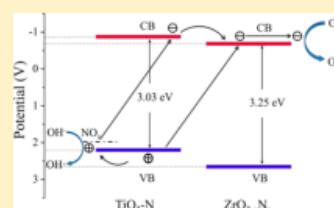




Adjustment and Control of Energy Levels for  $\text{TiO}_2\text{-N/ZrO}_{2-x}\text{N}_x$  with Enhanced Visible Light Photocatalytic ActivityYanlong Yu,<sup>†</sup> Peng Zhang,<sup>†</sup> Yuanjiang Kuang,<sup>†</sup> Yihong Ding,<sup>‡</sup> Jianghong Yao,<sup>†</sup> Jingjun Xu,<sup>†</sup> and Yaan Cao<sup>\*,†</sup><sup>†</sup>The MOE Key Laboratory of Weak Light Nonlinear Photonics, TEDA Applied Physics Institute and School of Physics, Nankai University, Tianjin 300457, P. R. China<sup>‡</sup>State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, P. R. China

## Supporting Information

**ABSTRACT:** We theoretically forecasted the narrowness of band gap for the nitrogen doped  $\text{ZrO}_2$ , implying a possible energy level matching at the interface between  $\text{TiO}_2$  and  $\text{ZrO}_2$ . Inspired by the theoretical simulation, the corresponding experiment was carried out and the band gap of  $\text{ZrO}_2$  is narrowed by doping nitrogen in substitutional mode. The  $\text{TiO}_2\text{-N/ZrO}_{2-x}\text{N}_x$  composite photocatalyst exhibited an excellent photocatalytic performance under visible-light irradiation. The enhancement is caused by the introduction of doping energy level as well as the electrons' transition at interface, which would enhance the visible absorption of composite photocatalyst and separate the photogenerated charge carriers efficiently. These results suggest that the selection of materials and dopants and the matching of energy levels at interface are of great importance to design and fabricate photocatalysts with high efficiency and performance.



## INTRODUCTION

$\text{TiO}_2$ , considered as one of the most promising photocatalysts, has been investigated extensively because of its stable and efficient photoelectric properties.<sup>1–5</sup> However, the catalytic performance is limited by the large band gap (3.2 eV for anatase) and high recombination efficiency for the photoexcited electrons and holes, impeding practical applications under solar light irradiation. Therefore, it is still a challenge to find a highly reactive photocatalyst to meet the present demands for environmental and fuel application.

Doping  $\text{TiO}_2$  with foreign elements is one of the most effective ways to extend the response into the visible-light region,<sup>6–12</sup> and it has been demonstrated that  $\text{TiO}_2$  modified with surface  $\text{NO}_x$  species ( $\text{TiO}_2\text{-N}$ ) is an effective photocatalyst for degradation of organic pollutants.<sup>13–16</sup> Moreover, combining  $\text{TiO}_2$  with other semiconductors to form the heterostructures possesses more advantages for separating the photogenerated charge carriers.<sup>17–20</sup> In previous studies,  $\text{TiO}_2$  coupled with zirconia has been investigated extensively in degradation of organic compounds.<sup>21–25</sup> Chary et al. prepared a series of copper supported  $\text{TiO}_2/\text{ZrO}_2$  for dehydrogenation reaction.<sup>21</sup> Fu et al. reported that  $\text{TiO}_2/\text{ZrO}_2$  presents an enhanced photocatalytic performance.<sup>22</sup> Wang et al. reported that  $\text{ZrO}_2/\text{TiO}_{2-x}\text{N}_x$  showed efficient catalytic activity under visible irradiation.<sup>26</sup> However, for the case of  $\text{TiO}_2/\text{ZrO}_2$  composite,  $\text{ZrO}_2$  can hardly work as an efficient visible-light photocatalyst because of its large band gap.<sup>27,28</sup> Moreover, on the basis of their band structures, there is almost no charge transfer between  $\text{TiO}_2$  and  $\text{ZrO}_2$ , which impedes the efficient

separation of charge carriers and inhibits the corresponding photocatalytic performance.<sup>29</sup> Therefore, it is necessary to design and regulate the band structure of  $\text{ZrO}_2$  to obtain a highly reactive  $\text{TiO}_2/\text{ZrO}_2$  composite photocatalyst with visible light response.

