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Article

Influence of Bi chemical state on the photocatalytic performance of Bi-doped NaTaO₃

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ABSTRACT

NaBiO₃ and Bi(NO₃)₃ were used to synthesize Bi-doped NaTaO₃. The influence of the Bi chemical state on the photocatalytic activity was investigated using X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and diffused reflectance spectroscopy to study the structure, chemical state and light absorption characteristics, respectively. The photocatalytic activity was evaluated by the H₂ evolution water splitting reaction. The monoclinic phase of NaTaO₃ remained intact for the two Bi-doped samples, but the Ta–O–Ta bond was distorted from 180° after Bi doping. XPS results indicated that Bi³⁺ was doped into NaTaO₃ with the Bi(NO₃)₃ precursor, while Bi⁵⁺ and Bi³⁺ were doped into NaTaO₃ with the NaBiO₃ precursor. The two samples showed identical light absorption, where doping with Bi extended the light absorption to long wavelength light as expected. However, Bi³⁺ doping did not promote the photocatalytic activity of NaTaO₃, while Bi⁵⁺ and Bi³⁺ doping did. The distorted Ta–O–Ta bond from 180° due to doping with Bi was detrimental for charge carrier transfer in the photocatalytic process. In contrast, the vacancies or defects in the NaTaO₃ lattice induced by Bi doping for charge balance were beneficial for charge carrier separation. The opposing action of these two factors resulted in the activity of the Bi³⁺-doped sample being comparable with pristine NaTaO₃. For Bi⁵⁺- and Bi³⁺-doped NaTaO₃, a high concentration of defects was induced by the high valence Bi⁵⁺ ion and this led to its higher photocatalytic activity. Our results indicated that charge carrier transfer is a priority factor in the photocatalytic process and the doping of a high valence ion in the ABO₃ structure is a way to promote the separation of charge carriers.

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1. Introduction

The photocatalytic water splitting reaction has been extensively studied as a conversion system to solve the energy issues nowadays [1,2]. A series of oxides with the ABO₃ perovskite structure (e.g. NaTaO₃ [2], AgTaO₃ [3], KNbO₃ [4], CaTiO₃ [5], and SrTiO₃ [6]) have been found to be highly active photocatalysts [7]. The ideal structure of the perovskite-type oxides

(ABO₃) is a network of corner-linked octahedra. The B cations are located at the center of the octahedra ([BO₆]) and the A cations are in the space coordinating with 12 oxygen atoms between the octahedra ([AO₁₂]). The [BO₆] octahedra is usually used for energy band construction when *d*⁰/*d*¹⁰ transition metal ions are the B-site [7]. For instance, it is believed that in ATaO₃ and ANbO₃ (A = Na and K), the valence band is formed by the O 2*p* orbital and the conduction band is formed by Ta 5*d*

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and Nb 4d orbital [8].

Although the ABO₃ perovskites are well known as promising photocatalysts in solar energy utilization, they still suffer from the problems of a restricted light response and highly inhibited photo-generated carrier activity. Doping a foreign element is a usual strategy to solve these problems and improve the photocatalytic performance [9,10]. In previous reports, visible light activity was observed when V⁵⁺ was substituted for Ta⁵⁺ in NaTaO₃ samples to extend the light response [11]. Doping Cu²⁺ at the B-site in NaTaO₃ also extended the light response, but excess Cu²⁺ would serve as a recombination center, which decrease the photocatalytic activity [12]. However, Zr⁴⁺ doping at the B-site mainly affected the behavior of the charge carriers instead of the energy band structure in KTaO₃ [4]. The A-site substitution can also influence the perovskite photocatalytic activity. Hwang's group [13] found in La_xNa_{1-x}TaO₃ samples that doping of La at the A-site caused little variation in the energy band structure, and the change in H₂ evolution rate was attributed to better charge carrier separation and migration. Similar results were also reported for Na_{1-x}K_xTaO₃ [14] and another NaTaO₃:La sample [15].

