

# Efficient Promotion of Anatase TiO<sub>2</sub> Photocatalysis via Bifunctional Surface-Terminating Ti–O–B–N Structures

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The surface structures of doped semiconductor photocatalysts play a vital role in determining visible light absorbance, transfer and redox potentials of charge carriers, as well as the inhibition of recombination. We examine the photocatalysis of anatase TiO<sub>2</sub> with surface terminating Ti–O–B–N structures from both experimental and computational perspectives. This codoped titania system shows much better photocatalytic activity in generating •OH radical species and degrading organic pollutants in comparison with B-doped anatase titania. We present indicative evidence that the Ti–O–B–N surface structures can exhibit bifunctionality in promoting photocatalysis, (i) supplying partially occupied localized states attributed to B–N coupling with spectral distribution that is advantageous for enhancing visible light absorption and (ii) acting as photocatalytic “hot sites” to support localization and separation of charge carriers at the surface. These results offer important implications for designing highly efficient photocatalysts based on codoping strategies.

## 1. Introduction

Anatase titanium dioxide (TiO<sub>2</sub>) with bandgap of 3.2 eV has been widely investigated in photoelectrochemical processes,<sup>1–5</sup> dye-sensitized solar cells,<sup>6–8</sup> and photocatalysis reactions<sup>9,10</sup> in response to growing environmental concerns and an increasing demand for sustainable energy technologies. Substantial effort has been devoted to using transition metal and nonmetal doping strategies to impart the normally UV-active TiO<sub>2</sub> with a visible-light active photocatalytic response.<sup>11–18</sup>

The additional visible light absorption of TiO<sub>2</sub> induced by doping can be considered to be the result of localized states of dopants formed in the band gap and/or a modification of the intrinsic band gap.<sup>12,18</sup> Such visible light absorption does not, however, always result in corresponding visible light photocatalytic activity and sometimes can even impair the UV activity.<sup>18</sup> Fundamentally, this issue can be understood in terms of (1) deleterious bulk recombination of charge carriers caused by the introduction of recombination centers; (2) a lack of favorable surface structures facilitating surface transfer and reactivity of carriers; (3) the spectral distribution of doping-induced localized states not being optimal to facilitate the photo-oxidation reactions.

Considering the current doping procedures for nonmetal elements and the surface-sensitive nature of X-ray photoelectron spectroscopy (XPS) as the main characterization technique for

dopants, it can be conjectured that most dopant species should be located at or near the surface of TiO<sub>2</sub>.<sup>19</sup> For example, even with ion implanting technique, it has been determined experimentally that the maximum depth of nitrogen dopant was around 3 nm from TiO<sub>2</sub> particle surface.<sup>20</sup> Batzill et al.<sup>21</sup> reported the simulated distribution of N atoms implanted at 500 eV to lie mainly within a depth of 2–4 nm of anatase and rutile titania surface, which is also the detectable sampling depth in XPS measurements.

Many experimental and theoretical investigations of metal–metal,<sup>22</sup> metal–nonmetal<sup>23</sup> and nonmetal–nonmetal<sup>24–32</sup> codoping have been conducted. The coupling of one dopant with the second has been proposed to enable a reduction in the number of carrier recombination centers by the proposed charge equilibrium mechanism,<sup>22c</sup> as well as enhancing visible light absorbance by increasing the solubility limit of dopants. For example, Ikeda et al.<sup>22c</sup> reported a synergistic effect of Cr<sup>3+</sup>/Sb<sup>5+</sup> codoping as a result of charge equilibrium mechanism, and Sanz et al.<sup>23g</sup> found increased solubility of nitrogen implanted in TiO<sub>2</sub> by Au surface preadsorption. In contrast to previously reported B, N codoping without the formation of B–N bond structure,<sup>31</sup> we recently demonstrated the vital role of surface Ti–B–N bond structure in enhancing visible light absorbance and surface separation probability of carriers.<sup>32</sup> It appears, then, that appropriate coupling between two dopants is the key to realizing synergistic effects of codoping.

In the previous investigation on synergistic effects of B, N codoping on photocatalytic activity of TiO<sub>2</sub>,<sup>32</sup> at least three important issues remain unclear. One is whether the B–N bond is still active in promoting photocatalytic activity when it ends on the exposed surface O atoms of TiO<sub>2</sub>. The second is how the B–N bonds acting as the “co-catalyst” trap carriers. The third is whether the photogenerated holes in B, N codoped TiO<sub>2</sub>

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can have sufficient oxidation power to be directly involved in photocatalysis reactions or indirectly generate important photocatalysis active species such as  $\bullet\text{OH}$  radicals. In this work, we have utilized a new route to synthesize codoped anatase titania with surface terminating Ti–O–B–N moieties. This codoped system is found to exhibit superior photocatalytic properties, and we explore by a combination of experimental characterization and electronic structure calculations the structural and mechanistic features underlying these advantageous properties. Significant insight is gained into the role of surface terminating Ti–O–B–N moieties in modifying and enhancing photon harvest, redox power, and surface transfer of photoinduced carriers on  $\text{TiO}_2$  so that a full image of the positive role of B and N codoping in promoting photocatalytic activity of  $\text{TiO}_2$  is achieved.

## 2. Experimental Section and Computational Details

**Sample Preparation.** Titanium tetrafluoride ( $\text{TiF}_4$ , Aldrich) and boric acid were employed as a titania precursor and a boron dopant precursor. In a typical synthesis procedure, 3 g of  $\text{TiF}_4$  powder precursor was dissolved into 100 mL of aqueous solution of 0.5 M  $\text{H}_3\text{BO}_3$ , followed by hydrothermal treatment in a Teflon-lined autoclave at 180 °C for 12 h. The collected samples were calcined in air at 400 °C for 2 h to obtain boron-doped titania. To realize nitrogen doping, boron doped titania was calcined at 600 °C in ammonia atmosphere for 30 min. For comparison, boron doped titania was also calcined at 600 °C in air for 30 min.

