is that InBO3 with a calcite structure can be used for water splitting under UV-light irradiation.7 There are no reports about InBO3 as a photocatalyst for degradation of organic contaminants. Here, we report that InBO3 can have a high photocatalytic activity on degradation of 4-CP under UV-light irradiation, for which the efficiency can be higher than that of as-prepared TiO2.

EXPERIMENTAL SECTION

Photocatalyst Preparation. At room temperature, 5.5 mL of indium(III) chloride solution (1 mol⋅L−1) was mixed with 50 mL of deionized water under vigorous stirring for 15 min, followed by addition of 720 mg of boric acid. A 16 mL of sodium hydroxide solution (1 mol⋅L−1) was then added dropwise. After aging for 24 h at room temperature, the resultant white precipitate was washed with deionized water to remove the unreacted reagent and dried at 373 K for 12 h. The obtained white powder was then divided equally into three parts and annealed in air for 2.5 h, respectively, at 723, 923, and 1073 K, which was, respectively, designated as IBO-723, IBO-923, and IBO-1073. The reference sample, TiO2, was prepared by a sol–gel method via hydrolysis of tetrabutyl titanate (Ti(OC4H9)4). At room temperature, 1 mL of concentrated HCl solution (12 mol⋅L−1) and 12 mL of Ti(OC4H9)4 were added dropwise to 40 mL of anhydrous ethanol under vigorous stirring. The mixture was continuously stirred until the TiO2 gel was formed. After aging at room temperature for 24 h, the as-prepared TiO2 gel was dried at 373 K for 12 h and then annealed in air at 723 K for 2.5 h.8 The deionized water (18.2 MΩ⋅cm) was used in all of the experiments. All the chemicals were purchased from Tianjin Letai Chemical Industry Co., Ltd.

Photocatalyst Characterization. X-ray diffraction (XRD) pattern was collected on a Rigaku D/max 2500 X-ray diffraction spectrometer (Cu Ka, λ = 1.54056 Å). The crystal size was...
The as-prepared photocatalysts were used to photodegrade 4-CP in a 100 mL photochemical reactor with 1 mg of photocatalyst suspended in 4-CP solution (5 × 10⁻⁵ mol·L⁻¹, pH = 5.74) under UV-light irradiation. A sunlamp (Philips HPA 400/30S, Belgium, λ = 380–400 nm) was used as light source. The UV-light intensity on the sample surface was 0.2 W·cm⁻². The reactor was perpendicular to the light beam and located 15 cm away from the light source. All the suspensions were stirred at 25 ± 2 °C in the dark for 30 min with continuously bubbled oxygen at a flux of 5 mL·min⁻¹ to reach adsorption equilibrium before photoirradiation. The solution concentration was monitored with a UV–vis spectrometer (UV-1601PC, Shimadzu) using 4-aminoantipyrine as the chromogenic reagent. The photodegradation was repeated at least three times with different batches of photocatalysts prepared using the same recipe. The control experiment was performed under identical conditions but without catalysts.

The concentration of organic species can be calculated by the determination of chemical oxygen demand (COD), which is performed using a COD reactor (DRB2000, HACH) via a semimicro modified dichromate method suitable for the determination of low COD concentrations (1–35 mg L⁻¹). Typically, the COD measurements were carried out before and after UV-light photodegradation of a 4-CP suspension containing 10 mg of photocatalyst. After a small fraction of suspension was taken out from the reactor at different time intervals, the particles inside were removed immediately by centrifugation and filtration. The COD values of the resultant solution were then determined by measuring the residual oxidizing agent after oxidation at 150 °C for 120 min in the COD reactor.

### RESULTS AND DISCUSSION

#### Structure and Morphology of Photocatalyst

Crystalline structure of different borates and TiO₂ reference sample was studied using XRD patterns (Figure 1). The TiO₂ annealed at 723 K exhibits an anatase structure. All the diffraction peaks for IBO-923 and IBO-1073 match well with the characteristic feature of InBO₃ crystal (JCPDS, No. 17-0933). The peaks at 24.3°, 31.6°, 37.4°, 45.0°, and 51.9° can be indexed to (102), (104), (110), (202), and (116) crystal planes of InBO₃, respectively. Hence, IBO-923 and IBO-1073 samples are in crystalline state with a hexagonal lattice and calcite structure. Only two weak peaks were observed at 24.3° and 31.6° for IBO-723 (Figure 1), indicating that it is largely in amorphous state. The values of specific surface area (Sₐ), cell volume and cell parameters of borate samples decrease with the increase of annealing temperature (Table 1).