The type of doped ion (e.g. alkali ions [14], alkaline earth ions [16], and lanthanides [17]), position of the doped ion (A- or B-sites) and the valence state of the doped ion in the perovskite are all factors that can affect the photocatalytic performance [18]. However, the function of the doped ion in the perovskite is still debated, and it is harder to discriminate the function of the doped ion when co-doping multi-valence metal ions into both A- and B-sites of ABO₃ [19–26]. The physico-chemical properties of the material are significantly altered by the accommodating site and the valence state of the doped cation. Hence, it is necessary to precisely control the occupation site and valence state of the doped ion in the ABO₃ structure to clarify its function in photocatalysis.

In this work, NaBiO₃ and Bi(NO₃)₃ were used as the Bi precursor to synthesize Bi-doped NaTaO₃ with different Bi chemical states, and the influence of the Bi ion chemical state on the photocatalytic activity was investigated. It was found that Bi doping mainly influenced charge carrier transfer in the photocatalytic process, and a high valence state ion dopant benefits defect generation to promote the separation of charge carriers.

2. Experimental

2.1. Materials and synthesis

Ta₂O₅ (>99%) was purchased from Aladdin Industrial Corporation (USA). The other reagents (analytically pure) were purchased from Guangzhou Chemical Reagent Factory. All reagents were used as received without further purification. Double distilled water was used in all experiments.

A solid state reaction was used to synthesize pristine and Bi-doped NaTaO₃. NaBiO₃·2H₂O and Bi(NO₃)₃·5H₂O were used as the Bi source for Bi doping of the NaTaO₃ samples. A typical solid state reaction is described in the following. A mixture of the starting materials of Ta₂O₅, Na₂CO₃, and Bi source was pressed into pellets, calcined in air at 1000 °C for 10 h and then

ground into fine powder. The powder was washed with distilled water, then filtered and dried at 120 °C for use. The molar ratio of Na:Ta:Bi was 1.05:1:0.02 in the starting mixture of Na₂CO₃, Ta₂O₅, and Bi precursor, where the 5% excess Na was to compensate the volatilization loss. The samples were denoted as V-0.02 and III-0.02, where V and III showed the valence state of the Bi source, and 0.02 is from the Bi:Ta ratio.

For comparison, Bi-doped NaTaO₃ with 0.02 molar ratio of Bi to Ta was prepared by the hydrothermal method based on the literature [25]. First, the starting materials of Ta₂O₅ and NaBiO₃·2H₂O were dispersed in NaOH aqueous solution (10 mol/L) by strong stirring for 2 h. Then, the slurry was poured into a Teflon-lined autoclave and heated at 180 °C for 48 h. After filtering and washing, the resulting powder was dried at 120 °C to get the final product. In this method, excess Na ion was introduced by a strong base. The sample was denoted as HV-0.02 NaTaO₃.

2.2. Characterization

The crystal structure of the samples was analyzed by an X-ray diffractometer (XRD, Bruker, D8 Advance, Germany) with a Cu K α radiation source at a scanning rate of 10°/min for all samples. Raman spectra were measured with a Laser Micro-Raman Spectrometer (Renishaw inVia) with a Ar⁺ laser with 633 nm excitation. The chemical environment of doped Bi was studied by X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra XPS, ESCALab250, American; hemispherical electron analyser, 120W Al K α X-ray source, *h* ν 1486.6 eV). The C 1s reference of 284.1 eV was chosen for calibration. Diffuse reflection spectra (DSR) were recorded on a UV-Vis spectrophotometer (Shimadzu, UV-3150, Japan, equipped with an integrating sphere) to study the optical properties of the samples.

