Improvement of visible-light photo catalytic activity of BiNbO$_4$ by Ti doping

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Abstract. Optimized doped BiNbO$_4$ is necessary for efficient visible light harvesting and perform excellent visible-light photocatalytic activity in degradation of organic pollutants. The Ti doped BiNbO$_4$ polycrystalline powders of BiNb$_{1-x}$TixO$_4$ (x = 0, 0.03, 0.05, 0.08, 0.10, 0.15) were synthesized by a traditional solid-state reaction method. The effects of Ti dopant on the structural, optical and visible-light photocatalytic properties were investigated. The X-ray diffraction (XRD) results show that all the samples maintain orthorhombic structure with a space group of Pnna without any impurity phases, suggesting the Ti ions were substitutionally incorporated in the BiNbO$_4$ lattice. With the increase of Ti concentration, the particle sizes and the specific surface area have no obviously variation, while the band gap (E$_g$) of each sample is slightly decreased compared with the pure BiNbO$_4$. Ti doped samples exhibits excellent visible-light photocatalytic properties and could be a potential candidate for photocatalytic degradation of organic pollutants. The improved visible-light photocatalytic activity could be attributed to the enhancement of oxidation-reduction power by a slight downshift of the conduction band and an upshift of the valence band.

1. Introduction

With the rapid development of industries, more and more people pay attention to the serious environmental pollutant remediation and energy shortage problems [1-3]. It is urgent for human to handle hardly degradable contaminants and find new green energy resource. Developing photo catalysts is a particularly effective way of organics degradation and producing hydrogen of clean energy. In 1972, Fujishima firstly used photo catalysts titanium dioxide (TiO$_2$) to decompose water into hydrogen and oxygen under ultraviolet irradiation [4]. However, the wide band gap of semiconductor TiO$_2$ makes it only be activated under UV light, which means less than 5% of sunlight energy could be utilized during photo catalytic reaction [5, 6]. Since then, various metal oxides semiconductor except titanium dioxide have been studied because of their non-toxic stable chemical properties, simple to preparation and low cost [7]. Among them, metal oxide compounds containing bismuth have been found the active photo catalytic performance even under visible light irradiation [8-10], which could be attributed to the suitable band gap caused by the O 2$p$ and Bi 6$s$ orbital hybridization [11].
Compared with the most popular photo catalytic material TiO₂, BiNbO₄ was reported more excellent photo catalytic efficiency for H₂ evolution under visible light [12]. However, the large band gap and the high recombination rate of photo generated charge carriers are the weak points of BiNbO₄, which limited its visible-light photo catalytic activity [13]. In order to enhance the visible-light photo catalytic performance, doping a foreign element is an effective way to adjust band gap for absorbing the visible light and change physical properties of materials, which beneficial to the photo-generated carrier migration [14]. Zou et al. observed that the BiTaₓ₋ₓNb₂O₅ samples could respectively decompose CH₃OH/H₂O aqueous solution and H₂O into hydrogen under UV irradiation, but it also showed optical absorption in visible light region, suggesting its promising visible-light photo catalytic activity [12, 15]. Nisar et al. studied that the BiNbO₄ co-doping with N and Mo was more stable than mono-doping and adjusted the band gap from 2.55eV to 1.74eV, which caused by the hybridization of N 2p and O 2p states with increasing the valance band maximum and the mixing of Mo 4d and O 2p state with decreasing the conduction band minimum [16]. Cristiane et al. reported the Cr dopant in BiNb (Ta) O₄ could enhance the photo catalytic ability of hydrogen evolution, while the Mo doping in BiNb (Ta) O₄ could enhance the photo catalytic ability of organic compounds degradation [17]. In this paper, we propose that doping a 3d transition metal element like titanium in BiNbO₄ may modify the electronic structure to improve its ability of visible-light response. And the doping of lower valance state of Ti⁴⁺ ion to replace the higher valance state of Nb⁵⁺ generates the more oxygen vacancy (Vo), which reduce the probability of photo-generated carriers recombination and enhance the visible-light photo catalytic properties.

