

Synergistic Effects of B/N Doping on the Visible-Light Photocatalytic Activity of Mesoporous TiO₂**

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The large bandgap of anatase titania (3.2 eV) restricts its photocatalytic applications to the UV range. To ensure visible-light photocatalytic activity of titania, it is therefore important to introduce visible-light absorption. Anion doping^[1–18] has shown great potential in introducing such absorption, and intensive efforts have been made to develop methods for synthesizing anion-doped titania-based photocatalysts with a visible-light response. However, visible-light absorption does not always result in visible-light photocatalytic activity—the key to enhancing photocatalytic activity lies in effectively combining the excitation, bulk diffusion, and surface transfer of photoinduced charge-carriers in the photocatalyst. While anion modification in titania changes the electronic structure and increases visible-light absorption, usually by introducing localized states in the bandgap, it also creates different surface structures that can intrinsically alter the surface transfer of carriers and hence the photocatalytic activity. For example, surface reconstruction of titania during N-doping has been demonstrated both experimentally and theoretically.^[19,20] Nitrogen doping of titania by thermal treatment under an ammonia atmosphere usually leads to very limited visible light activity but greatly impairs the UV activity.^[21]

Divergent results have been reported for the less-studied system involving B-doped TiO₂.^[7,22,23] For instance, Zhao et al.^[7] have demonstrated the effectiveness of sole B doping with a binding energy (BE) of about 191.6 eV in activating visible-light absorption, although they achieved only a very limited visible-light activity. In contrast, Lambert et al.^[23] have recently reported both efficient visible-light absorption and photocatalytic activity with low-level doping of B with a

BE of 190.6 eV, although they observed no synergistic effect of B/N doping. It is therefore highly important to design and construct effective photocatalyst surface structures that facilitate the separation and transfer of the carriers to develop efficient visible light photocatalysts.

Herein we demonstrate that there is a critical amount of B dopant in B-doped titania at which the binding energy (BE) of boron shifts from 192.1 to 191.5 eV and that the visible-light absorption of B-doped titania is dependent on the state of the doped boron. We also show that the limited visible-light activity of B-doped titania can be substantially enhanced by the formation of a B–N structure on the surface of titania. To the best of our knowledge, this is the first example to show the substantial role of B/N doping in enhancing the charge-carrier separation, and hence the photocatalytic activity, on the surface of the photocatalyst.

Mesoporous titania doped with different amounts of boron was synthesized in a modified two-step hydrothermal process and then calcined in air. N doping and B/N doping of the mesoporous titania were conducted with gaseous ammonia. The presence of B dopant seems to stabilize the structure, including the crystal size and specific surface area, relative to undoped titania during the N doping process. The optical absorption spectra of these photocatalysts are shown in Figure 1. There is a critical point for B doping at around 6 atom% B where an enhancement of the visible-light absorption between 400 and 600 nm is generated. The absorption intensity gradually increases as the amount of B increases to 14 atom% and is further enhanced upon additional N doping.

The photocatalytic activities of these photocatalysts were evaluated by monitoring the degradation of a model dye (Rhodamine B) upon irradiation with UV and visible light (> 420 nm) according to a procedure reported in the literature.^[24] The limited visible-light activity of B-doped titania is not sensitive to the amount of B dopant in the range 0.5 to 14 atom%, but the UV activity of B-doped titania gradually decreases compared to the undoped titania. Both the UV and visible-light activities for N-doped titania gradually weaken with an increase in N dopant, which is consistent with results reported previously.^[21] In summary, only a very limited visible-light photocatalytic activity is achieved for B- or N-doped mesoporous titania.

