



# The influence of pH values on the existing states of In and B ions in TiO<sub>2</sub>



Shaolong Huang<sup>a</sup>, Yanlong Yu<sup>a</sup>, Wenjun Zheng<sup>b,\*\*</sup>, Chunling Zhang<sup>a</sup>, Yaan Cao<sup>a,\*</sup>

<sup>a</sup> MOE Key Laboratory of Weak-Light Nonlinear Photonics, TEDA Applied Physics Institute and School of Physics, Nankai University, Tianjin 300457, China

<sup>b</sup> Department of Materials Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China

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## ABSTRACT

A series of In and B co-doped TiO<sub>2</sub> samples are prepared by sol–gel method under different pH values. The detailed existing states of introduced In and B ions are investigated via XRD, FT-IR, XPS and HRTEM. It is found that the B ions are mainly doped into TiO<sub>2</sub> in interstitial mode and In ions exist as surface O–In–Cl<sub>x</sub> species when the pH values are in the range of 0.31~0.65. With the increase of the pH values (0.82~3.40), the introduced In and B ions would react with each other to form InBO<sub>3</sub>. The existing states of In and B ions in TiO<sub>2</sub> can be easily changed by adjusting the pH values to achieve a new type of TiO<sub>2</sub> based materials with controlled structures.

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## 1. Introduction

TiO<sub>2</sub> has been extensively investigated owing to its wide applications, such as photocatalysis, photosynthesis and photoelectron-conversion [1–5]. However, due to the large band gap, it is still limited for TiO<sub>2</sub> to be applied for practical application under solar irradiation [2,6]. Doping TiO<sub>2</sub> with metal or nonmetal elements is considered to be one of the most efficient methods to make full use of solar light [7–16]. For example, B doped TiO<sub>2</sub> and In doped TiO<sub>2</sub> had attracted lots of attention in recent years. Zhao et al. reported that doping B ions in TiO<sub>2</sub> could narrow band gap and extend the absorption into the visible region [17]. Su et al. found that the doped B ions would retard the phase transition from anatase to rutile and exhibit enhanced photocatalytic activity under visible light irradiation [18,19].

Our previous work reported that a kind of unique surface O–In–Cl<sub>x</sub> species was formed on the surface of TiO<sub>2</sub> [20]. Yu et al. investigated the existing states of In and B ions in TiO<sub>2</sub> and their energy levels [21]. Besides, Yu et al. also reported the band structure of N–TiO<sub>2</sub>/InBO<sub>3</sub> heterostructure [22]. However, there are few reports about the influence of pH values on the structures of In and

B co-doped TiO<sub>2</sub>, and the existing states of In and B ions under different pH values. Therefore, it is expected to prepare a new type of TiO<sub>2</sub> doped with In and B ions with controlled structures via sol–gel method by simply adjusting the pH values.

Herein, a series of TiO<sub>2</sub> samples doped with In and B ions were prepared via a one-step sol–gel method under different pH values. The structures, existing states and their transform relationship of In and B ions in TiO<sub>2</sub> system were investigated in details. The transform mechanism of the existing states for In and B ions was also studied.

## 2. Experimental details

### 2.1. Catalyst preparation

The In and B ions co-doped TiO<sub>2</sub> nanoparticles were prepared by a simple one-step sol–gel method. In ice bath, 7.1 mL of InCl<sub>3</sub> solution (0.73 M) and 240 mg of H<sub>3</sub>BO<sub>3</sub> was mixed with 40 mL of anhydrous ethanol under vigorous stirring. Then 12 mL of tetrabutyl titanate was added dropwise into the mixed solution. Different amount of concentrated HCl solution (12 M) were added into the mixture to adjust the pH values. The obtained sol was stirred continuously until the formation of gel, and then aged for 24 h at room temperature. The gel was dried at 100 °C for 10 h, and then calcined at 450 °C for 2.5 h. The obtained TiO<sub>2</sub> based samples with the different pH values are denominated as In–B–TiO<sub>2</sub> pH<sub>x</sub>, and x is increasing pH from 0.31 to 3.40 (Table 1)

\* Corresponding author. Tel.: +86 22 66229431.

\*\* Corresponding author. Tel.: +86 22 23507951.

E-mail addresses: [zhwj@nankai.edu.cn](mailto:zhwj@nankai.edu.cn) (W. Zheng), [caoya@nankai.edu.cn](mailto:caoya@nankai.edu.cn) (Y. Cao).