**Characterization.** X-ray diffraction (XRD) patterns were recorded on Rigaku diffractometer using Cu irradiation. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were performed on Tecnai F30 and JEOL (6300) electron microscopy instruments. A UV–visible spectrophotometer (JASCOV550) was used to obtain the optical absorbance spectra of the samples. Raman spectra were recorded on LabRam HR 800. IR spectra were collected on a Nicolet 6700 with a resolution of 4  $\text{cm}^{-1}$  by using attenuated total reflectance (ATR) techniques. Chemical compositions of derived  $\text{TiO}_2$  were analyzed using XPS (Thermo Escalab 250, a monochromatic Al K $\alpha$  X-ray source). All binding energies were referenced to the C 1s peak (284.6 eV) arising from adventitious carbon.

**Photocatalytic Activity Tests.** The photocatalytic performance tests were carried out by adding 50 mg of photocatalysts into 100 mL of  $2 \times 10^{-5}$  M Rhodamine B (RhB) solution. The suspension was stirred in dark for 30 min to obtain saturated adsorption of RhB before illumination. The light source was a 300 W Xe lamp (Beijing Trustech. Co., Ltd., PLS-SXE-300UV) with cutoff by a combination of two glass filters with the wavelength of 200 to 770 nm and 420 to 770 nm, respectively. The measurements of the amount of  $\bullet\text{OH}$  were conducted according to the literature.<sup>33</sup> That is, 20 mg of photocatalyst was suspended in 80 mL of aqueous solution containing 0.01 M NaOH and 3 mM terephthalic acid (TA). Before exposure to visible light irradiation, the suspension was stirred in dark for 30 min. Then, 5 mL of solution was taken out after every 30 min and centrifuged for fluorescence spectra measurements. During the photoreactions, no oxygen was bubbled into suspension. The employed excitation light for recording fluorescence spectra is 320 nm.

**Computational Details.** All first-principles calculations were carried out using spin-polarized density functional theory (DFT) within the generalized-gradient approximation (GGA),<sup>34a</sup> with the exchange-correlation functional of Perdew–Burke–Ernzerhof

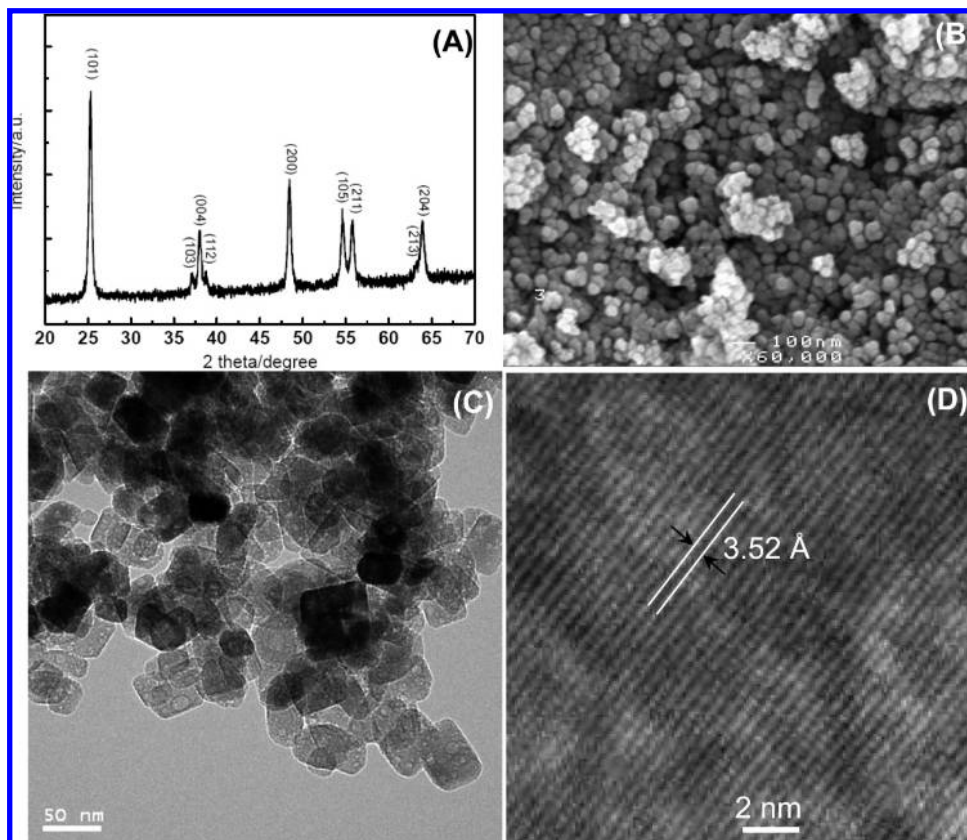
(PBE),<sup>34b,c</sup> based on the numerical double-numerical polarization (DNP) basis set, which has been implemented in the Dmol3 modules.<sup>34d,e</sup> More tests and the discussion regarding the efficiency and reliability of the DNP basis set can be found in Delley's work.<sup>34e</sup> Optimization of atomic positions were performed on alternate cycles using the BFGS method until the convergence criteria were met (maximum energy change per atom =  $1.0 \times 10^{-6}$  eV, maximum root-mean-square (rms) force = 0.03 eV  $\text{\AA}^{-1}$ , maximum rms stress = 0.02 GPa, and maximum rms displacement =  $5.0 \times 10^{-4}$   $\text{\AA}$ ). On the basis of the optimized structures, densities of states (DOS) and projected DOS were calculated using the CASTEP package.<sup>34f</sup> The electronic core wave function was described using the standard ultrasoft pseudopotentials available with the package. The k-point set used to sample the reciprocal space was generated using a Monkhorst-Pack grid ( $4 \times 4 \times 4$ ).<sup>34g</sup> PBE functional was used to model electronic exchange and correlation. The self-consistent field (SCF) tolerance was set as  $1.0 \times 10^{-6}$  eV/atom.