In this paper, theory calculation based on density functional theory (DFT) was carried out to predict the narrowness of band gap for nitrogen doped tetragonal  $\text{ZrO}_2$  ( $\text{ZrO}_{2-x}\text{N}_x$ ), implying a possible energy level match between  $\text{TiO}_2\text{-N}$  and  $\text{ZrO}_{2-x}\text{N}_x$  which would facilitate separation of photogenerated charge carriers, enhancing the visible light photocatalytic performance. It was revealed that the theoretical calculation was in good agreement with the experiment results. The band structure, the behaviors of charge carriers, and the photocatalytic mechanism for  $\text{TiO}_2\text{-N/ZrO}_{2-x}\text{N}_x$  catalysts are also studied and analyzed in details. The results may offer an example for development of semiconductors with advanced optoelectronic functions that may be applied in many fields, such as photosynthesis, solar cells, and photocatalysis.

## EXPERIMENTAL DETAILS

**Catalyst Preparation.** At room temperature and under vigorous stirring, 11.5 g of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  was mixed with 12 mL of deionized water for 1 h, and then 8 mL of ammonia was added. After 30 min, the precipitate was filtered and dried at

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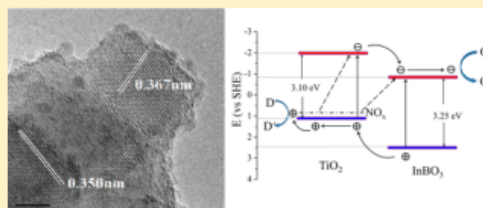
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Fabrication of N-TiO<sub>2</sub>/InBO<sub>3</sub> Heterostructures with Enhanced Visible Photocatalytic PerformanceYanlong Yu,<sup>†</sup> Yue Tang,<sup>†</sup> Jixiang Yuan,<sup>†</sup> Qiang Wu,<sup>†</sup> Wenjun Zheng,<sup>\*,‡</sup> and Yaan Cao<sup>\*,†</sup><sup>†</sup>Key Laboratory of Weak-Light Nonlinear Photonics, Ministry of Education, TEDA Applied Physics Institute and School of Physics, Nankai University, Tianjin 300457, China<sup>‡</sup>Department of Materials Chemistry, College of Chemistry, Nankai University, Tianjin 300457, China

## Supporting Information

**ABSTRACT:** A new type of heterostructured photocatalysts (N-TiO<sub>2</sub>/InBO<sub>3</sub>) were synthesized by coupling nitrogen-modified TiO<sub>2</sub> (N-TiO<sub>2</sub>) with indium borate (InBO<sub>3</sub>) via a one-step sol-gel method. It was revealed that N-TiO<sub>2</sub>/InBO<sub>3</sub> exhibited an improved photocatalytic performance compared with TiO<sub>2</sub>, N-TiO<sub>2</sub>, and InBO<sub>3</sub> under both UV and visible light irradiation because of the formation of a heterostructure at the interface as well as the introduction of surface NO<sub>x</sub> species and InBO<sub>3</sub>. These results may provide a paradigm to fabricate and design the optoelectronic functional materials with high efficiency and performance.



## INTRODUCTION

TiO<sub>2</sub> has been investigated extensively as one of the most promising photocatalysts due to its high chemical stability and good photoelectric performance.<sup>1–5</sup> However, the photocatalytic performance is still limited because of its large band gap (3.2 eV for anatase) and high recombination efficiency of photogenerated charge carriers, impeding the efficient usage of solar light in practical applications. Doping titania with metal or nonmetal elements is one of the most effective methods to extend the response into the visible region,<sup>3,6–12</sup> and compositing TiO<sub>2</sub> with other semiconductors to form the heterostructure can promote the separation of photogenerated electrons and holes efficiently.<sup>13–17</sup> Thus, the combination of doping and heterostructure would become more helpful to prepare and develop TiO<sub>2</sub>-based photocatalysts with high photocatalytic performance. We recently reported that indium borate exhibited better photocatalytic capabilities than TiO<sub>2</sub> in photodegradation of 4-chlorophenol,<sup>18</sup> with a longer lifetime of photogenerated electrons involved in the photocatalytic process. So, we expect to combine the nitrogen-modified TiO<sub>2</sub> (visible light response) with InBO<sub>3</sub> (excellent long lifetime charge carriers) and synthesize the N-TiO<sub>2</sub>/InBO<sub>3</sub> heterostructured photocatalysts, to achieve the advantages of doping and heterostructure and obtain photocatalysts with highly reactive activity under visible as well as UV light irradiation.

Herein, a new type of N-TiO<sub>2</sub>/InBO<sub>3</sub> heterostructure on nanoscale was synthesized by the sol-gel method. The molar ratios of InBO<sub>3</sub> and N-TiO<sub>2</sub> can be adjusted by controlling the pH value of the gel. The composition of InBO<sub>3</sub> with N-TiO<sub>2</sub> would extend the visible response, inhibit the recombination, and prolong the lifetime of photogenerated charge carriers.