**Table 1**  
Details of In-B-TiO<sub>2</sub> pHx samples.

Samples	InCl <sub>3</sub> solution (0.73 M)/mL	H <sub>3</sub> BO <sub>3</sub> /mg	Ti(OC <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> /mL	HCl (12 M)/mL
In-B-TiO <sub>2</sub> pH0.31	7.1	240	12	1.1
In-B-TiO <sub>2</sub> pH0.44	7.1	240	12	1.0
In-B-TiO <sub>2</sub> pH0.53	7.1	240	12	0.9
In-B-TiO <sub>2</sub> pH0.65	7.1	240	12	0.8
In-B-TiO <sub>2</sub> pH0.82	7.1	240	12	0.6
In-B-TiO <sub>2</sub> pH1.00	7.1	240	12	0.4
In-B-TiO <sub>2</sub> pH1.21	7.1	240	12	0.2
In-B-TiO <sub>2</sub> pH3.40	7.1	240	12	-

(In/(In + Ti) = 12.8%, B/(B + Ti) = 10%). For comparison, Pure TiO<sub>2</sub>, In-TiO<sub>2</sub> and B-TiO<sub>2</sub> powders were also prepared using the same procedure with or without the relative precursors. Pure indium borate powder (InBO<sub>3</sub>) was prepared by a sol-gel method as we reported [23]. All chemicals used were of analytical grade and water was deionized water (>18.2 MΩ cm<sup>-1</sup>).

## 2.2. Characterization

X-ray diffraction (XRD) patterns were collected on a Rigaku D/max 2500 X-ray diffraction spectrometer (Cu Kα, λ = 1.54056 Å). The crystal size was calculated using Scherrer equation ( $D = k\lambda/B\cos\theta$ ). The Fourier Transform Infra-Red (FT-IR) spectra were recorded for KBr disks containing the powder sample with an FT-IR spectrometer (MAGNA-560). X-ray photoelectron spectroscopy (XPS) measurements were carried out with an ESCA Lab 220i-XL spectrometer by using an unmonochromated Al Kα (1486.6 eV) X-ray source. All of the spectra were calibrated to the binding energy of the adventitious C1s peak at 284.8 eV. Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) analyses were conducted using a JEM-2010FEF, for which the samples were prepared by applying a drop of ethanol suspension onto an amorphous carbon-coated copper grid and dried naturally. The pH values in this work were measured by Model PHS-25 Meter.

## 3. Results and discussion

### 3.1. Structures of In-B-TiO<sub>2</sub> pHx

To investigate the crystal structures of the obtained samples, XRD technique was used. Fig. 1 shows the XRD patterns of pure TiO<sub>2</sub>, In-TiO<sub>2</sub>, B-TiO<sub>2</sub>, In-B-TiO<sub>2</sub> pHx and InBO<sub>3</sub> samples. Pure TiO<sub>2</sub> exhibits a typical anatase structure [12]. In case of In-TiO<sub>2</sub> and B-TiO<sub>2</sub>, they still remain anatase phase [20]. For In-B-TiO<sub>2</sub> pHx

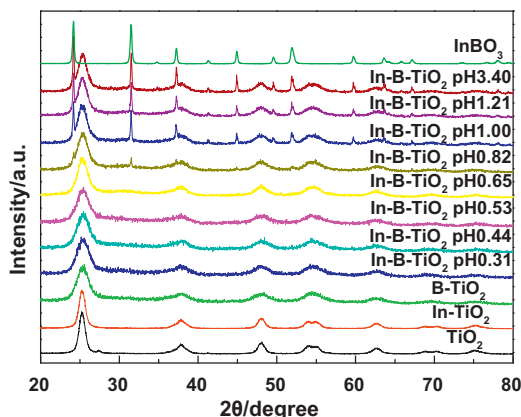


Fig. 1. XRD patterns of TiO<sub>2</sub>, In-TiO<sub>2</sub>, B-TiO<sub>2</sub>, In-B-TiO<sub>2</sub> pHx and InBO<sub>3</sub> samples.