A substantial enhancement in both the UV and visible-light photocatalytic activity for B-doped titania was achieved upon additional doping with N provided the amount of B dopant was higher than about 6 atom%. Titania doped with about 10 atom% B shows the highest visible-light activity upon additional doping with between 1 and 13 atom% of N. Figure 2 shows the kinetic degradation curves of Rhodami-

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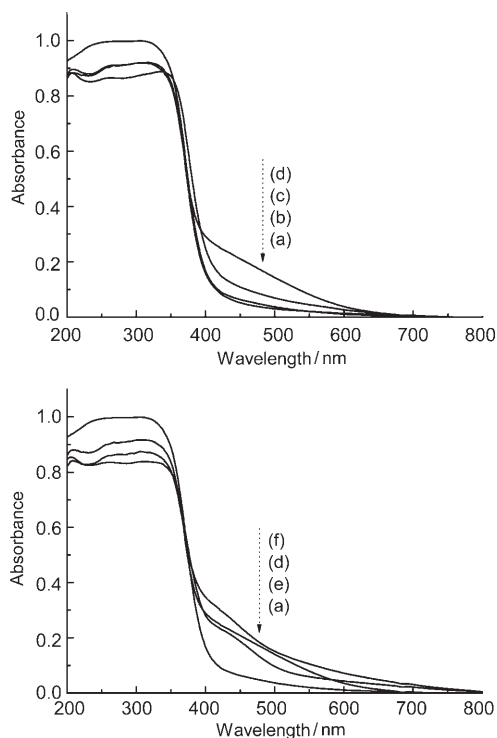


Figure 1. Top: UV/Vis absorption spectra of doped mesoporous titania with 0 (a), 2 (b), 6 (c), and 10 atom% boron (d). Bottom: UV-visible absorption spectra of N-doped mesoporous titania (e) and N-doped mesoporous titania (f) additionally doped with 10 atom% boron along with curves (a) and (d) from the top diagram.

ne B with different photocatalysts upon irradiation with UV/Vis and visible light, respectively. The kinetic constants normalized with respect to the specific surface area of each sample are given in Table 1.

The question now arose as to why this critical amount of B dopant strongly activates the visible-light absorption in B-doped titania and why additional doping with N enhances the photocatalytic activity. We therefore decided to examine the XPS spectra of these compounds (Figure 3) to determine the oxidation state of the dopants in these photocatalysts. The BE of the B 1s peak of B-doped titania shifts from 192.1 to 191.5 eV at around 6 atom% B when increasing the dopant content from 0.5 to 14 atom%, which is consistent with the onset (critical) point of visible-light absorption. The BE of the Ti 2p peak also shifts from 458.3 to 458.6 eV at this critical point. Three kinds of B dopants with BEs of about 191.6, 190.6, and 193 eV have been reported to date.^[7,22,23] The former two correspond to a O-Ti-B structure, which contributes to additional visible-light absorption, and the latter corresponds to a Ti-O-B structure, which only causes a blue-shift of the absorption edge. In our case, it is clear that the state of the B dopant is closer to the Ti-O-B structure before the critical point and the O-Ti-B structure after this point. New peaks with BEs of 190.0 and 397.7 eV appear in the B 1s and N 1s spectra, respectively, after additional N doping. Bulk BN can easily be formed from B₂O₃ and NH₃ above 500 °C. The BEs of the B 1s and N 1s peaks in bulk BN are 190.5 and

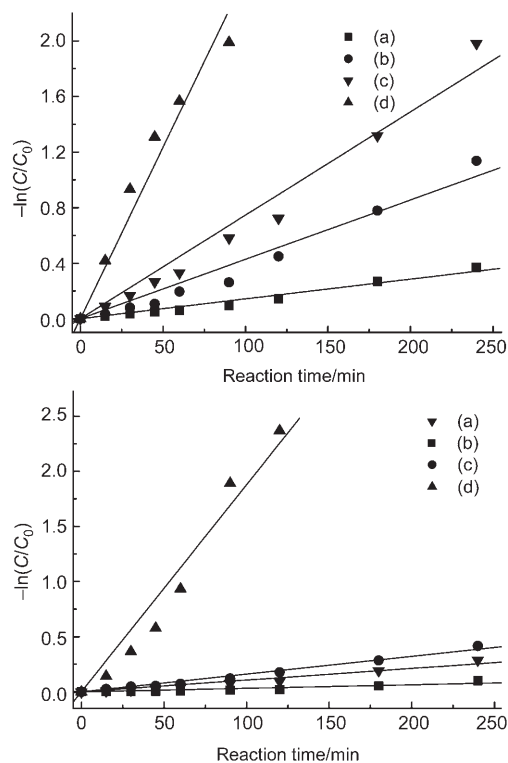


Figure 2. Kinetic photodegradation curves for Rhodamine B in the presence of B-doped titania (a), undoped titania (b), N-doped titania (c), and B/N-doped titania (d) upon irradiation with UV/Vis (top) and visible light ($\lambda > 420$ nm; bottom). The concentration of Rhodamine B was determined by monitoring the variation of the optical intensity at 554 nm.