## 3. Results and Discussion

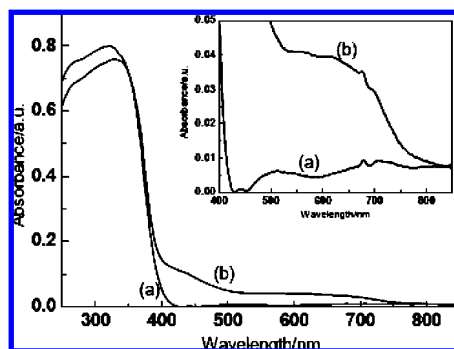
**3.1. Crystal Structure and Morphology.** The XRD patterns of boron-doped  $\text{TiO}_2$  by the hydrothermal process (Figure 1A) shows the crystal structure of pure anatase phase (space group  $I4_1/amd$ ). The average particle size determined from representative SEM (Figure 1B) and TEM (Figure 1C) images is around 50 nm. It is worth noting that there are some obvious cavities of the size of several nanometers on the surface of nearly rectangular  $\text{TiO}_2$  particles (Figure 1C). These surface cavities are formed as a result of the substantial etching of generated  $\text{F}^-$  from the hydrolysis of  $\text{TiF}_4$ .<sup>35</sup> Clear lattice fringes with a distance of around 3.52  $\text{\AA}$  can be ascribed to the most thermally stable and major anatase (101) facets. After nitrogen doping at 600 °C, both the morphology and crystal structure of  $\text{TiO}_2$  are well retained, and the crystallinity is further improved compared to the as-prepared  $\text{TiO}_2$  directly from the hydrothermal process.

**3.2. Optical Properties.** Figure 2 gives the UV–visible absorption spectra of B-doped  $\text{TiO}_2$  and B,N-codoped  $\text{TiO}_2$ . For the former, only very weak visible light absorption ranged from ca. 450 nm to infrared region (shown in the inset) is observed. Codoping of nitrogen results in two significant changes in the absorption spectrum. One is the appearance of a new absorption shoulder around 400–550 nm, and the other is the greatly enhanced absorbance in the range of 550–750 nm. Meanwhile, both the intrinsic absorption edge and the light response characteristics beyond 750 nm are retained. Nitrogen doping of  $\text{TiO}_2$  by thermal treatment in an ammonia atmosphere results in a visible light absorption shoulder in the range from 400 to 550 nm due to the introduction of some localized states in the intrinsic band gap.<sup>18</sup> In our B,N-codoped  $\text{TiO}_2$ , it appears that the increased shoulder in the range of 400–550 nm is directly related to the nitrogen doping, while the enhanced absorbance in the range of 550–750 nm arises from synergistic effects of B,N codoping on the electronic structure of  $\text{TiO}_2$ . The absorption spectra of B-doped  $\text{TiO}_2$  and B,N-codoped  $\text{TiO}_2$  will be further discussed in conjunction with the first-principles calculations below.

**3.3. Photocatalytic Activity.** Figure 3 shows the photocatalytic activity of B doped and B, N codoped  $\text{TiO}_2$  in decomposing organic pollutant RhB under both UV–visible and visible irradiation. In contrast to B-doped  $\text{TiO}_2$ , the degradation rate of RhB with B,N-codoped  $\text{TiO}_2$  is drastically improved under both UV–visible light and visible light irradiation. For example, compared to 18% with B-doped  $\text{TiO}_2$ , the degradation percentage with B,N-codoped  $\text{TiO}_2$  under the irradiation of UV–visible



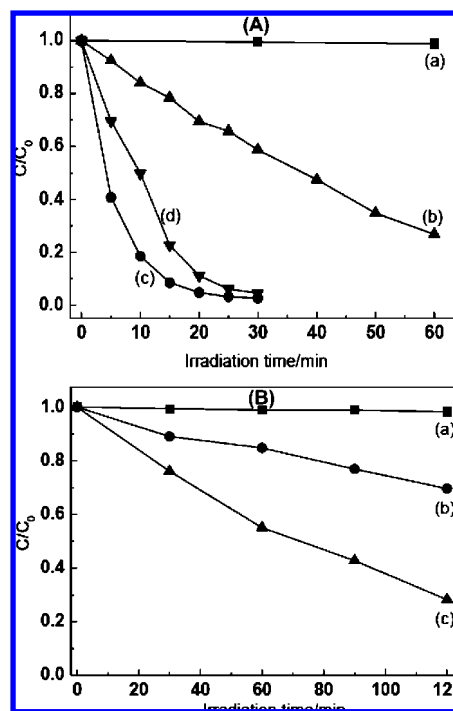
**Figure 1.** (A) XRD patterns, (B) SEM image, (C) TEM image, and (D) high-resolution TEM image of resultant TiO<sub>2</sub>.



