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Theoretical and experimental studies on electronic structure and optical properties of Bi-doped anatase TiO_2

Zhanhong Ma [a,b,*], Fengzhang Ren [a,**], Zhouya Yang [a], Alex A. Volinsky [c]

[a] School of Materials Science and Engineering, Henan University of Science and Technology, Luoyang, China
[b] Henan Collaborative Innovation Centre of Non-Ferrous Generic Technology, Luoyang 471023, China
[c] Department of Mechanical Engineering, University of South Florida, Tampa, FL 33620, USA

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ABSTRACT

In this paper, Bi-doped TiO_2 was prepared by electrochemical method. XRD results show that the crystal structure was not changed after Bi doping. All of them were anatase TiO_2. And there were no strontium peak. The microscopic morphology of the nanotube has little effect. The optical property test results show that the Bi doping causes a significant red shift of anatase TiO_2, which promotes light absorption in the visible range. This is consistent with the theoretical results. The band gap of pure anatase TiO_2 calculated by GGA+*U* method is 3.22 eV. After Bi enters the lattice, it will introduce impurity level in the TiO_2 bandgap and reduce the band gap of TiO_2.

1. Introduction

Anatase TiO_2 has a band gap of 3.2 eV, and its photogenerated electrons and holes have stronger reduction and oxidation capabilities, thus having best photocatalytic activity [1–3]. However, in practical application, due to the wide band gap of anatase TiO_2, most visible light in the sun cannot be fully utilized. Therefore, how to effectively extend the photoresponse range of TiO_2 to the visible light region has become a hot issue not only experimentally but also theoretically [4,5]. The TiO_2 band gap can be engineered by creating lattice defects, such as vacancies, substitution, and interstitial space, which in turn change its electrical, thermal, magnetic, and optical properties. Ion doping using metals or nonmetals is one of the most effective modification methods and has attracted extensive attention from scientific researchers. The impurity level introduced by doping will become a shallow trap potential well of photo-generated electron-hole pairs, which can promote the effective separation of photo-generated electron-hole pairs and increase the carrier lifetime. In recent years, the research on Bi doping has been more active in experiments. The research results show that the introduction of appropriate amount of Bi element can inhibit the growth of anatase titanium dioxide and effectively improve the photocatalytic activity of TiO_2 [6–10]. Li revealed Bi doping will reduce the band gap of titanium dioxide [8], while Zhou [11] research on Bi doping will increase the band gap of titanium dioxide. In view of the differences in research results, there is less theoretical and experimental combination. In order to solve this problem, this paper adopts anodic oxidation method to prepare bismuth-doped titanium dioxide nanotube arrays. At the same time, the optical properties of bismuth-doped titanium dioxide are calculated by the first principle. Combining theory with experiment, the influence of Bi doping on the electronic structure and optical properties of TiO_2 is systematically studied, providing theoretical reference for the optical properties of bismuth-doped titanium dioxide.

* Corresponding author at: School of Materials Science and Engineering, Henan University of Science and Technology, Luoyang, China.
** Corresponding author.
E-mail addresses: mazhanhong@163.com (Z. Ma), renfz@haust.edu.cn (F. Ren).

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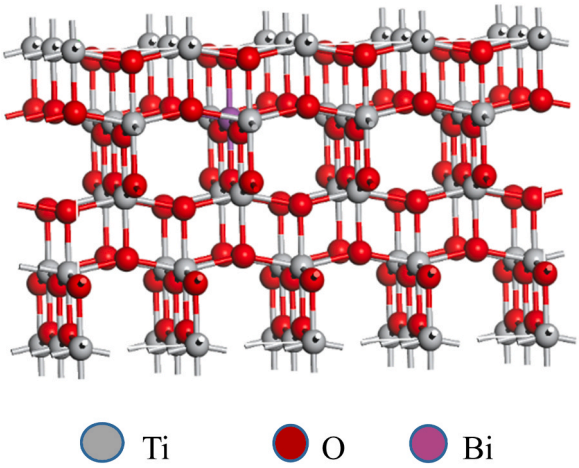

Fig. 1. 4 × 2 × 1 supercell structure of Bi- TiO_2.