Therefore, N-TiO<sub>2</sub>/InBO<sub>3</sub> represents a better photocatalytic performance than N-TiO<sub>2</sub> and InBO<sub>3</sub> under both visible and UV light irradiation.

## EXPERIMENTAL DETAILS

**Catalyst Preparation.** The N-TiO<sub>2</sub>/InBO<sub>3</sub> heterostructures were synthesized via a one-step sol-gel method. All the chemicals used are of analytical grade, and water is deionized water (>18.2 MΩ cm). At room temperature, 7.1 mL of InCl<sub>3</sub> solution (0.73 mol·L<sup>-1</sup>) was mixed with 40 mL of anhydrous ethanol. Then 240 mg of H<sub>3</sub>BO<sub>3</sub> was added into this mixed solution under vigorous stirring for 15 min. The mixtures were added dropwise with 1 mL of concentrated HCl solution (12 mol L<sup>-1</sup>) and then 12 mL of Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>. After stirring continuously for 15 min, 3 mL of ammonia was added, and the white precipitate was observed immediately. After filtering and washing, the white precipitate was dried at 373 K after aging at room temperature for 24 h and then calcined at 723 K in a muffle for 150 min. The pH value of the gel could be easily adjusted by changing the amount of HCl solution to obtain N-TiO<sub>2</sub>/InBO<sub>3</sub> heterostructures with different molar ratios. For comparison, pure TiO<sub>2</sub>, N-TiO<sub>2</sub>, and InBO<sub>3</sub> powders were prepared with the same procedure with relative precursors.

**Characterization.** The XRD patterns were collected on a Rigaku D/max 2500 X-ray diffraction spectrometer (Cu Kα, λ = 1.54056 Å). Corresponding crystal size was calculated using the Scherrer equation ( $D = k\lambda/B \cos \theta$ ). The high-resolution transmission electron microscopy (HRTEM) analyses were

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# The Design of TiO<sub>2</sub> Nanostructures (Nanoparticle, Nanotube, and Nanosheet) and Their Photocatalytic Activity

Yanlong Yu,<sup>†</sup> Peng Zhang,<sup>†</sup> Limei Guo,<sup>†</sup> Zhandong Chen,<sup>†</sup> Qiang Wu,<sup>†</sup> Yihong Ding,<sup>‡</sup> Wenjun Zheng,<sup>§</sup> and Yaan Cao<sup>\*,†</sup>

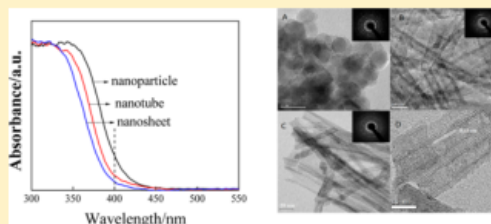
<sup>†</sup>MOE Key Laboratory of Weak-Light Nonlinear Photonics, TEDA Applied Physics Institute and School of Physics, Nankai University, Tianjin 300457, China

<sup>‡</sup>State Key Lab of Theoretical and Computational Chemistry, Jilin University, Changchun 130023, China

<sup>§</sup>Department of Materials Chemistry, College of Chemistry, Nankai University, Tianjin, 300457, China

## Supporting Information

**ABSTRACT:** Density functional theory (DFT) calculation is carried out to access the band structure and density of states (DOS) based on the models of TiO<sub>2</sub> nanoparticle, nanotube, and nanosheet, predicting the order of the photocatalytic activity for three different nanostructures. Sol-gel method and hydrothermal method are used to achieve desired morphologies: nanoparticles, nanotubes, and nanosheets (fragmentized nanotubes). The photocatalytic activity ranks in the order of nanosheets > nanotubes > nanoparticles, which is consistent with theoretical prediction. It was revealed that the enlargement of band gap is caused by the quantum confinement effect; the prolonged lifetime of photogenerated electrons and increased specific surface areas are dependent on the morphology of the nanostructure. All these factors contribute to the improvement of the photocatalytic activity for nanostructures. Our results can guide the design and selection of low-dimensional nanomaterials with desired morphology and improved photoelectric functional properties, which can be used in many fields, such as solar cells, photocatalysis, and photosynthesis.