**Figure 2.** Optical absorption spectra of B doped TiO<sub>2</sub> (a) and B, N codoped TiO<sub>2</sub> (b). The inset is the enlarged curves between 400 and 850 nm.

light can reach 80% within 10 min, which is also better than P25 TiO<sub>2</sub>. Even with the irradiation of visible light (420–770 nm), the degradation percentage can increase from 30% to 73% within 2 h. Clearly, a significant synergistic effect of B,N codoping in enhancing the photocatalytic efficiency is evidenced.

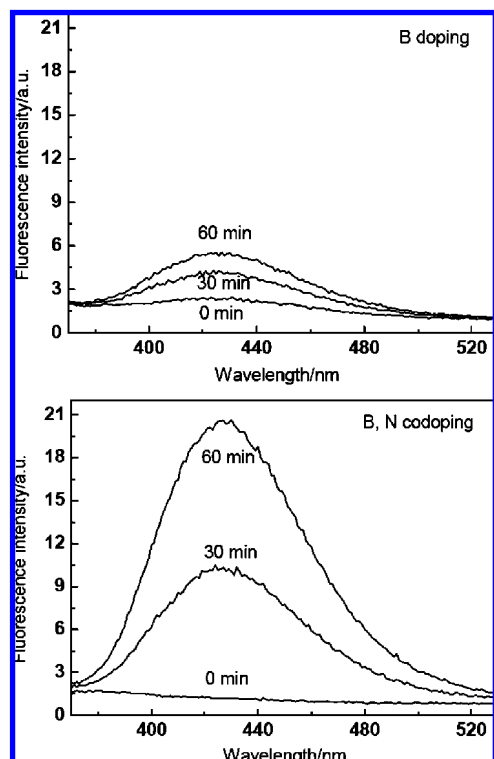
Subsequent to photoexcitation, electron holes with sufficient oxidation power in the VB, or in localized states within the band gap, can either be directly involved in the photocatalytic degradation reactions or, alternatively, may generate active species such as hydroxyl radical  $\cdot\text{OH}$  by reacting with surface adsorbed water and hydroxyl groups.<sup>9</sup> It is known that  $\cdot\text{OH}$  reacts with TA in basic solution and generates 2-hydroxy terephthalic acid (TAOH), which emits a unique fluorescence signal with the peak at 426 nm.<sup>33</sup> As shown in Figure 4, obvious fluorescence spectra associated with TAOH are generated upon the visible light 420–770 nm irradiation of B-doped TiO<sub>2</sub> and of B,N-codoped TiO<sub>2</sub> suspended in TA solution. This indicates that the holes generated by the visible light excitation possess



**Figure 3.** Comparison of photocatalytic activity of photocatalysts under the irradiation of (A) 220–770 nm and (B) 420–770 nm: (a) no photocatalyst; (b) B-doped TiO<sub>2</sub>; (c) B,N-codoped TiO<sub>2</sub>; and (d) commercial P25 TiO<sub>2</sub>.

sufficient oxidation power and can be transferred to surface-adsorbed water molecules and/or hydroxyl groups at the surface in the presence of dopant sites. The B,N-codoped TiO<sub>2</sub> shows 4 times higher visible light activity in generating  $\cdot\text{OH}$  than B-doped TiO<sub>2</sub>. In addition, it should be pointed out that, besides





**Figure 4.** Fluorescence spectra measured for the visible-light (420–770 nm) irradiated B-doped TiO<sub>2</sub> and B,N-codoped TiO<sub>2</sub> suspension in 3 mM TA at different irradiation times.

the dominant route of holes attacking water or hydroxyl groups, another secondary route to produce hydroxyl radicals is also possible via the following reactions:<sup>19,36</sup>



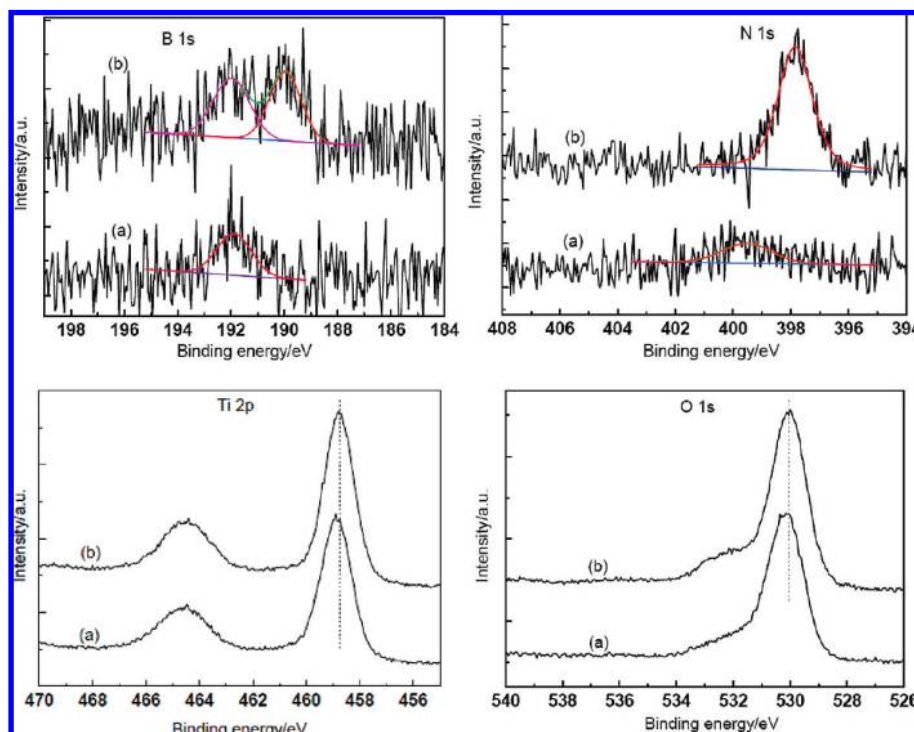
The key in this route is the involvement of protons in the second step. However, the probability of this step can be very low as a result of the basic solution employed in this work.