We investigated deeply the structures, morphologies, the specific surface areas and optical properties of BiNbₓ₋ₓTiₓO₄ (x = 0, 0.03, 0.05, 0.08, 0.10, 0.15) prepared by the solid states reaction method. The visible-light photo catalytic properties were evaluated with the degradation of methyl violet (MV) under visible light irradiation.

2. Experiments

2.1. A. Catalyst preparation

BiNbₓ₋ₓTiₓO₄ (x = 0-0.15) were synthesized by a traditional solid states reaction process. We used Bi₂O₃ (AR), Nb₂O₅ (99.9%), TiO₂ (99%) as raw materials for the preparation of BiNbₓ₋ₓTiₓO₄ (x = 0-0.15) samples. The mixture was putted in a agate jar with an alcohol moderate medium, milled at 300 r·min⁻¹ for 12 hours. After milling, slurries were dried at 80°C to become powder samples. Finally, sintering powders at 950°C for 12 hours with the heating rate of 10°C·min⁻¹ in a controlled atmosphere furnace.

2.2. Characterization

(1). The crystal structure of the samples was observed by a Bruker D8 ADVANCE X-ray diffractometer (λ=1.5418 Å) using Cu Kα radiation. The morphology characteristics of the samples were detected under a Field Emission Scanning Electron Microscopy (Zeiss Merlin). The specific surface area was measured by a Brunauer-Emmett-Teller method on a surface area apparatus (Beckman Coulter SA3100) using N₂ adsorption/desorption method at liquid nitrogen temperature (77 K). The UV-Visible (UV-vis) absorption spectra over a range of 300-1000 nm wavelength were tested by an Ocean Optical Fiber Spectrometer (USB 4000) equipped with integration sphere.

(2). The photo catalytic performance of the BiNbₓ₋ₓTiₓO₄ (x = 0-0.15) powders was characterized by for the degradation rate of methyl violet (MV) under visible light irradiation at the natural pH condition. The original concentration of MV was 10 mg/L. The suspension mixed with 0.04g photo catalyst and 40 mL MV solution was agitated for two hours in the absence of light to achieve the adsorption equilibrium. After dark process, a 500W Xe lamp (GXZ500, SHANGHAIJIJIGUANG) was turned on as a visible light simulator and liquid samples was measured every 30 minutes. Each time before the absorption measurement, the sample solution should be centrifuged twice at 6000 rpm for 5 minutes in order to separate the sample particles from the MV solution. An Ocean Optical Fiber
Spectrometer (USB4000) was used to monitor the degradation process through the residual dye MV concentration, which could be analyzed by measuring the characteristic absorption peak at 582 nm [18].

3. Results and discussion

Figure 1 reveals XRD patterns of BiNb\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{4} \((x = 0.0, 0.03, 0.05, 0.08, 0.1, 0.15)\) at room temperature. By contrast with the standard powder diffraction file database [JCPDS No. 16-0295], all diffraction peaks of the samples are identified as the orthorhombic structure with a space group of \(Pnma\). With the increase of Ti doping, there is no obvious sign of phase transition from the XRD patterns. Moreover, no trace of any typical diffraction peak related to crystalline TiO\textsubscript{2} and other Ti oxides appear, indicating a single phase of the samples [19]. Therefore, we can assume that Ti ions were substitutionally incorporated in the BiNbO\textsubscript{4} lattice.

![Figure 1. XRD patterns of BiNb\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{4} with different x values (x = 0-0.15)](image)

The surface microstructures of different Ti concentration in BiNbO\textsubscript{4} compositions are observed by Field Effect Scanning Electron Microscopy (FESEM). The morphologies of samples seem irregular in Figure 2. Calculated by Nano-Measurer, table.1 has shown that the average particle sizes of the samples are about 1.5-2 \(\mu\text{m}\) in diameter and have no obvious variation with increasing of Ti doping.