Table 1: The specific surface area and normalized kinetic constants of photocatalysts under UV/Vis and visible light: a) undoped titania, b) N-doped titania, c) B-doped titania, and d) B/N-doped titania.

Sample	BET surface area [m ² g ⁻¹]	Normalized kinetic constant ^[a] [$\times 10^{-6}$ min ⁻¹]	
		UV/Vis	Vis
a	190	40.3	1.7
b	90	56	17.9
c	200	9.7	4.9
d	170	918.5	110.6

[a] Normalized with respect to the specific surface area.

398.1 eV, respectively, therefore we propose the formation of a O-Ti-B-N structure on the surface of B-doped TiO₂ due to nitridation; the two new peaks are direct proof of this. Moreover, the existence of such a surface structure can also be confirmed by the broadened X-ray diffraction peaks and weakened Raman-active modes (shown in the Supporting Information) of the N/B-doped titania.

We carried out quantum mechanical calculations to further confirm the possibility of such a bonding situation. The geometries, total energies, and electronic structures of undoped anatase, B-doped anatase, N-doped anatase, and B/N-doped anatase titania samples were investigated by density functional calculations. Ultrasoft pseudopotentials were expanded within a plane-wave basis set with a cut-off

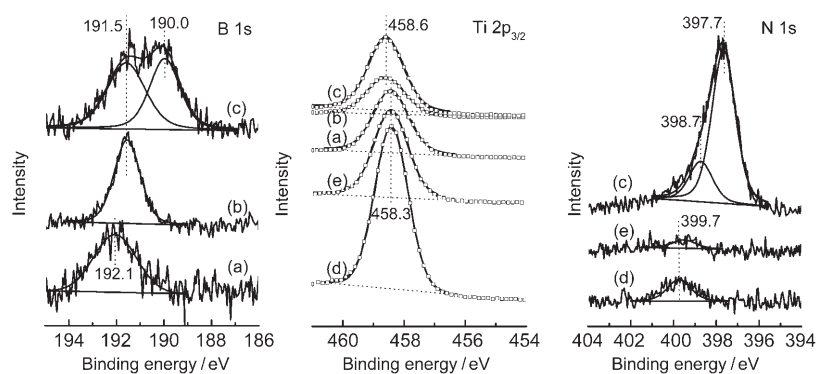


Figure 3. XP spectra showing the B 1s, Ti 2p, and N 1s bands for 2 atom% B-doped titania (a), 10 atom% B-doped titania (b), 10 atom% N/B-doped titania (c), undoped titania (d), and N-doped titania (e).

energy of 380 eV. The electron exchange-correlation was described by the generalized gradient approximation in the revised Perdew–Burke–Ernzerhof functional.^[25] The band structures and densities of states (DOS) were calculated for Γ points only. The calculations were considered to be converged when the total energy change was below 10^{-5} eV per atom and the stress change was less than 10^{-4} GPa.

The (001) surface of anatase was employed for two reasons: 1) it is a typical surface with unsaturated Ti atoms which can serve as absorption sites for B to form the B–Ti bonds observed in our XPS experiments; 2) the effect of oxygen atoms in the bulk anatase on the bonding of B or N can be neglected, which means that modeling can be simplified. Possible surface structures derived from the (001) surface are illustrated in Figure 4. It should be stressed, however, that the structures proposed here are only possibilities that explain the XPS results. The adsorption energies of the structures **B–F** are 6.23, 12.38, 11.38, 7.72, and 11.68 eV, respectively. These results suggest that: 1) B prefers to be adsorbed at the center of four Ti atoms; 2) the adsorption of B does not prevent the adsorption of N; and 3) the adsorption of N is preferred to that of B. It can therefore be deduced from the above results that B and N can be doped on the pristine surface of TiO_2 .