**3.4. Composition and Chemical State Analysis.** To understand the unique visible light absorption characteristics and enhanced photocatalytic activity of B,N-codoped TiO<sub>2</sub>, we first investigated the chemical states of boron and nitrogen dopants on the titania surface by high-resolution XPS. The spectra of B 1s and N 1s are shown in Figure 5. The as-prepared B-doped TiO<sub>2</sub> was surface-enriched in F species with the binding energy of 684.6 eV (not shown here), which is usually observed in surface fluorinated TiO<sub>2</sub> systems as TiOF<sub>2</sub> or ≡Ti–F species on a TiO<sub>2</sub> crystal surface.<sup>37</sup> After a simple calcination in air or ammonia atmosphere, the surface F species on a B-doped surface can be easily removed as reported.<sup>37</sup> For B-doped TiO<sub>2</sub>, the peak at 191.8 eV in the B 1s spectrum originates from Ti–O–B bonds,<sup>38</sup> and the very weak peak at 399.6 eV in the N 1s spectra is from surface-adsorbed nitrogen species, which were commonly observed in both pure and nitrogen-doped TiO<sub>2</sub>.<sup>12a</sup> After additional nitrogen doping in B-doped TiO<sub>2</sub>, a new peak with its center at 190.0 eV appears in the B 1s spectrum besides the original peak shift from 191.8 to 192.0 eV. Meanwhile, a new N chemical state is determined in the N 1s spectrum with its peak at 397.8 eV. As proposed in the previous work,<sup>32</sup> these two new peaks can be clearly related to

the formation of B–N bonds. In this case, two possibilities for the formation of B–N bonds exist, namely Ti–N–B by replacing O in Ti–O–B bonds with N and Ti–O–B–N by reacting exposed B in Ti–O–B during nitridation. However, considering the likely free energy cost of substituting O for N in the Ti–O–B structure and the fact that the Ti–N–B structure would not make any contribution to visible light absorption (Figure 8, to be discussed further below), it is anticipated that the Ti–O–B–N structure will predominate. We did not observe an additional N peak potentially attributed to nitrogen dopant in the TiO<sub>2</sub> matrix, possibly because it is too low in concentration to be detected by XPS.<sup>18</sup> Comparing Ti 2p and O 1s spectra, no obvious binding energy shift is observed after N codoping. The amounts of boron and nitrogen in B,N-codoped TiO<sub>2</sub> are ca. 5.88 at. % and 3.89 at. %. On the basis of the above results, it can be concluded that Ti–O–B and Ti–O–B–N bond structures are formed respectively at the surfaces of B-doped anatase TiO<sub>2</sub> and B,N-codoped anatase TiO<sub>2</sub>.

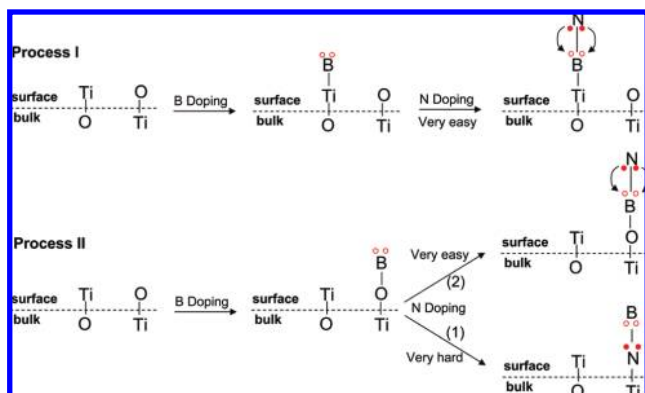
We can reasonably explain why B and N have similar XPS peak positions in Ti–B–N and Ti–O–B–N structures. The key to understanding this issue is that the binding energies of B 1s and N 1s are intrinsically determined by the *inner* electron states, which are also affected by their bonding states with other elements via the interaction of their *outer* electrons (valence electrons). Because of the unsaturated coordination of B atom and the unpaired electrons of N atom, the interaction of B with N can be much stronger as evidenced by both experimental (the substantially enhanced amount of N dopant in Figure 5) and theoretical (The strong B and N electron state coupling in Figure 8h presented below) results than that of B with O or Ti. In this situation, the B–N unit in either the Ti–B–N structure or the Ti–O–B–N structure can give a similar characteristic to bulk crystalline BN so that the nearly identical B 1s and N 1s binding energies are observed in both structures. In addition, the strong bonding interaction between B and N plus the saturated coordination of O may make it harder or nearly impossible to replace the O of a Ti–O–B structure with N into a Ti–N–B structure. The above understanding is summarized in Scheme 1.