**Table 2**  
The lattice parameters, cell volume and crystal size of all samples.

Sample	Cell parameters (Å)		Cell volume (Å <sup>3</sup> )	Crystallite size (nm)
	a = b	c		
Pure TiO <sub>2</sub>	3.789	9.498	136.40	10
In-TiO <sub>2</sub>	3.789	9.499	136.39	9.5
B-TiO <sub>2</sub>	3.808	9.575	138.84	4.5
In-B-TiO <sub>2</sub> pH0.31	3.805	9.585	138.77	2.8
In-B-TiO <sub>2</sub> pH0.44	3.801	9.586	138.50	3.6
In-B-TiO <sub>2</sub> pH0.53	3.798	9.576	138.13	4.3
In-B-TiO <sub>2</sub> pH0.65	3.800	9.523	137.51	4.5
In-B-TiO <sub>2</sub> pH0.82	3.795	9.524	137.17	4.7
In-B-TiO <sub>2</sub> pH1.00	3.793	9.547	136.85	5.0
In-B-TiO <sub>2</sub> pH1.21	3.797	9.471	136.55	5.7
In-B-TiO <sub>2</sub> pH3.40	3.791	9.498	136.50	6.5

samples, only anatase is observed when the pH values increase from 0.31 to 0.65. For In-B-TiO<sub>2</sub> pH0.82 sample, besides the anatase peaks, a few new diffraction peaks at 24.3°, 31.6°, 37.4°, 45.0° and 51.9° are found, corresponding to (1 0 2), (1 0 4), (1 1 0), (2 0 2) and (1 1 6) crystal planes of InBO<sub>3</sub> [23,24], respectively. This indicates that a small amount of InBO<sub>3</sub> is formed in the In-B-TiO<sub>2</sub> pH0.82 sample when the pH value is 0.82. Furthermore, the peak intensities of InBO<sub>3</sub> increase with the increase of the pH values from 0.82 to 3.40, suggesting the increase of pH values is benefit to the formation of InBO<sub>3</sub> for In-B-TiO<sub>2</sub> pHx samples. There is no other characteristic diffraction peaks (such as InCl<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>) detected for all samples. The XRD patterns are used to determine the lattice parameters, cell volume and crystal size of samples by Scherrer equation ( $D = k\lambda/B\cos\theta$ ), which are summarized in Table 2. It is found that the lattice parameters and cell volume of In-TiO<sub>2</sub> are almost the same as those of pure TiO<sub>2</sub>, which suggesting In ions are not doped into TiO<sub>2</sub> lattice. Most likely, it has been demonstrated by our previous works that the In links with O and Cl to form O-In-Cl<sub>x</sub> (x = 1 or 2) species on the surface of TiO<sub>2</sub> [20]. Moreover, compared with pure TiO<sub>2</sub>, the lattice parameters and cell volume of B-TiO<sub>2</sub> increase, implying B ions are doped into TiO<sub>2</sub> lattice in interstitial mode [25]. Compared with B-TiO<sub>2</sub>, the lattice parameters and cell volume remain almost unchanged after the addition of In ions for In-B-TiO<sub>2</sub> pH0.31 sample, implying that the B ions are still doped into TiO<sub>2</sub> lattice in interstitial mode and the In ions might exist as unique surface O-In-Cl<sub>x</sub> species. For In-B-TiO<sub>2</sub> pHx samples, the crystal sizes of all samples are smaller than that of pure TiO<sub>2</sub>, suggesting that the introduction of In and B ions could inhibit the grain growth of TiO<sub>2</sub> effectively because of dissimilar boundaries [21]. In addition, with the increase of pH values, the lattice parameters and cell volume decrease gradually while the crystal size of increases, accompanied with the occurrence of InBO<sub>3</sub> which further become stronger (Fig. 1) for In-B-TiO<sub>2</sub> pHx samples. These results imply the transition of the existing states for In and B ions in TiO<sub>2</sub> from doping mode to InBO<sub>3</sub> with the increase of pH values in preparation process. The chemical states and the doping mode of In and B ions for In-B-TiO<sub>2</sub> pHx will be confirmed by FT-IR, HRTEM and XPS.

### 3.2. Existing states of In and B ions in In-B-TiO<sub>2</sub> pHx

#### 3.2.1. FT-IR

Fig. 2 shows FT-IR spectra of TiO<sub>2</sub>, In-TiO<sub>2</sub>, B-TiO<sub>2</sub>, In-B-TiO<sub>2</sub> pHx and InBO<sub>3</sub>. The bands at about 3430 cm<sup>-1</sup> and 1630 cm<sup>-1</sup> were assigned to stretching vibration and the bending vibration of H<sub>2</sub>O adsorbed on TiO<sub>2</sub> surface, respectively [26]. For B-TiO<sub>2</sub> sample, the band at about 1340 cm<sup>-1</sup> was assigned to the B-O stretching vibrations of interstitial doped B (B links with three O atoms) in TiO<sub>2</sub> [19,27]. The band at about 1240 cm<sup>-1</sup> was assigned to the B-O stretching vibrations of [BO<sub>3</sub>] unit in the InBO<sub>3</sub> [28]. Furthermore,

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