2. Theoretical methods and experimental details

2.1. Experimental details

In this work, Bi-doped TiO_2 nanotubes are prepared by anodic oxidation method. Firstly, 0.25% NH_4F and 2.5% mixed solution of deionized water and ethylene glycol are put into a beaker, stirred by magnetic force for 12 h, and allowed to stand for 1 h to prepare electrolyte. Pure titanium foil is washed with dilute hydrochloric acid, acetone and deionized water in turn for 5 min. Then titanium foil is anodized in the electrolyte with an oxidation voltage of 50 V and an oxidation time of 1.5 h h. Then the anodized Ti foil is ultrasonically cleaned for 60 min and dried for later use. Then the second anodic oxidation was carried out with an oxidation voltage of 50 V and an oxidation time of 3 h. The sample after secondary oxidation is dipped in 3% bismuth nitrate for 20 min, and then annealed at 500°C for 3 h in an annealing furnace. The Bi-doped titanium dioxide nanotube array is prepared. Undoped samples are annealed directly without immersion.

The morphology of the samples was examined by the field-emission scanning electron microscopy (FESEM, JSM-7800 F, JEOL). The X-ray diffraction data was acquired using a Bruker D8 Advance powder X-ray diffractometer (XRD, Bruker), the X-ray tube produced Cu Kα radiation (λ = 1.5406 Å), and the generator was set to 40 kV and 40 mA during data collection. Data was collected from 20° to 80° (2θ). A UV–visible spectrophotometer (UV-2600, Shimadzu) was utilized to obtain the transmittance spectra and absorption spectra of the TNA films. The photoluminescence (PL) spectra experiments were performed using a WFY-28 Fluorescence spectrophotometer (Tianjin Tuo Pu Instrument Co., Ltd).

2.2. Model construction

The calculation model in this paper are pure TiO_2(1 ×1 × 1) unit cell model; $Bi_{0.031}Ti_{1.969}O$ (4 ×2 ×1) with a Bi atom replacing Ti atom (the corresponding amount 3.1%), and the crystal structure is shown in Fig. 1.

The calculations are based on the ultrasoft and norm-conserving pseudopotentials available in the CASTEP code to optimize the models and obtain the authentic optical properties [12,13]. The valence electron configurations used for the construction are O $2s^2 2p^4$, Ti $3s^2 3p^6 3d^2 4s^2$, Bi $5d^{10} 6s^2 6p^3$ respectively. In the calculation of pure anatase TiO_2, the exchange correlation energy is GGA approximation and the pseudopotential function is gradient correction function PBE. The calculation is carried out in reciprocal space. At the end of the self-consistent process, the overall energy of the structure converges to 2 × 10^{-6} eV/atom, the force on each atom is less than 0.05 eV/nm, the tolerance deviation is 0.0002 nm, and the stress deviation is 0.1 GPa. The K Point in Brillouin zone are set to 2 × 2 × 3 respectively. When calculating energy, electrons are treated by spin polarization. Since the conventional GGA method underestimates the band gap width of metal oxide in calculating electronic structure, the GGA+U method is used to correct the 3d state of Ti and 2p state of O in all systems of band gap [14–18]. U = 5.5 eV(U^{Ti} d = 5.5 eV) and U= 6 eV(U° p = 6 eV) are taken respectively. In the calculation, the crystal structure is optimized first, and the electronic structure and optical properties are calculated according to the obtained structural parameters.

3. Results and analysis

3.1. Analysis of experimental results

Fig. 2 is an XRD direction pattern of titanium dioxide nanotubes prepared by anodic oxidation method. It can be seen from Fig. 2 than the main crystal phase before and after doping is anatase, and no peak of Bi is found after doping, but the diffraction intensity and

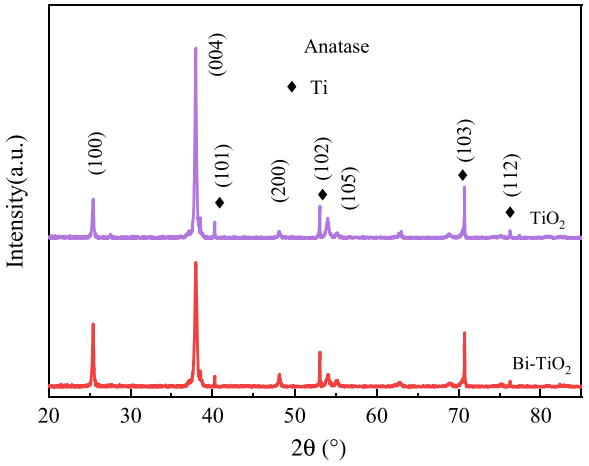

Fig. 2. XRD patterns of sample.