**3.5. ATR-IR and Raman Spectroscopy.** The effects of additional nitrogen doping on the surface structure properties of B-doped anatase TiO<sub>2</sub> were further investigated by ATR-IR and Raman spectra because of their high sensitivity to local surface bond structures.<sup>39</sup> As shown in Figure 6, the main infrared active bands at 400–700 cm<sup>−1</sup> in referenced anatase TiO<sub>2</sub> (Aldrich), B-doped anatase TiO<sub>2</sub> and B,N-codoped anatase TiO<sub>2</sub> are attributed to Ti–O stretching and Ti–O–Ti bridging modes.<sup>40</sup> In contrast to the reference undoped TiO<sub>2</sub>, a new band at 1273–1500 cm<sup>−1</sup>, which is attributed to asymmetric stretching of the B–O vibration,<sup>41a</sup> appears in both B-doped TiO<sub>2</sub> and B,N-codoped TiO<sub>2</sub>. The shift from 1396 to 1380 cm<sup>−1</sup> of B–O stretching band after nitrogen doping is likely caused by some degree of mixing of local mode B–O and B–N vibrations. A similar shift of the overlapped stretching band of B–O and Si–O toward lower frequency upon the formation of B–N and Si–N bonds was also observed in SiO<sub>2</sub>–B<sub>2</sub>O<sub>3</sub> aerogels.<sup>41b</sup> The region of 1500–1750 cm<sup>−1</sup> can be attributed to the bending vibration of O–H. The broadband in the region of 2800–3400 cm<sup>−1</sup> originates from the vibration of O–H for surface-absorbed water molecules and hydroxyl groups, which are conventionally considered as important factors in affecting photocatalytic activity.<sup>42</sup> Upon nitrogen doping, the intensity of surface-absorbed water molecules and hydroxyl groups on B-doped TiO<sub>2</sub> remarkably decreased.



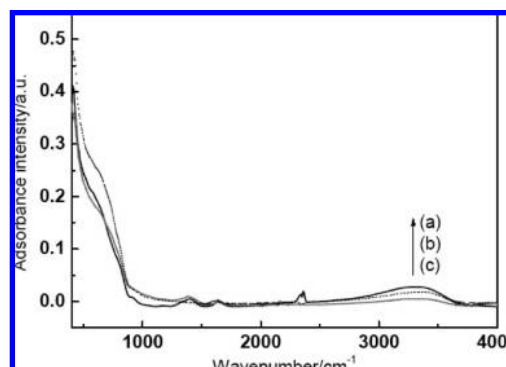
**Figure 5.** High-resolution XPS spectra of B 1s and N 1s, Ti 2p and O 1s in boron-doped TiO<sub>2</sub> (a) and N,B-codoped TiO<sub>2</sub> (b).

#### SCHEME 1: B-Doping and Subsequent N-Doping Process on the Exposed TiO<sub>2</sub> Surfaces<sup>a</sup>

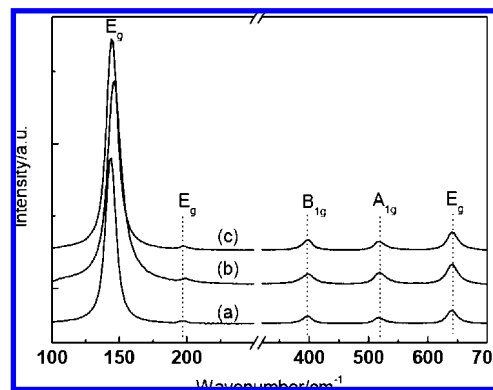


<sup>a</sup> Process I proposes the formation of a Ti–B–N surface structure, and Process II gives the formation of Ti–N–B (1) and Ti–O–B–N (2) surface structures. For simplicity, the coordination numbers of surface Ti and O atoms are not considered here.

Figure 7 gives Raman spectra of five typical active modes of anatase TiO<sub>2</sub>: E<sub>g</sub> (146 cm<sup>-1</sup>), E<sub>g</sub> (199 cm<sup>-1</sup>), B<sub>1g</sub> (397 cm<sup>-1</sup>), A<sub>1g</sub> (519 cm<sup>-1</sup>), and E<sub>g</sub> (642 cm<sup>-1</sup>), existing in B-doped anatase TiO<sub>2</sub>. In contrast to the reference anatase TiO<sub>2</sub>, its two E<sub>g</sub> modes at 146 cm<sup>-1</sup> and 199 cm<sup>-1</sup> are shifted by 3 cm<sup>-1</sup> toward higher wavenumbers. However, these two shifted E<sub>g</sub> modes can be recovered again by the surface Ti–O–B–N structure formed in B,N-codoped TiO<sub>2</sub>. The surface Ti–O–B structure formed on anatase TiO<sub>2</sub> inevitably impairs the symmetry of Ti–O–Ti network and thus changes some force constants, which intrinsically determine the wavenumbers of corresponded active Raman modes. In the previous work,<sup>43</sup> the replacement of Ti with I also leads to the similar shift of E<sub>g</sub> mode at 144 to 149 cm<sup>-1</sup>. In the current case, it may be anticipated that the introduction of the N atom at the end of Ti–O–B structure to create the Ti–O–B–N moiety may significantly weaken the B–O binding