To further understand the effect of B/N doping on the electronic structures of TiO_2 , the densities of states corresponding to the structures **A–F** were calculated (lower portion of Figure 4). It can be concluded that: 1) the nature of the pure TiO_2 surface results in a couple of electronic states around the Fermi level due to the dangling bonds; 2) B/N doping can change these states dramatically when the dangling bonds are terminated by B and N and, at the same time, both B 2p and N 2p introduce new states around the upper valence band close to the Fermi level; and 3) B/N doping introduces more surface electronic states and changes the gaps between these states, which may have an important influence on the lifetime of excitons. Moreover, it can be seen that, with respect to the bulk doping, the changes of the electronic structures related to the surface modification focus on the states around the Fermi level.

The calculated results clearly indicate the role of O–Ti–B–N bonding in the formation of additional impurity states

which can contribute to the enhanced visible-light absorption after doping of N into B-doped titania. The possible contribution of both substitution of O for N and concomitant oxygen vacancies in the titania matrix to additional visible-light absorption should also be considered. This is because both the localized states of N 2p formed above the valence band maximum of O 2p,^[21] and the states below the conduction band minimum resulting from oxygen vacancies,^[26–28] can result in additional visible-light absorption.

The effective doping of N into the titania matrix was confirmed by the N 1s peak of

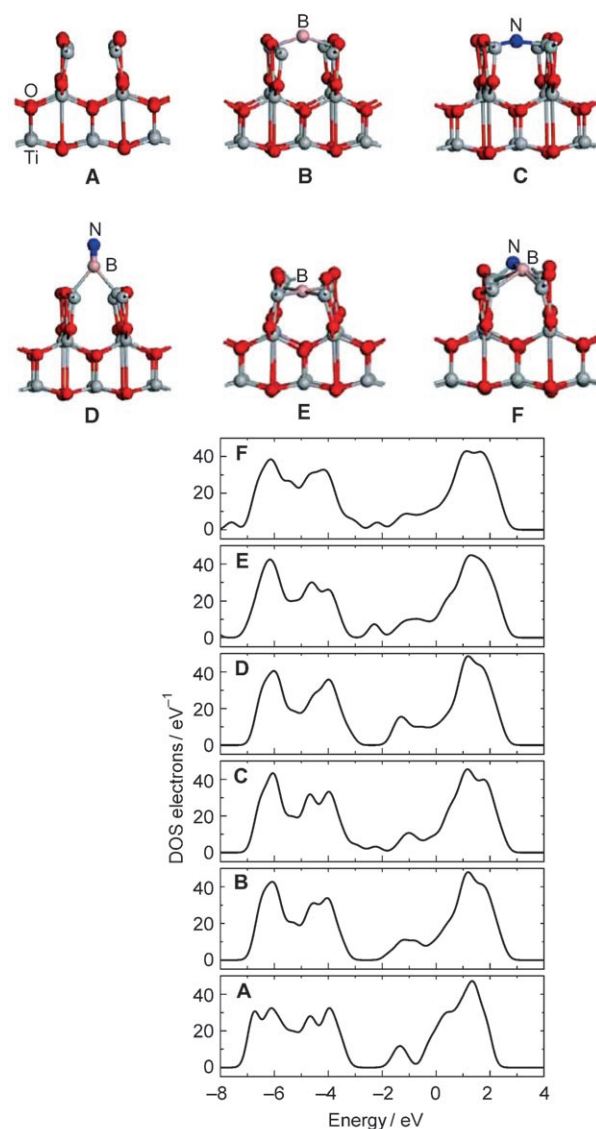


Figure 4. Top: Optimized geometries for the (001) surface upon adsorption of B and N: **A**) pure surface; **B**) bridge adsorption of B; **C**) bridge adsorption of N; **D**) on-top adsorption of N after the bridge adsorption of B; **E**) B at the fourfold vacancy; **F**) on-top adsorption of N after adsorption of B at the fourfold vacancy. Bottom: Densities of states for **A–F**.