2.3. Photocatalytic evaluation

The photocatalytic activity of the samples was examined in a closed gas circulation and evacuation system. Typically, 0.1 g catalyst powder was dispersed in 100 mL methanol aqueous solution (20 vol%) in a Pyrex reaction cell. Pt was photodeposited on the catalyst with 0.3 wt% loading in situ using a H₂PtCl₆·6H₂O precursor under irradiation. The light source was a 300 W Xe lamp (Beijing Changtuo, PLS-SXE-300UV) with an intensity of 200 mW/cm². The light absorption spectra were shown elsewhere [27]. The amount of produced hydrogen was analyzed using an online gas chromatograph (Shanghai Tianmei, GC-7890II, China) with a thermal conductivity detector and a molecular sieve 5A column and N₂ carrier.

3. Results and discussion

3.1. Crystal structure of Bi doped NaTaO₃

Figure 1 shows the XRD patterns of the NaTaO₃ and Bi-doped NaTaO₃ samples. The XRD pattern of NaTaO₃ was in agreement with PDF #74-2480 (*P2/m* with *a* = *c* = 0.3907 nm, *b* = 0.3904 nm, and $\alpha = \gamma = 90^\circ$, $\beta = 90.1^\circ$), and indicated the crys-

Fig. 1. XRD patterns of NaTaO₃ (1), V-0.02 NaTaO₃ (2) and III-0.02 NaTaO₃ (3).

tal structure to be the monoclinic phase. For the Bi-doped NaTaO₃ samples, the diffraction patterns were similar to pristine NaTaO₃, and no additional peak was detected. This suggested that the monoclinic phase of NaTaO₃ remained intact and no impurity existed in Bi-doped NaTaO₃. It was reported that the Na/Ta molar ratio of the starting materials affects the site occupancy of Bi at the A- or B-site in the NaTaO₃ lattice, and Bi predominantly occupied the Na-site under a Na-deficient condition [24]. In our case, though 5% excess Na ion was introduced in the synthesizing process, the Na:Ta molar ratio in pristine NaTaO₃ was 1:1.9 from the quantitative analysis by XPS. Thus, it was proposed that the Bi ion was located at the A site because of the low Na/Ta ratio.

3.2. Raman spectra

Figure 2 shows the Raman spectra of the NaTaO₃ and Bi-NaTaO₃ samples. Two distinct peaks at 578 and 860 cm⁻¹ were observed for both the V-0.02 and III-0.02 samples, which were absent from pristine NaTaO₃. These two peaks corresponded to the Stokes-shifted signals from the transverse and longitudinal optical phonons [28]. The appearance of these two

Fig. 2. Raman spectra of NaTaO₃ (1), V-0.02 NaTaO₃ (2) and III-0.02 NaTaO₃ (3).

peaks indicated that Bi ion doping induced a band gap change in NaTaO₃ [29].

In addition to the energy band structure, Raman spectroscopy of solids is extremely sensitive to the local deviation from the average periodicity, thereby making it a valuable probe of the local structure. The region of 850 to 950 cm⁻¹ was assigned to the valence vibrations of the Ta–O–Ta bridges that were inactive in the Raman spectra for the centrosymmetric structure [30]. The appearance of 860 cm⁻¹ for Bi-doped NaTaO₃ indicated a distorted B–O–B bond from the bond angle of 180°, which has an impact on the photo-induced charge carrier migration in the photocatalyst [14].

3.3. Chemical state of Bi in NaTaO₃

The chemical environment and oxidation state of Bi in NaTaO₃ were studied by X-ray photoelectron spectroscopy (XPS). Figure 3 shows XPS spectra of the samples. The Bi 4f_{7/2} and 4f_{5/2} peaks were at 158 and 164 eV, respectively. For comparison, the XPS spectra of Bi 4f in Bi₂O₃, NaBiO₃, BiTaO₄ and HV-0.02 (synthesized with the hydrothermal method) were also measured to deduce the position and valence state information of the doped Bi ion. The binding energy (BE) of Bi 4f_{7/2} for all the samples is summarized in Table 1.