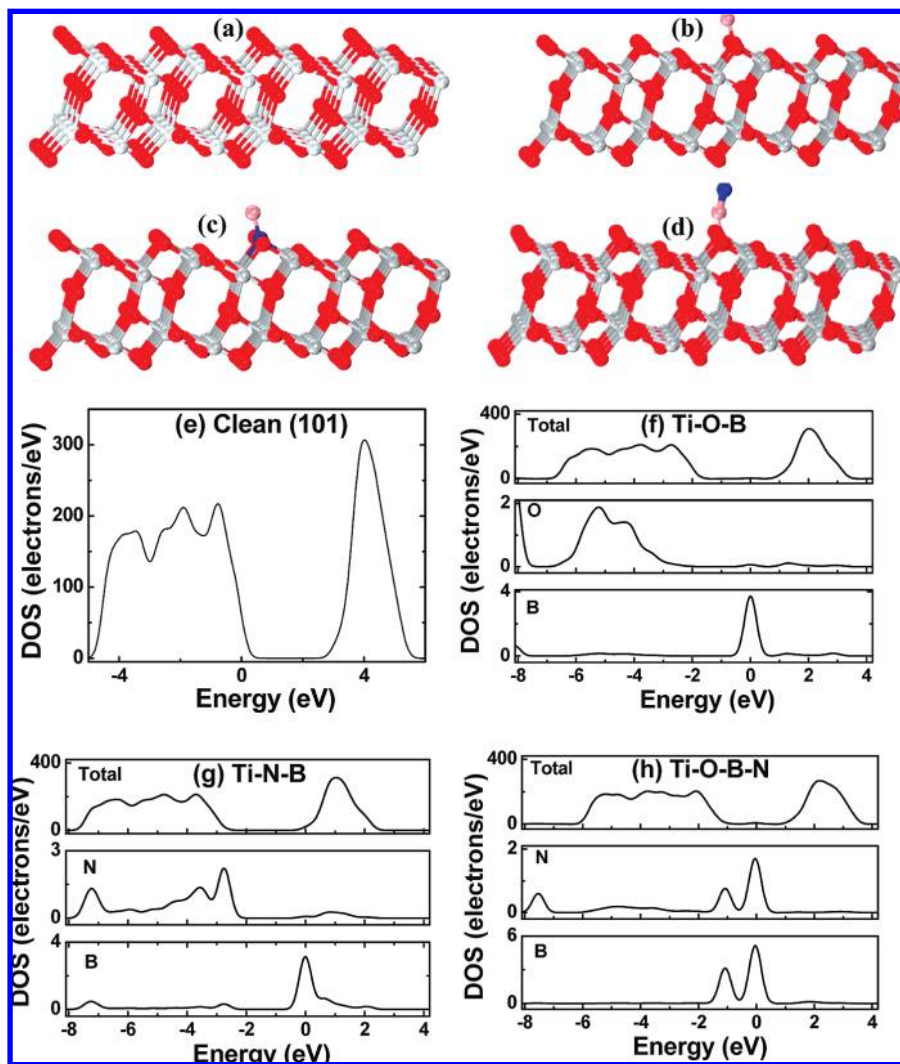
**Figure 6.** ATR-IR spectra of B-doped TiO<sub>2</sub> (a), reference anatase TiO<sub>2</sub> (b), and B,N-codoped TiO<sub>2</sub> (c).



**Figure 7.** Raman spectra of reference anatase TiO<sub>2</sub> (Aldrich) (a), B-doped TiO<sub>2</sub> (b) and B,N-codoped TiO<sub>2</sub> (c).

and thereby reduce the effect of the B atom in disrupting the symmetry of the Ti–O–Ti network.

**3.6. First-Principles Calculations.** To investigate the synergistic effect of B/N codoping, theoretical analysis of the electronic structures of various B/N adsorption configurations, including Ti–O–B, Ti–N–B, and Ti–O–B–N, was carried



**Figure 8.** Structural models and calculated electronic structures. (a) Clean (101) surface, (b) Ti-O-B structure on (101) surface, (c) Ti-N-B structure on (101) surface, and (d) Ti-O-B-N structure on (101) surface. Oxygen, titanium, boron, and nitrogen atoms are indicated by red, gray, pink, and blue spheres, respectively. (e-h) Calculated DOS and local DOS, corresponding to structures a-d.

out, with clean (101) surface as the reference. Surface structures are described by periodic  $4 \times 4$  slab models, as shown in Figure 8a-d, with Ti, O, B, and N labeled as gray, red, pink, and blue spheres, respectively. The calculated band structures, DOS, and local DOS are shown in Figure 8e-h, corresponding to the four surface conditions listed above. Analysis of the calculated results reveals three important features: (i) local states are introduced between VB and CB as a result of the B/N adsorption; (ii) the local DOS contributed by B atoms is localized at around Fermi level, independent of the adsorption configuration, whereas the local DOS contributed by N atoms is sensitive to the adsorption configuration; and (iii) the Ti-O-B-N moiety shows a unique double-peak feature in the introduced DOS, due to the strong O-B and N-B interactions.

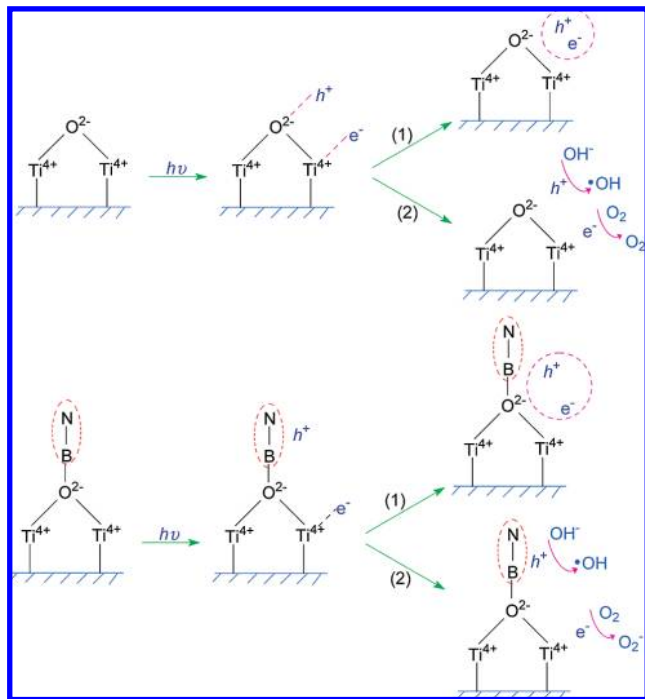
**3.7. Discussion.** It is dramatically apparent from Figures 3 and 4 above that B,N-codoped anatase TiO<sub>2</sub> with surface terminating Ti-O-B-N moieties shows much better photocatalytic activity than B-doped anatase TiO<sub>2</sub> with the surface Ti-O-B structure. These two anatase TiO<sub>2</sub>-based photocatalysts possess nearly the same morphology (rectangular particles), particle size (ca. 50 nm), crystallinity and specific surface area (ca.  $45 \text{ m}^2 \text{g}^{-1}$ ), which, therefore, cannot be responsible for the remarkable photocatalytic activity difference. Surface adsorbed water molecules and hydroxyl groups, which can trap holes to