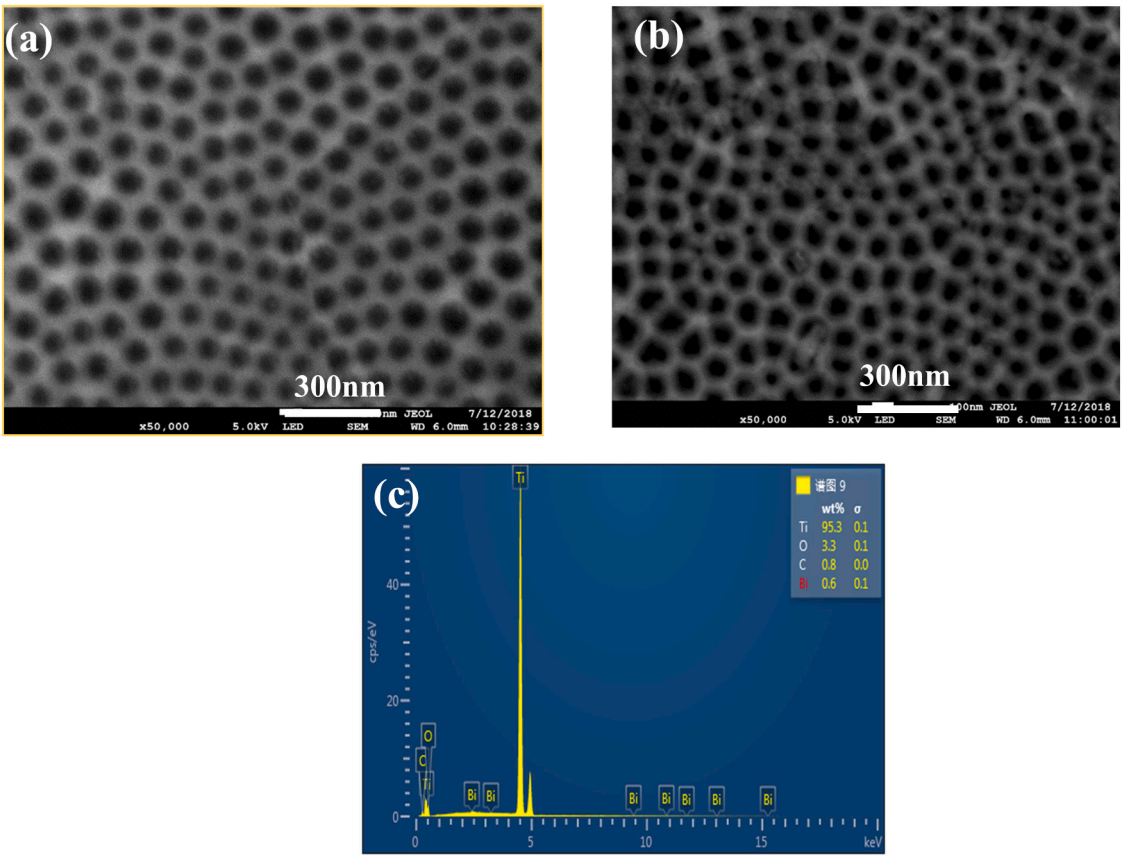

Fig. 3. FESEM of TiO_2 nanotubes. (a): TiO_2; (b): Bi-TiO_2; (c): EDS of Bi-TiO_2.

width of the peak have slightly changed, which may be because the ionic radius of Bi^{3+} is 94 nm and the radius of Ti^{4+} is 68 nm. The ionic radii of the two are quite different, Bi^{3+} is easy to destroy the original crystal lattice of TiO_2, thus causing lattice distortion [19].