In the reference samples, Bi₂O₃ and NaBiO₃ were the precursors of Bi with the +3 and +5 chemical valence, respectively. The BE positions of Bi 4f_{7/2} in Bi₂O₃ and NaBiO₃ were 158.3 and 158.8 eV, respectively, and the 0.5 eV chemical shift was ascribed to the oxidation state difference. For BiTaO₃ with the perovskite structure, the Bi ion is located at the A-site with +3

Fig. 3. XPS spectra of Bi 4f_{7/2} and Bi 4f_{5/2} of Bi₂O₃, HV-0.02 NaTaO₃, NaBiO₃, III-0.02 NaTaO₃, BiTaO₄ and V-0.02 NaTaO₃.

Table 1

Bi 4f_{7/2} binding energy of Bi₂O₃, HV-0.02 NaTaO₃, NaBiO₃, III-0.02 NaTaO₃, BiTaO₄ and V-0.02 NaTaO₃.

Sample	Binding energy of Bi 4f _{7/2} (eV)
V-0.02 NaTaO ₃	159.0, 159.5
III-0.02 NaTaO ₃	158.9
BiTaO ₄	159.0
NaBiO ₃	158.8
Bi ₂ O ₃	158.3
HV-0.02 NaTaO ₃	158.7

chemical valence. The BE position of BiTaO₃ was 159.0 eV, which was higher than 158.3 eV for Bi³⁺ in Bi₂O₃ and 158.8 eV for Bi⁵⁺ in NaBiO₃. This suggested that the Bi chemical environment exhibited more influence on its BE than its oxidation state, and the A-site Bi substitution for Na can significantly increase the BE.

For HV-0.02 NaTaO₃, the Bi ion is located at the B-site in NaTaO₃ with the +5 chemical valence [25]. HV-0.02 NaTaO₃ was synthesized by the hydrothermal method with the strong base of sodium hydroxide, where the low hydrothermal temperature avoided the decomposition of NaBiO₃ to Bi³⁺ and excess sodium ion in the strong base made the Bi⁵⁺ substituted for Ta⁵⁺ at the B-site in NaTaO₃. The position of the BE in HV-0.02 NaTaO₃ was 158.7 eV, which was comparable to the 158.8 eV for Bi⁵⁺ in NaBiO₃. Thus, it was proposed that the B-site Bi substitution for Ta in NaTaO₃ had little impact on the BE position of the Bi ion.

For the III-0.02 NaTaO₃ sample synthesized with the Bi₂O₃ precursor, the position of the BE was 158.9 eV, which was close to 159.0 eV for Bi³⁺ at the A-site in BiTaO₃. Therefore, it was deduced that Bi³⁺ substituted for Na⁺ at the A-site in the III-0.02 sample. For the V-0.02 sample synthesized with the NaBiO₃ precursor, the BE position was higher than for III-0.02 in Fig. 3. Due to the pyrolysis of NaBiO₃, it was reasonable that Bi³⁺ and Bi⁵⁺ would coexist in the V-0.02 sample under the high temperature synthesis condition. Therefore, the XPS curve of V-0.02 was fit by two peaks with the BE positions at 159.0 and 159.5 eV. The lower BE at 159.0 eV was the same as the BE for Bi³⁺ at the A-site in BiTaO₃, therefore, this peak was identified as the Bi³⁺ substitution for Na in the V-0.02 sample. For the other peak at 159.5 eV in V-0.02, three possible assignments should be taken into account. First is the A-site Bi⁵⁺ substitution for Na in V-0.02, second is the B-site Bi⁵⁺ substitution for Ta in V-0.02, and third is the Bi³⁺ in a different chemical environment reported in a previous work [31].