generate the photocatalytically important active species  $\bullet\text{OH}$ , are considered as important factors in mediating photocatalytic activity. In the previous work,<sup>42</sup> the higher amount of adsorbed water molecules and surface hydroxyl groups for undoped anatase TiO<sub>2</sub> was proposed to be a factor in its higher photocatalytic activity compared with rutile TiO<sub>2</sub>. Recently, however, we have demonstrated in the case of nitrogen-doped TiO<sub>2</sub> with mixed phases of anatase and rutile that the amount of adsorbed water molecules and surface hydroxyl groups is not an exclusively determinant factor in high photocatalytic activity. Also playing a vital role is the abundance and efficacy of induced electronic surface states in promoting the surface transfer of carriers.<sup>44</sup> In the current study, the amount of adsorbed water and surface hydroxyl groups on B,N-codoped TiO<sub>2</sub> is much lower than that of B-doped TiO<sub>2</sub>, as evidenced by ATR-IR in Figure 6; yet the photocatalytic efficiency is greater, further underlining the conclusions of the earlier work.<sup>44</sup>

Motivated by the experimental results and theoretical insight presented above, we suggest that the markedly enhanced photocatalytic activity of B,N-codoped anatase TiO<sub>2</sub> under both UV and visible light irradiation can be rationalized in terms of three key features. The first feature is the increased absorbance in the visible range 400–750 nm (Figure 2) by localized electronic states associated with the surface Ti-O-B-N



**SCHEME 2:** Schematic of Photoexcitation of Carriers, Surface Recombination Process (Step 1) of Photoinduced Electrons and Holes, and Surface Transfer Process (Step 2) of Carriers by Trapping Carriers with an Electron Donor (i.e., OH<sup>−</sup>) and Acceptor (i.e., O<sub>2</sub>) on Anatase TiO<sub>2</sub> (Upper) and B,N-Codoped Anatase TiO<sub>2</sub> (Below)<sup>a</sup>



<sup>a</sup> For simplicity, the coordination numbers of surface Ti and O atoms are not considered here.

structure. These states originate from electronic coupling between the codoped B and N, as shown in Figure 8, suggesting that the effect is indeed synergistic. Second, the spectral distribution of these states is such that they possess more positive potentials than the OH<sup>−</sup>/•OH redox potential, evidenced by the effective generation of •OH radicals off the B,N-codoped TiO<sub>2</sub> particles under visible light irradiation. As illustrated in Figure 8, the occupied localized states from the B atom in the band gap of B-doped TiO<sub>2</sub> are close to the conduction band minimum (corresponding to a relatively lower oxidizing potential for holes created by optical excitation). On the contrary, the occupied localized states from the coupled B, N atoms locate more closely to the valence band maximum, indicating more oxidative power of holes in these states upon photon excitation. Third, the surface Ti–O–B–N moieties may act as a “hot sites” for trapping holes to promote surface transfer and separation of electrons and holes. Holes with more positive potential generated in the valence band upon UV excitation can presumably be easily transferred into the localized states of the surface Ti–O–B–N structure. In doing so, the spatial overlap of the charge carriers is reduced to retard their recombination probability due to the nature of localization.<sup>45</sup> Surface B–N structures acting as oxidation sites (i.e., OH<sup>−</sup> → •OH) are further from the surface Ti reduction sites (i.e., O<sub>2</sub> → O<sub>2</sub><sup>−</sup>) than surface lattice O, thereby reducing the surface recombination probability of trapped electrons and holes.

In summary of these ideas, Scheme 2 gives a schematic representation of photoexcitation, surface recombination and transfer processes of carriers on the surface of anatase TiO<sub>2</sub> and B, N codoped anatase TiO<sub>2</sub>.

#### 4. Conclusions

B,N-codoped anatase TiO<sub>2</sub> crystals with an average particle size of ca. 50 nm have been prepared via a facile hydrothermal route and subsequent thermal treatment in an ammonia atmosphere. The superior photocatalytic activity in comparison with B-doped anatase TiO<sub>2</sub> under both UV–visible and visible light irradiation is attributed to the unique electronic properties of the surface Ti–O–B–N bonding structure. This structure generates partially occupied localized states in the band gap with spectral distributions that allow for (a) enhanced visible light absorption and (b) the creation of electron holes of sufficient oxidizing power to allow for photo-oxidation reactions. Equally importantly, the Ti–O–B–N moiety can act as a photocatalytic “hot site” to promote surface separation and transfer of carriers by trapping holes. This is due to the localized nature of the Ti–O–B–N states contributing to a more effective physical separation of surface reduction and oxidation reactions by minimizing the state overlap that would contribute to electron hole recombination. Collectively, the present study not only presents a very efficient codoped TiO<sub>2</sub> photocatalyst but also derives significant insight into the synergistic effects of codoping of B and N as well as proposing rational models by which the enhanced photocatalytic behavior may be understood.

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