#### Table 1. Cell Parameters and BET Surface Area for Different Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>(a = b) (nm)</th>
<th>(c) (nm)</th>
<th>Cell Volume (\left(10^⁵\text{nm}³\right))</th>
<th>(S_{\text{BET}}) (m²·g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBO-723</td>
<td>0.4823</td>
<td>1.5457</td>
<td>311.42</td>
<td>55.3</td>
</tr>
<tr>
<td>IBO-923</td>
<td>0.4823</td>
<td>1.5450</td>
<td>311.24</td>
<td>3.9</td>
</tr>
<tr>
<td>IBO-1073</td>
<td>0.4820</td>
<td>1.5441</td>
<td>310.71</td>
<td>1.0</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.3792</td>
<td>0.9499</td>
<td>136.59</td>
<td>63.8</td>
</tr>
</tbody>
</table>

As the crystal size increases with the increase of annealing temperature due to crystal growth, the BET surface area decreases with the increase of annealing temperature and, thereby, the amount of crystalline phase of borate.

Figure 2 shows TEM and HRTEM images of IBO-1073 sample. Accurate structural information about crystal structure and planar spacing can be extracted via 2D fast Fourier transform (FFT) analysis of HRTEM image. Fringe spacing of (104) and (110) crystallographic plane for hexagonal lattice structure are determined to be 2.86 Å (Figure 2B) and 2.42 Å (Figure 2C), respectively. FFT analysis (Insets of Figure 2) clearly reveals the bright spots for both (104) and (110) planes, indicating that a single crystal of IBO-1073 has been successfully prepared.

![Figure 1. XRD patterns of samples for different borates and TiO₂ reference.](dx.doi.org/10.1021/es203333k/Environ. Sci. Technol. XXX, XXX, XXX—XXX)
Photophysics of Photocatalyst. Figure 3 shows the electronic band structure (along high symmetry lines in Brillouin zone) of InBO₃ obtained by DFT calculation. The zero energy level lies in the top of valence band (VB), corresponding to the highest state occupied by electrons. Hence, all electrons are located in the VB. The band structure indicates that the photoabsorption can arise from both indirect and direct bandgap transition. The top of VB was H point (−0.333, 0.667, 0.500), and the bottom of conduction band (CB) was G point (0.0, 0.0, 0.0). The direct bandgap at H point is calculated to be ~4.60 eV, and the indirect bandgap is ~2.31 eV.

Figure 4 shows the projected contributions to total DOS from O (2s²2p⁴), In (4d¹⁰5s²5p¹), and B (2s²2p¹) are also included in the figure. It is found that, as expected, the top of VB is dominated by O 2p states, as well as a small fraction of contribution from B 2p, In 5p, In 4d, and In 5s. The bottom of CB is dominated by In 5s states, with a small fraction of contribution from O 2s, In 5p, B 2s, and B 2p. The O 2p states also partially contribute to the CB. Except In 5s, all the states contribute to the CB at high energy levels. The contribution of O 2p states to CB may make its level rise, resulting in widening the bandgap.
Figure 5 is the diffuse reflectance UV–visible absorption spectra of TiO$_2$, IBO-723, IBO-923, and IBO-1073 samples. The strong absorption peak at 340 nm for TiO$_2$ is attributed to the band-to-band transition, for which the absorption onset edge is $\sim$400 nm, corresponding to a bandgap of $\sim$3.10 eV.\textsuperscript{8,9} The absorption edge for the borates when the annealing temperature increases since the crystallinity of borate increases with annealing temperature, as evidenced by XRD. The strong absorption peak at 340 nm for TiO$_2$ is attributed to the photoabsorption is very weak since its energy is very high. Hence, the contribution to photocatalysis from the direct bandgap is no longer considered in this work.

**Photocatalytic Degradation of 4-CP.** The photocatalysts have been used to photodegrade 4-CP under UV-light irradiation (Figure 6A). Both TiO$_2$ and borates have a very low adsorption capability of 4-CP after 1 h (about 2–4%, inset of Figure 6A). The 4-CP can hardly be degraded in the control experiment (photolysis). The TiO$_2$ shows a degradation rate ($\ln(C_0/C)$) of $\sim$66.0% after 1 h irradiation (Table 2). The TiO$_2$ shows a degradation rate ($\ln(C_0/C)$) after 1 h irradiation for IBO-723, IBO-923, and IBO-1073 is about 40.0%, 67.3%, and 96.0%, respectively. Hence, IBO-923 and IBO-1073 exhibit a higher photocatalytic activity than TiO$_2$, while IBO-723 is lower. Both specific photocatalytic activity and photodegradation rate of IBO-1073 are $\sim$1.5 times of that of TiO$_2$ (Table 2).