In the above paragraph, it was discussed that the BE of Bi⁵⁺ substitution for Ta in HV-0.02 was 158.7 eV, which is far lower than 159.5 eV. So the second possibility of the B-site Bi⁵⁺ substitution for Ta was excluded. Based on the BE difference of Bi₂O₃ and III-0.02 (Bi³⁺ in A-site), and of NaBiO₃ and HV-0.02 (Bi⁵⁺ in B-site), it was proposed that the A-site substitution can more significantly increase the BE of the Bi ion than the B site, and the chemical environment had a more significant influence on the BE than the oxidation state. For Bi³⁺ in a different chemical environment proposed in the literature [31], the BE should not be as high as 159.5 eV, considering its +3 oxidation state and that the chemical environment was different from the A-site. That is, the third possibility of Bi³⁺ in a different chemical environment was also excluded. Therefore, we assigned the 159.5 eV peak to the A-site Bi⁵⁺ substitution for Na from an overall consideration of the chemical states. This remains to be further explored in future work.

Thus, we identified that the Bi³⁺ doping occurred at the A-site in the III-0.02 sample, while Bi³⁺ and Bi⁵⁺ co-doping at the A-site occurred in the V-0.02 sample. It was worth mentioning that the Bi⁵⁺ content in V-0.02 was far smaller than Bi³⁺ from the two components of the XPS fitting in Fig. 3. That is,

most of NaBiO₃ was pyrolysed to Bi³⁺, and only a small amount of Bi⁵⁺ was doped into the NaTaO₃ cell. The Bi³⁺ and Bi⁵⁺ co-existence in NaTaO₃ induced the production of Na vacancies or interstitial O atoms in the lattice for charge compensation, which will have an impact on the photocatalytic process and interstitial charge migration [23].

3.4. Optical absorption of Bi-doped NaTaO₃

Diffused reflectance spectra of pristine and Bi-doped NaTaO₃ samples are shown in Fig. 4. The steep edges and intense absorption of NaTaO₃ originated from the transition from the valence band to the conduction band. A shoulder peak on the steep absorption edge of NaTaO₃ was observed in the Bi-doped V-0.02 and III-0.02 samples, which indicated that doped Bi ions extended the absorption edge to a longer wavelength. The valence band (VB) was mainly composed of O 2*p* orbitals while the conduction band (CB) mainly consists of Ta 5*d* orbitals for NaTaO₃ [18]. This shoulder peak in the absorption spectra can be attributed to the transition from the localized impurity state of the Bi ion dopant. An isolated donor energy state was formed in the forbidden band of NaTaO₃ during Bi doping, from considering the energy structure of BiTaO₄ [32].

3.5. Photocatalytic H₂ generation

The photocatalytic activity of pristine and Bi-doped NaTaO₃ samples were examined by splitting water into H₂ under simulated solar light. For all samples, H₂ generation was linear with irradiation time as shown in Fig. 5. The highest activity was observed for the V-0.02 sample, and the photocatalytic activity of the III-0.02 sample was comparable with that of NaTaO₃.

In the absorption spectra, almost similar absorption profiles were observed for the V-0.02 and III-0.02 samples. The photocatalytic activity distinctly increased with the V-0.02 sample, but remained unchanged with III-0.02. Due to the low Bi ion content in NaTaO₃, the slight extending of light absorption to the visible region contributed little to the photocatalytic activity. In addition to light absorption for charge carrier generation, charge transfer inside the photocatalyst is an important factor

Fig. 4. UV-Vis diffused reflectance spectra of NaTaO₃ (1), V-0.02 NaTaO₃ (2) and III-0.02 NaTaO₃ (3).

Fig. 5. Photocatalytic H₂ evolution of NaTaO₃ (1), V-0.02 NaTaO₃ (2) and III-0.02 NaTaO₃ (3).

that affects the photocatalytic activity. The Raman results indicated that Bi ion doping induced a distorted B–O–B bond from the bond angle of 180°, which was detrimental for charge carrier migration in NaTaO₃. The Bi ion dopant induced the generation of a Na vacancy or an interstitial O in the lattice for charge compensation. These defects served as charge traps that promote the separation of the charge carriers and therefore the photocatalytic activity [27]. The separate actions of the positive and negative factors in the III-0.02 sample led to unchanged photocatalytic activity compared to pristine NaTaO₃. For the V-0.02 sample, it was found in the XPS data that both Bi⁵⁺ and Bi³⁺ ions were doped into the A-site. Compared to the III-0.02 sample, there were more defects in the V-0.02 sample that existed as high valence state Bi⁵⁺ ions in the lattice. That is, the separation efficiency of the charge carriers in the V-0.02 sample was higher than III-0.02. Therefore, a higher photocatalytic activity was obtained with V-0.02. Our result indicated that the occupation by a high valence ion at the A-site in the ABO₃ per-

ovskite structure was more favorable for the enhancement of photocatalytic activity.