Fig. 3 is FESEM image of the nanotube. Fig. 3(a) is a TiO_2 nanotube and (b) is a Bi doped titanium dioxide nanotube. As can be seen from the Figure, the uniform diameter of the TiO_2 nanotube is about 90 nm, and bismuth doping has little influence on the morphology of the nanotube. (c) is EDS of Bi-TiO_2. It can be seen that bismuth does exist in the nanotubes. Combined with XRD analysis, Bi may have entered the lattice of titanium dioxide.

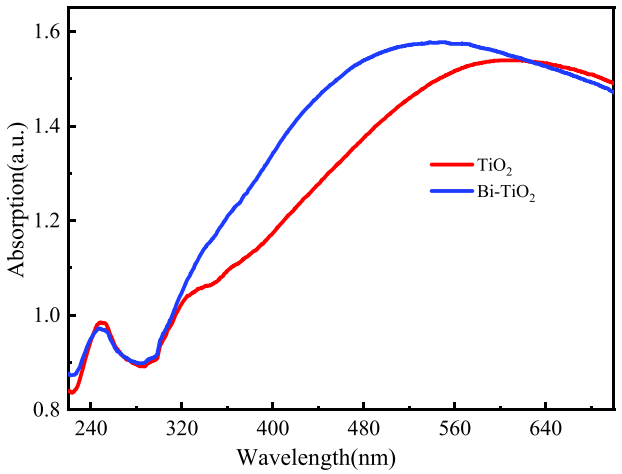

Fig. 4. Absorption spectrum of Bi doped TiO_2.

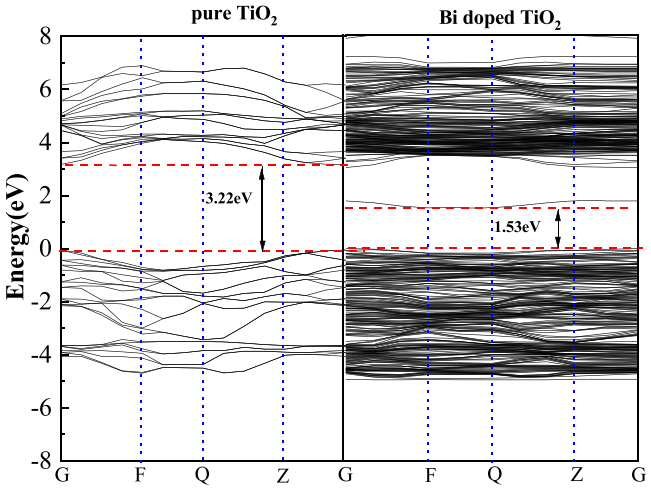

Fig. 5. Band structure of Bi doped TiO_2.

3.2. Optical performance analysis

Fig. 4 is the ultraviolet-visible light absorption spectrum of bismuth doped titanium dioxide nanotubes. it can be seen from the figure that the absorption band edge shows obvious red shift after doping, and the corresponding band gap decreases. in the visible light range, its light absorption value increases obviously.

3.3. Theoretical calculation results

Fig. 5 shows the band structure of pure anatase TiO_2 and bismuth doped TiO_2. The band gap of anatase TiO_2 is 3.22 eV, which is very close to the theoretical value [20]. The minimum point of anatase TiO_2 conduction band bottom and the maximum point of valence band top are not in a straight line, Indicating that the anatase TiO_2 is an indirect band gap semiconductor. Fig. 5(b) is an energy band structure of Bi doped TiO_2. It can be seen that the for band gap of TiO_2 is obviously smaller after Bi doping. when doping, an impurity energy level appears in the middle of the band gap. the existence of the impurity energy level greatly reduces the energy required for electrons to transition from valence band to conduction band. The decrease of band gap will lead to red shift of absorption band edge and increase photocatalytic activity of TiO_2 in visible light range.