398.7 eV (Figure 3). To evaluate the role of oxygen vacancies, we treated the B-doped titania with hydrogen. Despite an increase in the visible-light absorption at longer wavelengths upon formation of oxygen vacancies, the photocatalytic activity appeared unchanged within experimental error. This suggests that the oxygen vacancies introduced in B-doped titania are partially responsible for the additional visible-light absorption but not the enhanced photocatalytic activity.

The increased activity of B-doped titania upon additional N doping can be explained based on our experimental data. The concept of a co-catalyst is very important for the development of highly efficient photocatalysts, especially for photocatalytic water splitting. Besides the use of Ag, Au, Pt, RuO₂, and NiO as effective co-catalysts^[29–33] in photocatalytic water splitting, a mixed oxide of rhodium and chromium has been shown to be an extraordinary co-catalyst.^[34] Zhao et al. have also shown that Ni₂O₃ is an effective co-catalyst for the B-doped titania system.^[7] The co-catalysts present during photocatalysis strongly promote the effective transfer of photo-induced carriers by acting as an antenna to collect the electrons or holes formed by the Fermi level equilibration upon light-excitation, thereby enhancing the efficiency of the charge-transfer process.^[35] In our case, it seems that the presence of an O-Ti-B structure contributes to the visible-light absorption and that the O-Ti-B-N structure on the photocatalyst surface acts as an effective co-catalyst. The synergistic effects of creating visible-light absorption and then promoting visible-light-induced carriers are responsible for the high visible-light photocatalytic activity for this B/N doped titania. The formation of an O-Ti-B-N structure leads to the construction of a favorable surface structure that facilitates the separation and transfer of charge carriers, thereby promoting the photocatalytic activity.

Finally, we address the reasons why the B/N doping of titania reported here is so effective whereas no synergistic effect of B/N doping was observed in the work of Lambert et al.^[23] There are three key differences between these two studies, namely the high level of B dopant, and its different oxidation state, and the doping process itself. The B dopant in our work, which has a BE of 191.5 eV, was inserted by a hydrothermal process and the nitridation was achieved by thermal treatment under ammonia, whereas Lambert et al. used a wet chemistry route.^[16] These differences are likely to be responsible for the formation of the O-Ti-B-N surface structure.

In summary, we have used a simple strategy to obtain B/N-doped titania with a greatly enhanced visible-light absorption and high visible-light photocatalytic activity. We propose that the surface separation and transfer of visible-light-induced carriers is enhanced by a new O-Ti-B-N structure on the surface. This work not only further advances the understanding of doped titania but could also open up a new route to the design and synthesis of highly efficient visible-light photocatalysts and co-catalysts.

Experimental Section

Ti[OCH(CH₃)₂]₄ (5 mL, Aldrich, 97%) was dissolved in isopropyl alcohol (40 mL) and the resulting solution added dropwise to a

solution of HNO₃ (50 mL, 9 × 10⁻² M) containing a known amount of boric acid. The resultant translucent sol was aged for 10 h at room temperature and then transferred into a Teflon-lined autoclave at 85 °C for the first step of the hydrothermal treatment. After 5 h, the gel was cooled to room temperature. It was then added dropwise to a 10 wt % aqueous solution (20 mL) of the block copolymer Pluronic P123 (EO₂₀PO₇₀EO₂₀) at 40 °C and stirred vigorously for 2 h before being transferred into the autoclave again. This mixture was heated at 110 °C for 20 h. The resultant gel was dried at 200 °C for 10 h to partially remove water and organic matter and then calcined at 400 °C for 2 h in air to give the B-doped mesoporous titania. Nitridation was conducted by annealing the B-doped titania samples at 600 °C under an ammonia atmosphere.

Undoped mesoporous titania was prepared in a similar manner to the B-doped titania but without adding boric acid to the HNO₃ solution; N-doped titania was prepared by annealing mesoporous titania under an ammonia atmosphere at 600 °C. Both the undoped mesoporous titania and B-doped titania were also calcined at 600 °C in air before characterization for comparison.

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