## INTRODUCTION

TiO<sub>2</sub> has been investigated extensively for optical, electrical, and photochemical applications, due to its chemical stability and good performance.<sup>1–5</sup> In recent years, one-dimensional TiO<sub>2</sub> has enormous potential as photocatalysts, solar cells, nanodevices, and sensors because of their peculiar properties, which originate from their low dimensionality.<sup>6–10</sup> Quan et al. reported an improved photoconversion ability by modified anatase nanotubes.<sup>11</sup> Zhang and his co-workers reported on highly ordered anatase nanotube array electrodes with enhanced photoelectrocatalytic activity due to their large specific surface areas and numerous surface defects.<sup>12</sup> In addition, Yu et al. reported on an improved photoelectric conversion efficiency in dye-sensitized solar cells based on an anatase nanosheet.<sup>6</sup> Zhang et al. also reported on an anatase TiO<sub>2</sub> nanosheet with exposed (0 0 1) facet and its application in solar cells.<sup>13</sup> It was demonstrated that the nanostructure played an important role in the photocatalytic and photoconversion performance. However, the insight of the connection between the low-dimensional nanostructure and band structure as well as their effects on the behaviors of photogenerated charge carriers has not been explored up theoretically and experimentally until now, which is of great importance to design and develop new efficient photoelectric functional materials.

In this work, the models of nanoparticle, nanotube, and nanosheet are designed, and corresponding band structure and density of states (DOS) are calculated theoretically. The calculation results that imply the photocatalytic activity may rank in the order of nanosheet > nanotube > nanoparticle. The desired TiO<sub>2</sub> nanostructures were synthesized, and the experiment results confirmed the theoretical forecast about the band structure and photocatalytic activity. The detailed band structure for TiO<sub>2</sub> nanoparticles, nanotubes, and nanosheets and the behaviors of photogenerated charge carriers as well as the photocatalytic mechanism are analyzed and studied.

## EXPERIMENTAL DETAILS

**Calculation.** The calculations were performed using a first-principle calculation software package CASTEP. Generalized gradient approximation (GGA)-based density functional theory (DFT) was used to calculate the electronic band structure and density of states (DOS) for TiO<sub>2</sub> nanoparticles, nanotubes, and nanosheets, respectively. The plane wave energy cutoffs were taken to be 340 eV, and the k-point set was 3 × 2 × 3. The core

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## Short Communication

A new Ni/Ni<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>/NiO heterostructured photocatalyst with efficient reduction of CO<sub>2</sub> into CH<sub>4</sub>Yanlong Yu<sup>a</sup>, Limei Guo<sup>a</sup>, Han Cao<sup>b</sup>, Yuekai Lv<sup>b</sup>, Enjun Wang<sup>c</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> College of Physics and Material Science, Tianjin Normal University, Tianjin 300387, China<sup>c</sup> Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031, China

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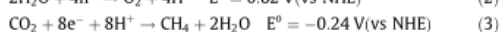
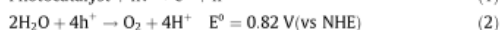
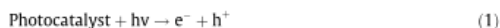
## ABSTRACT

A new Ni/Ni<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>/NiO heterostructured photocatalyst was synthesized. Owing to the formation of the heterostructure, the photo-excited charge carriers are utilized efficiently for the redox reaction, resulting in an enhanced photocatalytic activity on reduction of CO<sub>2</sub> with H<sub>2</sub>O into CH<sub>4</sub>.

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The reduction of CO<sub>2</sub> into CH<sub>4</sub> by photocatalysis is one of the most valuable methods to solve the energy crisis and global warming problems [1]. Amounts of semiconductors, such as TiO<sub>2</sub> [2–4], Zn<sub>2</sub>GeO<sub>4</sub> [5,6], Bi<sub>2</sub>WO<sub>6</sub> [7], InTaO<sub>4</sub> [8] and CeO<sub>2</sub> [9], have been reported as effective photocatalyst for the reduction of CO<sub>2</sub>. Besides, many strategies have been explored to improve the photo-reduction of CO<sub>2</sub>, e.g., the addition of noble metal onto the photocatalyst [3] and combination with other metal oxide to form heterostructure [10]. However, the photocatalytic activity is still too low to be applied in practice. Therefore, new photocatalysts with high photocatalytic performance is necessary to further improve the photo-reduction of CO<sub>2</sub>.