Fig. 6 is the result of density of states. it can be seen from Fig. 6(a) that the valence band of anatase TiO_2 is mainly composed of 2p state of O, while the conduction band is mainly contributed by 3d state of Ti, and both the valence band and conduction band of anatase TiO_2 contain 2p state of O and 3d state of Ti, it can be judged that there is a covalent components of partial covalent bond between Ti atoms and O atoms of anatase TiO_2, which is consistent with the results reported in the literature [7,21,22]. After Bi doping, a small density of states peak appears in the bandgap of TiO_2, which corresponds to the impurity level in the middle of the bandgap in

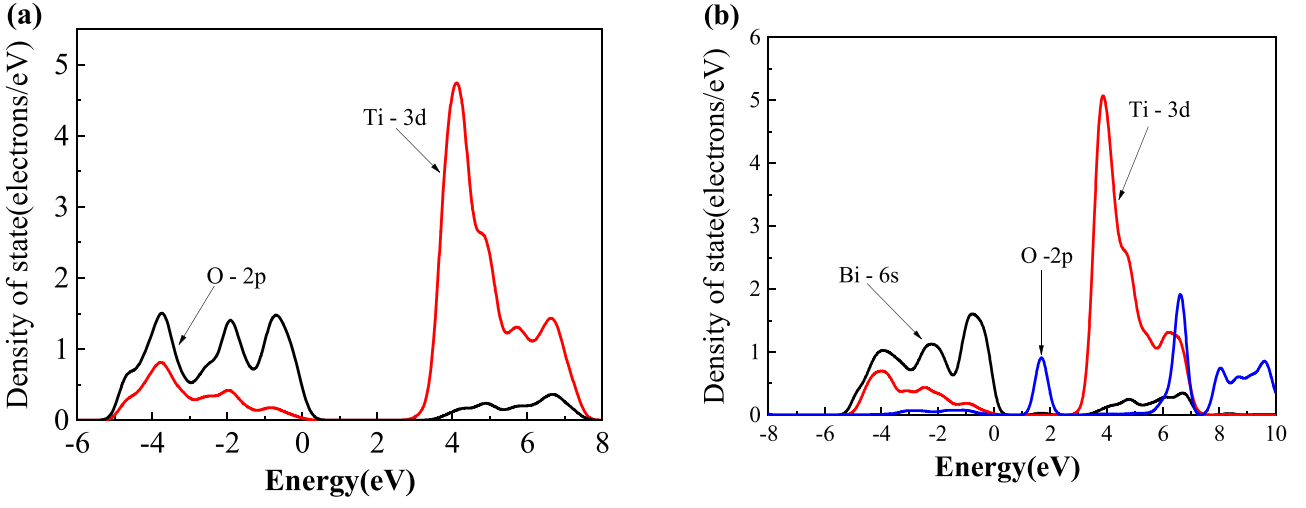

Fig. 6. Density of states (a) pure TiO_2; (b) Bi-TiO_2.

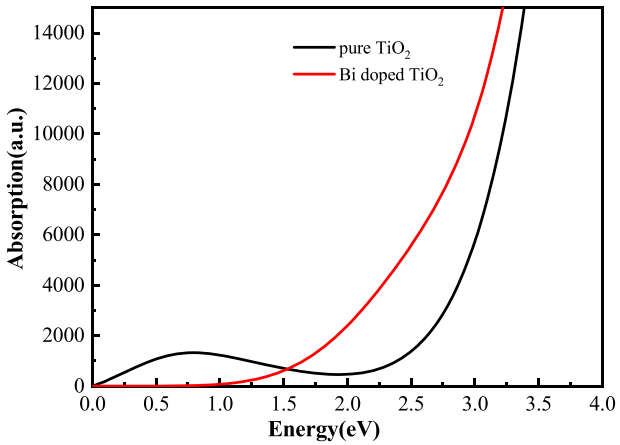

Fig. 7. Absorption spectrum.

the energy band structure. According to analysis, the impurity level is mainly composed of electrons in the 6s state of Bi, the 2p state of O and the 3d state of Ti. The existence of impurity energy levels causes the valence band to move toward low energy, thus reducing the band gap relative to pure TiO_2. The band gap of the material doped with Bi is 1.53 eV, and the light absorption range is just in the visible light range, which is beneficial to increase the utilization rate of the material to visible light, thus increasing the photocatalytic activity of TiO_2 in the visible light range. This result is consistent with the previous optical performance analysis results.

Fig. 7 is the absorption spectrum calculated by the first principle. After bismuth doping, obvious red shift occurs, which is consistent with the experimental results.