4. Conclusion

Doping of Bi ion into NaTaO₃ extended the light response to the visible light region. At the same time, it induced a distorted Ta–O–Ta bond and the generation of defects in the lattice, which influenced the charge carrier migration. Bi³⁺ substitution for Na did not increase the photocatalytic activity as expected. On the other hand, the occupancy by high valence state Bi⁵⁺ at the A-site increased the photocatalytic activity. Our results indicated that the charge transfer process is the key factor for the enhancement of photocatalytic activity, and it was more important than the extending of the range of light response. It was proposed that increasing the defect amount by doping with a high valence state ion in the A-site of the perovskite structure is a strategy to promote the separation of the charge carriers and thus the enhancement of photocatalytic activity.

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Graphical Abstract

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Influence of Bi chemical state on the photocatalytic performance of Bi-doped NaTaO₃

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Doping of Bi⁵⁺ and Bi³⁺ in NaTaO₃ substituting for Na⁺ promoted the separation of charge carriers, and the photocatalytic for H₂ evolution was enhanced.

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Bi掺杂NaTaO₃中Bi的化学价态对其光催化性能的影响

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摘要: 分别采用NaBiO₃和Bi(NO₃)₃为Bi源制备了Bi掺杂NaTaO₃光催化剂,研究了Bi离子的价态对NaTaO₃光催化分解水制氢性能的影响。采用X射线衍射(XRD)、拉曼光谱、X射线光电子能谱(XPS)和紫外-可见吸收光谱研究了催化剂的晶体结构、Bi离子的化学状态和催化剂的光学吸收性能。以光催化分解水制氢反应研究了Bi离子掺杂NaTaO₃的催化性能。XRD结果表明,对于两个不同Bi源掺杂的NaTaO₃样品,Bi离子的掺杂没有改变催化剂的单斜相结构,但拉曼光谱证实Bi离子的掺杂致使Ta–O–Ta键角偏离了180°。XPS结果表明,以Bi(NO₃)₃为Bi源时,Bi离子以Bi³⁺掺杂于NaTaO₃的A位;当以NaBiO₃为原料时,Bi³⁺和Bi⁵⁺共掺杂于NaTaO₃的A位。两种不同Bi源掺杂得到的样品在紫外-可见吸收光谱中给出了相似的光学吸收,但Bi³⁺的掺杂对NaTaO₃光催化性能影响不大,而Bi³⁺和Bi⁵⁺共掺杂大大提高了NaTaO₃的光解水制氢性能。Bi离子取代Na离子在A位的掺杂,在NaTaO₃结构中引入了能够促进载流子分离的空位和缺陷;与此同时,Bi的掺杂导致Ta–O–Ta键角偏离180°而不利于载流子迁移。对于Bi³⁺掺杂的NaTaO₃样品,这两种作用相互抵消,使得其催化性能与NaTaO₃相比没有变化;而Bi³⁺和Bi⁵⁺的共掺杂和高价态Bi⁵⁺的掺杂引入了更多的空位和缺陷,提高了光生电子-空穴的分离效率,从而提高了光催化产氢性能。研究表明,光催化过程中载流子的迁移是影响催化性能的重要因素,而在ABO₃钙钛矿结构的A位引入高价态离子是促进光生载流子分离的有效途径。

关键词: 光催化剂; 钽酸钠; Bi掺杂; 化学价态; 水分解

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