Similar phenomena were observed by the change in COD before and after the photodegradation of 4-CP (Figure 6B), which can reveal the degree of mineralization and/or degradation of an organic upon irradiation.\textsuperscript{13} Considering photocatalysis may lead to stoichiometric photomineralization of organic compounds,\textsuperscript{13} the COD of a given photocatalyst can be assessed, by tracing the change of dissolved oxygen concentration under the photocatalytic conditions. The reduction of COD value after 1 h irradiation for the control, TiO$_2$, IBO-723, IBO-923, and IBO-1073 is about 2.5%, 58.3%, 37.5%, 60.0%, and 92.5%, respectively, so 4-CP can not only be degraded but also be mineralized efficiently by the borates.

Table 2. Photodegradation of 4-CP under UV-Light Irradiation

<table>
<thead>
<tr>
<th>sample</th>
<th>degradation rate ($\Delta C/C_0$)\textsuperscript{a}</th>
<th>$k$ (min$^{-1}$)\textsuperscript{b}</th>
<th>$t_{1/2}$ (min)</th>
<th>specific photocatalytic activity (mol g$^{-1}$ h$^{-1}$) \textsuperscript{c}</th>
</tr>
</thead>
</table>
| control      | 0.043                                          | 7.25 $\times$ 10$^{-4}$            | 956.1          | *
| IBO-723      | 0.400                                          | 0.85 $\times$ 10$^{-2}$            | 81.5           | 0.80 $\times$ 10$^{-4}$\textsuperscript{d}       |
| IBO-923      | 0.673                                          | 1.86 $\times$ 10$^{-2}$            | 37.3           | 1.35 $\times$ 10$^{-4}$\textsuperscript{d}       |
| IBO-1073     | 0.960                                          | 5.36 $\times$ 10$^{-2}$            | 12.9           | 1.92 $\times$ 10$^{-4}$\textsuperscript{d}       |
| TiO$_2$      | 0.660                                          | 1.80 $\times$ 10$^{-2}$            | 38.5           | 1.32 $\times$ 10$^{-4}$\textsuperscript{d}       |

\textsuperscript{a}After reaction for 1 h. \textsuperscript{b}Apparent rate constant deduced from the linear fitting of $\ln(C_0/C)$ versus reaction time. \textsuperscript{c}Control refers to the photolysis of 4-CP.

Figure 5. Diffuse reflectance UV–visible spectra for TiO$_2$, IBO-723, IBO-923, and IBO-1073 samples.

Figure 6. Photocatalysis of different catalysts. (A) Concentration of 4-CP as a function of UV-light irradiation time during photodegradation with different catalysts. (B) The corresponding change in COD before and after the photodegradation. Inset of (A) is the adsorption ratio of 4-CP with different catalysts in dark after 1 h.
Therefore, the borate can be an effective catalyst for 4-CP photodegradation.

**Mechanism of 4-CP Photodegradation.** As an effective photocatalyst, its potential of VB and CB should be located in an appropriate position so that photogenerated charge carriers can take part in decomposing organic molecules. Here, IBO-1073 is used as an example for borate catalysts. Figure 7 is the XPS VB spectra for TiO₂ and IBO-1073 samples, which can be used to determine the VB position in a semiconductor. As shown in Figure 7, the energy level of defects in IBO-1073 is determined to be +2.40 V (vs SHE) and in TiO₂ to be +2.85 V (eq 2), which can further react with the electrons to produce OH⁻ and ⋅OH (eq 3). The ⋅OH can also be obtained via the reaction of holes with OH⁻ or surface hydroxyl (eq 4). The 4-CP molecules absorbed on the catalyst surface can be oxidized by both O₂⁻ and ⋅OH (eqs 5 and 6), as well as directly by the holes (eq 7) since their potential is positive enough. Eventually, the 4-CP molecules can be photodegraded into CO₂ and H₂O. The energy level of defects in IBO-1073 is determined to be +2.40 V. Here, the hump at ~515–540 nm is not discussed. Similarly, the energy levels of defects in TiO₂ are determined to be ~0.58 V (480 nm) and ~0.36 V (525 nm) (Figure 8B). Under UV-light irradiation, the photogenerated electrons in the defects and CB can be directly captured by the adsorbed O₂ as their potential is negative enough, resulting in formation of O₂⁻ (eq 1). The O₂⁻ can react with electrons to form H₂O₂ (eq 2), which can further react with the electrons to produce OH⁻ and ⋅OH (eq 3). The ⋅OH can also be obtained via the reaction of holes with OH⁻ or surface hydroxyl (eq 4). The 4-CP molecules absorbed on the catalyst surface can be oxidized by both O₂⁻ and ⋅OH (eqs 5 and 6), as well as directly by the holes (eq 7) since their potential is positive enough. Eventually, the 4-CP molecules can be photodegraded into CO₂ and H₂O.