Fig. 8 is the complex dielectric function of pure TiO_2 and Bi-TiO_2. Re is the real part of the dielectric function, indicating the reflection state of the material to light and the process of releasing children or photons when excited electrons transition to low energy level. Im is the imaginary part of the dielectric function, indicates the light absorption of photoelectrons from valence band to conduction band. The larger the imaginary part, the greater the probability of electrons absorbing photons, and the stronger the absorption energy of materials to light. The real part and imaginary part of the dielectric function comprehensively reflect the light utilization rate of the material. Fig. 8(a) is the complex dielectric function of pure anatase TiO_2. It can be seen that the imaginary part of the system starts to reflect at 1.9 eV, indicating that the material has poor response capability in the visible light range. Fig. 8(b) is the complex dielectric function of Bi-TiO_2. As can be seen from the figure, the imaginary part peak of the system shows red shift compared with the undoped TiO_2 system. This is due to the impurity energy level in the system after doping, which reduces the photon energy that electrons need to absorb in the transition process, resulting in obvious left shift of the imaginary part peak of the dielectric function. This is consistent with the light absorption results above.

4. Conclusion

In this work, titanium dioxide nanotubes can be successfully prepared by anodic oxidation. Bi doping has little effect on the microstructure of titanium dioxide nanotubes. The main crystal phase before and after doping is anatase titanium dioxide. Experimental and theoretical calculation results show that bismuth doping causes anatase titanium dioxide to undergo obvious red shift for optical properties, and promotes light absorption in visible light range. The band gap of pure anatase TiO_2 calculated by GGA+U method is 3.22 eV. After Bi enters the crystal lattice, impurity level will be introduced into the TiO_2 band gap to reduce the band gap of TiO_2.

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Author contributions

Zhanhong Ma drafted the manuscript and performed the experiments. Fengzhang and Ren Zhouya Yang contributed to the conception of the study. Alex A. Volinsky performed the data analyses and revised the manuscript.

Declaration of Competing Interest

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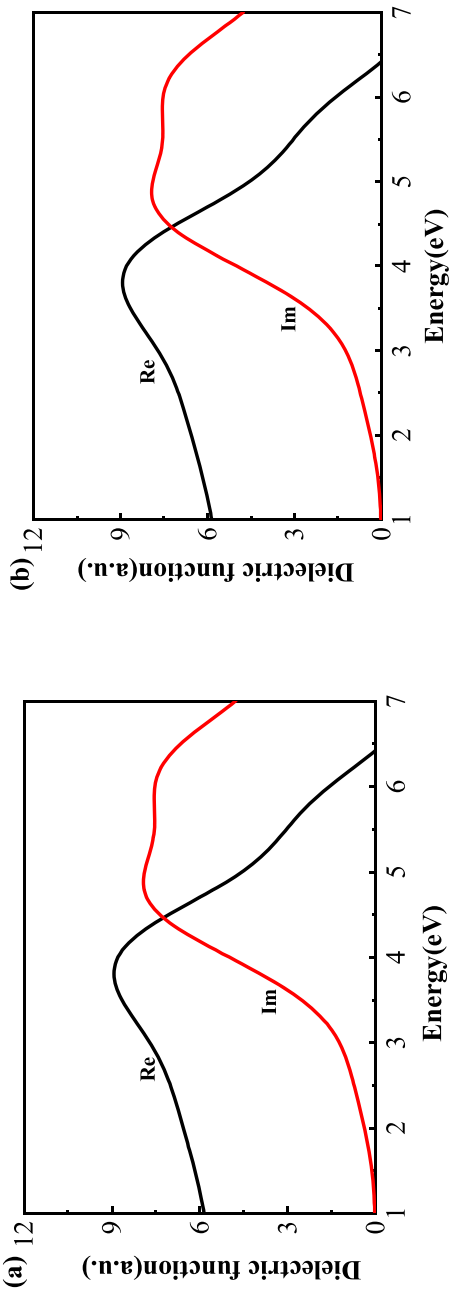

Fig. 8. Dielectric function of Bi doped TiO_2. (a) pure TiO_2; (b)Bi -TiO_2.

conficts of interest.

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