![Figure 2. FESEM images of BiNb\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{4} with x = 0-0.15](image)

The high specific area could provide more active sites for the oxidation-reduction reaction and make the degraded molecules reach the particle surface easier during the degradation process [20]. Table. 1 summarizes the average grain sizes and the specific surface areas of BiNb\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{4} powders. It can be clearly seen that the surface area of Ti doped samples show no obvious variation, which is consistent to the results of the average particle sizes. The results indicate that all of the samples have similar adsorption ability.
Table 1. The grain size, specific surface area and band gap of BiNb$_{1-x}$Ti$_x$O$_4$ ($x = 0$- 0.15).

| Ti concentration | $x = 0.0$ | $x = 0.03$ | $x = 0.05$ | $x = 0.08$ | $x = 0.10$ | $x = 0.15$ |
|------------------|-----------|------------|------------|------------|------------|------------|
| Grain size (μm)  | 1.67      | 2.03       | 2.02       | 2.08       | 1.43       | 1.46       |
| Specific surface area (m$^2$/g) | 4.749 | 4.178 | 4.161 | 6.777 | 4.848 | 3.786 |
| Band gap (eV)    | 3.09      | 3.02       | 3.0        | 2.99       | 2.98       | 2.93       |

The selected room temperature UV-Vis absorbance spectra of BiNb$_{1-x}$Ti$_x$O$_4$ ($x = 0$, 0.03, 0.08, 0.10, 0.15) samples are shown in the Figure 3. The absorption edge of pure BiNbO$_4$ is at about 450 nm, which have the ability to respond the visible light ($\lambda > 400$ nm). Compared to the pure sample, the absorption edge occurs slightly red shift with increasing of Ti concentration.

According to the UV-vis absorption spectra, we can use the Tau’s formula to get the band gap values ($E_g$) of the samples. There is Tau’s relation: $\alpha h\nu = C(h\nu-E_g)^n$, where $\alpha$ is the absorption coefficient, $h$ is Planck constant, $\nu$ is frequency of the light and $C$ is a constant [21]. BiNbO$_4$ is the direct band gap, so the parameter $n$ should be equal to 1/2 [22]. Extending of the tangent line of these graphs to $(\alpha h\nu)^2 = 0$ could calculate the values of $E_g$ as shown in the inset of Figure 3. The plot of $E_g$ against Ti concentration $x$ are displayed in Figure 4 and the data of the band gap are also shown in table 1. A monotonic decline of $E_g$ with the increasing Ti concentration was observed. The valence band of BiNbO$_4$ consists mainly of O 2p states and Bi 6s states, while the conduction band edge is composed of Nb 4d state [23]. When doping with Ti, the hybridization of Ti 3d and Nb 4d orbital will decrease conduction band bottom, contributing to slightly narrowing of band gap.

**Figure 3.** UV-vis absorption spectra of BiNb$_{1-x}$Ti$_x$O$_4$ with $x = 0$-0.15 and plots of $(\alpha h\nu)^2$ versus $h\nu$ for the absorption spectra (inset), giving the value of corresponding band gaps ($E_g$).

The photo catalytic performance of BiNb$_{1-x}$Ti$_x$O$_4$ ($x = 0$-0.15) was characterized by the degradation of methyl violet (MV) under visible light irradiation. In order to exclude particle adsorption factors, the suspensions were magnetically stirred in the dark to achieve the adsorption/desorption equilibrium. We focus on the intensity changes of the MV characteristic adsorption peak at 582 nm. Figure 5 shows that UV-vis absorption spectral of MV aqueous solutions changes over visible-light irradiation time in the sample of BiNb$_{1-x}$Ti$_x$O$_4$ ($x = 0.1$). With increasing visible-light irradiation time, the intensity of the major absorbance decreased caused by degradation process. The characteristic adsorption peak was shifted to low wavelength because both chromophores and aromatic rings of MV have been destroyed, instead of being simply decolorized by adsorption [24].
Figure 4. The variation of the band gap $E_g$ with Ti concentration $x$.

Figure 5. UV-vis absorption spectra of BiNb$_{1-x}$Ti$_x$O$_4$ ($x = 0.10$) in MV solution (1g/L) under visible irradiation.