The process of photocatalysis reduction of CO<sub>2</sub> into CH<sub>4</sub> with semiconductor as well as the redox potential ( $E^0$ ) can be shown as follows [11]:



Under irradiation, the photocatalyst creates photo-excited electrons and holes in the conduction band (CB) and valence band (VB), respectively. The holes on the VB would react with the adsorbed H<sub>2</sub>O to form H<sup>+</sup> and oxygen. Meanwhile, the electrons on the CB

are captured directly by the surface adsorbed CO<sub>2</sub> molecules to form CO and oxygen. The resultant CO would further react with electrons and H<sup>+</sup> to generate the final product, CH<sub>4</sub>. According to the aforementioned mechanism, the conduction band edge should be slightly above the reduction potential of Eq. (3) ( $E^0 = -0.24 \text{ V}$ , vs NHE), while the valence band edge should be slightly below the oxidation potential of Eq. (2) ( $E^0 = 0.82 \text{ V}$ , vs NHE), to provide energetic electrons and holes for the redox reaction. Owing to the appropriate energy level band, the photo-excited electrons and holes participate in the redox reaction on the surface more easily, leading to a high photocatalytic activity.

Borates have been reported as low-cost and stable photocatalyst with excellent catalytic performance. Our previous work has reported InBO<sub>3</sub> and its application in photodegradation of 4-chlorophenol [12]. Besides that, Pang et al. reported the synthesis of Ni<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> nanoribbons with good antimicrobial activities [13]. However, as far as we know, there is no reports about Ni<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> based photocatalyst with enhanced photocatalytic activity on the reduction of CO<sub>2</sub> into CH<sub>4</sub>.

In this work, we reported a new Ni/Ni<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub>/NiO heterostructured photocatalyst with enhanced photocatalytic activity. Owing to the formation of heterostructure, the photogenerated charge carriers are separated effectively, especially after the addition of elemental Ni. The band structure of photocatalyst is tuned to match the redox potential, as a result, leading to a significant enhanced photocatalytic activity for the photo-reduction of CO<sub>2</sub> into CH<sub>4</sub>.

\* Corresponding author.



## Enhanced photocatalytic activity of titania with unique surface indium and boron species



Yanlong Yu, Enjun Wang, Jixiang Yuan, Yaan Cao\*

MOE Key Laboratory of Weak-Light Nonlinear Photonics, TEDA Applied Physics School and School of Physics, Nankai University, Tianjin 300457, China

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### ABSTRACT

Indium and boron co-doped TiO<sub>2</sub> photocatalysts were prepared by a sol–gel method. The structure and properties of photocatalysts were characterized by XRD, BET, XPS, UV–vis DRS and PL techniques. It is found that boron is mainly doped into the lattice of TiO<sub>2</sub> in interstitial mode, while indium is present as unique chemical species of O–In–Cl<sub>x</sub> (x = 1 or 2) on the surface. Compared with pure TiO<sub>2</sub>, the narrowness of band gap of TiO<sub>2</sub> doped with indium and boron is due to the mixed valence band formed by B2p of interstitial doped B ions hybridized with lattice O2p. And the surface state energy levels of O–In–Cl<sub>x</sub> (x = 1 or 2) and B<sub>2</sub>O<sub>3</sub> species were located at about 0.4 and 0.3 eV below the conduction band respectively, which could lead to significant absorption in the visible-light region and facilitated the effectually separation of photogenerated carriers. Therefore, indium and boron co-doped TiO<sub>2</sub> showed the much higher photocatalytic activities than pure TiO<sub>2</sub>, boron doped TiO<sub>2</sub> (TiO<sub>2</sub>–B) and indium doped TiO<sub>2</sub> (TiO<sub>2</sub>–In) under visible and UV light irradiation.

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### 1. Introduction

In recent years, great efforts have been devoted to make TiO<sub>2</sub>-based photocatalysts more sensitive to visible light for utilizing solar energy efficiently [1–5]. So far, many strategies have been adopted in this field, such as doping metal or nonmetal elements [6–9], combination with a narrow-bandgap semiconductor [10–14] and surface modification [15]. Doping TiO<sub>2</sub> with metal or nonmetal elements is considered as one of the most promising methods to enhance photocatalytic activity. The introduction of doping states is able to extend catalytic absorption to visible light region, and suppress the recombination of photogenerated charge carriers (electron and hole pairs), due to the narrowness of band gap and/or creation of doping energy levels in band gap [16–19]. However, the amount of doped ions incorporation is usually quite low, which limits visible light absorption and separation efficiency of photogenerated charge carriers. For the boron doped TiO<sub>2</sub> [9], because of only small amounts of boron incorporation, visible light absorption and separation efficiency of photogenerated charge carriers are limited, as a result, the catalysts show a poor visible-light photocatalytic activity.