**Photocatalytic Activity.** The alignment of energy levels can be used to explain why IBO-1073 exhibits a higher activity than as-prepared TiO₂, which is drawn according to the aforementioned results of UV-vis absorption spectra, valence band XPS, and PL spectra. Here, it is noted that the energy levels for TiO₂ are different from the literature, which is ascribed to that TiO₂ can exhibit different energy levels if they are prepared by different methods.

The energy level of CB bottom (indirect) for IBO-1073 locates closer to the energy level of O₂/O₂⁻ (~−0.78 V vs SHE) than that for TiO₂ and the energy level of defects in IBO-1073 locates closer to the energy level of O₂/H₂O₂ (~−0.38 V) than that for TiO₂. This may facilitate the formation of O₂⁻ and ⋅OH (eqs 1–3). Moreover, the potential of VB top for IBO-1073 is positive than that for TiO₂, leading to a higher oxidation capacity and, thereby, also in favor of the formation of ⋅OH (eq 4). It is suggested that ⋅OH may play a major role in the photodegradation process.

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**Figure 7.** Valence band XPS spectra for TiO₂ and IBO-1073 samples. The Fermi level (Ef) is shown too.

**Figure 8.** The PL spectra of (A) different borate catalysts and (B) TiO₂.
The photocatalytic activity is closely related to the behavior of photogenerated electrons and holes. The photogenerated electrons first fall into the defects from the CB via a nonradiative process and then recombine with the holes in VB to give rise to fluorescence emission. Hence, the lifetime of electrons in the defects can be used to evaluate the photocatalytic activity, which is measured by PL technique. 

27 The photocatalytic activity is generally related to the band gap (eq 7). Thus, IBO-1073 exhibits a higher activity than as-prepared TiO2, albeit its band gap is slightly wider than that of TiO2. This may be related to the increase of crystallinity with the increasing temperature as well as the change in surface states. Further study is undergoing to elucidate this.

Table 3. Values of the Calculated Decay Time Constant $\tau_1$ and $\tau_2$ through Double Exponential Decay Fitting for the Corresponding Samples

<table>
<thead>
<tr>
<th></th>
<th>TiO2</th>
<th>IBO-723</th>
<th>IBO-923</th>
<th>IBO-1073</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_1$ (ns)</td>
<td>0.442 ± 0.036</td>
<td>0.468 ± 0.097</td>
<td>0.626 ± 0.122</td>
<td>1.289 ± 0.084</td>
</tr>
<tr>
<td>$\tau_2$ (ns)</td>
<td>1.528 ± 0.182</td>
<td>1.312 ± 0.007</td>
<td>2.612 ± 0.233</td>
<td>4.538 ± 0.577</td>
</tr>
</tbody>
</table>

Figure 9. Schematic diagram for the alignment of energy levels for IBO-1073 and TiO2 (not drawn to scale).

Figure 10. The time-resolved PL decay curve for different catalysts, excited at 400 nm and monitored at 470 nm for borates and 480 nm for TiO2.

The nonradiative relaxation process related to defects of materials, and the longer PL lifetime range ($\tau_2$) arises from the radiative process related to the recombination of photogenerated electrons and holes. The $\tau_1$ and $\tau_2$ values of different samples have been calculated via double exponential decay fitting (Table 3). Results show that the $\tau_2$ value for IBO-1073 is 4.538 ns, which is longer than that for TiO2 (1.528 ns). This slow PL decay indicates a prolonged recombination process in IBO-1073 and, thus, results in a higher photocatalytic activity than TiO2. Similarly, the $\tau_2$ value for IBO-923 (2.612 ns) is longer than that for TiO2 and, accordingly, exhibits a higher activity. The $\tau_2$ value for IBO-723 (1.312 ns) is shorter than that for TiO2 and shows a lower activity.

It is noted that photocatalytic activity of borate photocatalyst increases with the increase of annealing temperature (Table 2), which correlates to the PL results. The IBO-1073 has the longest $\tau_2$ value, followed by IBO-923, and IBO-723 has the shortest $\tau_2$ (Table 3). Since the PL intensity is sensitive to the lifetime, accordingly, IBO-1073 exhibits the weakest PL intensity, followed by IBO-923, and IBO-723 has the strongest PL intensity (Figure 8). This may be related to the increase of crystallinity with the increasing temperature as well as the change in surface states. Further study is undergoing to elucidate this.

ACKNOWLEDGMENTS

This work is supported by National Natural Science Foundation of China (50872056, 51072082, and 51043010). T.H. also thanks National Research Fund for Fundamental Key Projects No. 973 (2011CB93200), Ministry of Science and Technology of China (2010DFA64680), and the Hundred-Talent Program of Chinese Academy of Sciences. We thank Prof. Ying Ma from Institute of Chemistry, Chinese Academy of Sciences, for helping us to carry out the theoretical calculation.

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