The photo catalytic activities of samples that the vary of C/Co over time under visible-light irradiation is shown in Figure 6. After 3h of visible-light irradiation, the MV solution with pure BiNbO$_4$ only decomposed about 45%. However, in the same experimental condition, the doping samples at $x = 0.03, 0.05, 0.08, 0.1$ and 0.15 with the decomposition of MV were about 74%, 79%, 81%, 90% and 88% respectively. The results obviously show that the visible-light photo catalytic activity of BiNbO$_4$ doped with Ti have significantly improved.
Figure 6. Photo catalytic degradation of MV over BiNb$_{1-x}$Ti$_x$O$_4$ ($x = 0$-0.15) under visible light irradiation.

The proposed mechanism of MV degradation over BiNb$_{1-x}$Ti$_x$O$_4$ ($x = 0$-0.15) under visible light is shown in Figure 7. Doing Ti ions would introduce a new Ti 3$d$ states hybridized with Nb 4$d$ states in the electronic structure, slightly decreasing conduction band minimum. Under visible light irradiation, the electrons would be excited from the valence band comprised of O 2$p$ and Bi 6$s$ to the conduction band composed of Nb 4$d$ and Ti 3$d$, causing the separation of electron and hole. The most Photo-generated carriers recombine and disappear during migration, while the survived electrons and holes would migrate to the particle surface of the samples and participate in the oxidation-reduction reactions. The transferred electrons can be captured by the surface adsorbed O$_2$ molecules to give O$^-$ and the positive holes can oxidize the adsorbed MV molecules or react with the adsorbed OH$^-$/H$_2$O for generating OH$^-$ species to oxidize the organic compounds.

Figure 7. Photo catalytic degradation of MV over BiNb$_{1-x}$Ti$_x$O$_4$ ($x = 0$-0.15) under visible light irradiation.

The conduction band and valence band potentials of BiNb$_{1-x}$Ti$_x$O$_4$ ($x = 0$, 0.03, 0.08, 0.10, 0.15) at the point of zero charge can be calculated by the following empirical equation [25]: $E_{VB} = X - E^e + 0.5E_g$. Here, $E_{VB}$ is the valence band edge potential and X is the electronegativity of the semiconductor which is the geometric mean of the electronegativity of the constituent atoms. The electronegativity of an atom is the arithmetic mean of the atomic electron affinity and the first ionization energy. $E^e$ is the energy of free electrons on the hydrogen scale (~4.5 eV), $E_g$ is the band gap energy of the semiconductor, and $E_{CB}$ can be determined by $E_{CB} = E_{VB} - E_g$. The calculated energy level of the samples is shown in Figure 8. The results show that with the increasing Ti concentration, the decrease of band gap could be attributed to the downshift of conduction band because of the doping Ti 3$d$ orbits and the upshift of valence band caused by O 2$p$ orbits hybridization. With the
suitable band gap, the electrons and holes are easily excited and migrate to the surface instead of recombination, which results in an increased lifetime of the charge carriers and more charge transfer to adsorbed organic molecules, enhancing the photo catalytic properties of the material.

**Figure 8.** Schematic illustration for the calculated energy level diagram indicating the conduction and valence band potentials of BiNb$_{1-x}$Ti$_x$O$_4$ ($x = 0-0.15$).

4. Conclusion

In summary, the structure, optical and photo catalytic properties of the BiNb$_{1-x}$Ti$_x$O$_4$ ($x = 0-0.15$) was studied systematically. All samples exhibit an orthorhombic structure with $Pnna$ space group according to the XRD patterns. All the samples have similar particle sizes and the specific surface area, providing more absorptive and photo catalytic active sites during the degradation process. With the increasing of doping Ti in BiNbO$_4$, the band gaps of samples are slightly decreased compared to pure BiNbO$_4$, extending absorption region and increasing the oxidation reduction power. From calculated data of the conduction band and valence band potentials, we find the suitable band gap for absorb visible light enhance the photo catalytic activity for the degradation of methyl violet (MV) in water under visible light irradiation.

Acknowledgments

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