In addition, it has been proved that modification of unique chemical species on TiO<sub>2</sub> surface can accelerate an improvement of visible-light photocatalytic activity. Our previous work [15] has

shown that a unique chemical species, O–In–Cl<sub>x</sub> (x = 1 or 2), present on the surface of indium doped TiO<sub>2</sub>. The surface state energy level of O–In–Cl<sub>x</sub> (x = 1 or 2) species is located at 0.3 eV below the conduction band of TiO<sub>2</sub>, which can lead to the visible-light absorption. Furthermore it allows an efficient transfer of photogenerated electrons to the surface and suppresses the recombination of photogenerated charge carriers. Consequently, the indium doped TiO<sub>2</sub> showed improved photocatalytic activity for photodegradation of 4-chlorophenol compared to pure TiO<sub>2</sub> under visible light irradiation.

Furthermore, the visible-light absorption and photocatalytic activity of photocatalyst can be further improved by doping TiO<sub>2</sub> with multidopants since the contribution can come from all the dopants. This has been demonstrated in several systems, such as (B Ni) [9], (N W) [16] and (N Sn) [17]. Thus, it is expected to establish a promising method to promote photocatalysis by introducing both the doping ions and the surface species into TiO<sub>2</sub>. This introduction would be able to further improve the visible light absorption and suppress the recombination of photogenerated charge carriers efficiently. In this work, we prepared a TiO<sub>2</sub>-based photocatalyst co-doped with indium and boron prepared via a sol–gel method. Boron is incorporated into the TiO<sub>2</sub> lattice in interstitial mode, and the B<sub>2</sub>O<sub>3</sub> species formed by surplus B ions exist on the surface of photocatalyst, while indium exists as surface unique O–In–Cl<sub>x</sub> species. Moreover, as expected, it exhibits much better visible and UV light photocatalytic activity than pure TiO<sub>2</sub>, indium doped TiO<sub>2</sub> and boron doped TiO<sub>2</sub>. The mechanism is also discussed in this contribution.

\* Corresponding author. Tel.: +86 22 66229598.

E-mail address: [caoyaana@yahoo.com](mailto:caoyaana@yahoo.com) (Y. Cao).

# Structure of Nitrogen and Zirconium Co-Doped Titania with Enhanced Visible-Light Photocatalytic Activity

Peng Zhang,<sup>†,§</sup> Yanlong Yu,<sup>†</sup> Enjun Wang,<sup>‡</sup> Jingsheng Wang,<sup>†</sup> Jianghong Yao,<sup>†</sup> and Yaan Cao<sup>\*,†</sup>

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

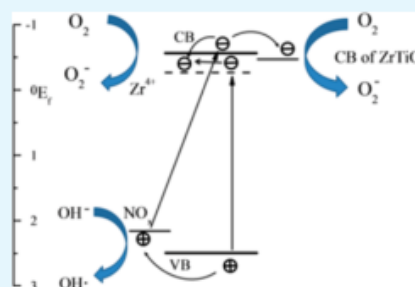
<sup>‡</sup>Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031, China

<sup>§</sup>China Electronics Technology Group Corporation 54th Research Institute, Shijiazhuang 050000, China

## Supporting Information

**ABSTRACT:** Nitrogen and zirconium co-doped TiO<sub>2</sub> (TiO<sub>2</sub>-N-x% Zr) photocatalysts were synthesized via a sol-gel method. The existing states of the dopants (N and Zr) and their corresponding band structures were investigated via XRD, Raman, BET, XPS, TEM, FT-IR, UV-vis DRS, and PL techniques. It was found that N existed only as a surface species (NO<sub>x</sub>) and Zr<sup>4+</sup> was doped in a substitutional mode; the doping of Zr<sup>4+</sup> ions and modification of N extended the absorption into the visible region and inhibited the recombination of electrons and holes. Moreover, the excess Zr<sup>4+</sup> ions existed as the ZrTiO<sub>4</sub> phase when the content of Zr was sufficiently high, which could also contribute to the separation of the charge carriers. Therefore, the TiO<sub>2</sub>-N-x%Zr samples show enhanced visible-light photocatalytic activity compared with single-doped TiO<sub>2</sub>. These results offer a paradigm for the design and fabrication of optoelectronic functional materials such as solar cells and photocatalysts.

**KEYWORDS:** TiO<sub>2</sub>, surface NO<sub>x</sub> species, substitutional Zr<sup>4+</sup> ions, ZrTiO<sub>4</sub>, visible-light photocatalysis, 4-chlorophenol degradation



## 1. INTRODUCTION

Titanium dioxide (TiO<sub>2</sub>) is considered to be one of the most attractive semiconductors to date and has been applied as a photocatalyst for the purification of pollutants.<sup>1–4</sup> However, limited by its large band gap (anatase, 3.2 eV),<sup>5,6</sup> TiO<sub>2</sub> shows no response to solar light, which impedes the effective usage of solar illumination in its practical applications. In spite of this, TiO<sub>2</sub> presents quite a low quantum yield as a result of its high recombination rate of photogenerated electrons and holes.<sup>7,8</sup>

Doping TiO<sub>2</sub> with foreign ions is a promising approach to extend its response to the visible-light region;<sup>9–20</sup> a breakthrough in this regard was made in 2001 via the doping of TiO<sub>2</sub> with nitrogen.<sup>11</sup> From that point forward, nitrogen-doped TiO<sub>2</sub> has been investigated widely by many other researchers owing to its great potential for enhancing visible-light activity.<sup>15,21–25</sup> As a titanium subgroup element, Zr possesses the same valence shell structure (n-1)d<sup>2</sup>ns<sup>2</sup> and valence state as Ti. Accordingly, Zr<sup>4+</sup>-doped TiO<sub>2</sub> has attracted the interest of many researchers because of its benefits for use in increasing the photocatalytic activity of TiO<sub>2</sub>.<sup>14,20,26–28</sup>

Furthermore, doping TiO<sub>2</sub> with multiple dopants has become an effective and promising approach to improve the photocatalytic performance of TiO<sub>2</sub>.<sup>6,8,29–31</sup> Our recent work has demonstrated that TiO<sub>2</sub> co-doped with (N, Sn)<sup>6</sup> or (N, In)<sup>32</sup> exhibits improved visible-light photocatalytic activity in

comparison with nitrogen-doped TiO<sub>2</sub>. In addition, TiO<sub>2</sub> doped with N and Zr has been investigated by some researchers. For example, Liu et al.<sup>33</sup> prepared nitrogen and zirconium co-doped TiO<sub>2</sub> nanotube arrays that exhibited improved photocatalytic efficiency. Gao et al.<sup>34</sup> synthesized nitrogen-doped Ti<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> that demonstrated an extended visible-light response. However, the existing states of the dopants for Zr and N co-doped TiO<sub>2</sub> and their corresponding band structures have still not been explored, and the influence of the dopants' existing states on the absorption and behavior of the photogenerated carriers as well as the photocatalytic mechanism of the photocatalysts still needs to be investigated further.

In this work, TiO<sub>2</sub> doped with nitrogen and zirconium catalysts were prepared via a sol-gel method. It was found that the modified N was present as a surface species (NO<sub>x</sub>) and the introduced Zr<sup>4+</sup> ions were weaved into the anatase lattice in a substitutional mode, whereas the excess Zr<sup>4+</sup> ions formed ZrTiO<sub>4</sub> on the surface. The doped Zr<sup>4+</sup> ions in the substitutional mode and the surface NO<sub>x</sub> species both contributed to the remarkable absorption of these catalysts in

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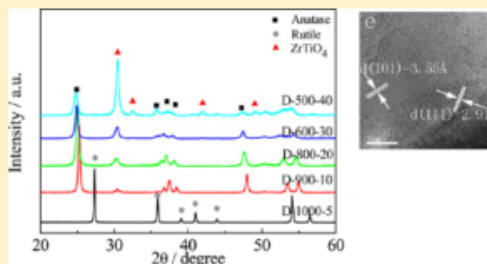
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Doping Behavior of  $\text{Zr}^{4+}$  Ions in  $\text{Zr}^{4+}$ -Doped  $\text{TiO}_2$  NanoparticlesJingsheng Wang,<sup>†</sup> Yanlong Yu,<sup>†</sup> Sha Li,<sup>†</sup> Limei Guo,<sup>†</sup> Enjun Wang,<sup>‡</sup> and Yaan Cao<sup>\*,†</sup><sup>†</sup>The MOE Key Laboratory of Weak Light Nonlinear Photonics, TEDA Applied Physics Institute and School of Physics, Nankai University, Tianjin 300457, China<sup>‡</sup>Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei 230031, China

## Supporting Information

**ABSTRACT:**  $\text{TiO}_2$  nanoparticles doped with different concentrations of  $\text{Zr}^{4+}$  ions were prepared by the sol–gel method and annealed at different temperatures. X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and high resolution transmission electron microscopy (HRTEM) techniques were used to investigate the existing states and doping mechanism of dopants as well as the phase transition of the  $\text{Zr}^{4+}$ -doped  $\text{TiO}_2$  samples. It was revealed that the doping behavior of introduced  $\text{Zr}^{4+}$  ions was closely related to the doping concentration. The  $\text{Zr}^{4+}$  ions would replace the lattice  $\text{Ti}^{4+}$  ions directly in substitutional mode at a certain annealing temperature. Moreover, if the concentration of doped  $\text{Zr}^{4+}$  ions is high enough, excess  $\text{Zr}^{4+}$  ions would form  $\text{ZrTiO}_4$  on the surface of  $\text{TiO}_2$ . In addition, the phase transition temperature from anatase to rutile increases significantly after doping  $\text{Zr}^{4+}$  ions, due to their larger electropositivity and radius than those of  $\text{Ti}^{4+}$  ions. Our results may afford a better understanding on the doping mechanism and aid in the preparation of  $\text{Zr}$ -doped  $\text{TiO}_2$  with high photoelectric performance.



## 1. INTRODUCTION

As one of the most important functional materials,  $\text{TiO}_2$  has been extensively investigated for its wide applications from catalysis to photoelectrochemistry.<sup>1–10</sup> However, owing to its large band gap, pure  $\text{TiO}_2$  cannot use solar energy efficiently, especially visible light. Doping  $\text{TiO}_2$  with metal or nonmetal elements is considered to be one of the most efficient methods to make full use of solar light. Asahi et al. found that nitrogen-doped  $\text{TiO}_2$  exhibits enhanced visible-light response and improved photocatalytic activity under visible-light irradiation.<sup>11</sup> Zhao et al. reported that doping B in  $\text{TiO}_2$  could extend the spectral response to the visible region.<sup>12</sup> Choi and co-workers reported that doping  $\text{TiO}_2$  with Fe, Mo, Ru, Os, Re, V, Rh, Co, and Al is an effective method to enhance photocatalytic activity.<sup>13,14</sup> A series of other metal or rare earth ions such as  $\text{W}^{6+}$ ,  $\text{V}^{5+}$ ,  $\text{Ce}^{4+}$ ,  $\text{Zr}^{4+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{La}^{3+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ag}^+$ ,  $\text{Sm}^{3+}$ ,  $\text{Nd}^{3+}$ , and  $\text{Pr}^{3+}$  have been also investigated.<sup>15–20</sup> As a titanium subgroup element, Zr has the same valence shell structure ( $(n-1)d^{ns^2}$  and valence state as Ti, so  $\text{Zr}^{4+}$ -doped  $\text{TiO}_2$  has attracted much interest from researchers. Chang and Doong<sup>21</sup> prepared a series of  $\text{Zr}^{4+}$ -doped  $\text{TiO}_2$  via a sol–gel method. Venkatachalam et al.<sup>22</sup> reported that  $\text{Zr}^{4+}$  doping of  $\text{TiO}_2$  presented enhanced catalytic activity. Lukáč et al.<sup>23</sup> researched the influence of different temperature treatments on the photocatalytic performance of  $\text{Zr}^{4+}$ -doped  $\text{TiO}_2$ . Liu et al.<sup>24</sup> reported the synthesis and photocatalytic activity of  $\text{Zr}$ -doped  $\text{TiO}_2$  nanotube arrays. However, there are few systematic reports on the doping mechanism of  $\text{Zr}^{4+}$  ions in  $\text{TiO}_2$ , such as

the influence of  $\text{Zr}^{4+}$  doping on the structure and the phase transition of  $\text{TiO}_2$ , and the existing states of  $\text{Zr}^{4+}$  ions under different conditions.

In this work, a series of  $\text{TiO}_2$  doped with different concentrations of  $\text{Zr}^{4+}$  ions were prepared via the sol–gel method and annealed at different temperatures. We studied the doping mode and existing states of  $\text{Zr}^{4+}$  ions in  $\text{TiO}_2$  and the conversion from substitutional doping  $\text{Zr}^{4+}$  ions to  $\text{ZrTiO}_4$  as well as the influence on the phase transition temperature of  $\text{TiO}_2$ .

## 2. EXPERIMENTAL METHODS

**2.1. Sample Preparation.** At room temperature, a certain amount of  $\text{ZrOCl}_2$  was added into 50 mL of anhydrous ethanol solution. After mixing equally under vigorous stirring, 15 mL of tetrabutyl titanate and 3 mL of deionized water were added dropwise into the ethanol solution. The pH of the mixture was 0.8, controlled by adding concentrated HCl (12 mol/L). The obtained sol was stirred continuously until the formation of gel, which was aged for 24 h at room temperature. The as-prepared gel was dried at 100 °C for 10 h, and then triturated to powder in an agate mortar. The powder was calcined at different temperatures for 2.5 h. A series of zirconium-doped  $\text{TiO}_2$

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