Experimental and Theoretical Investigations on the Activity and Stability of Substitutional and Interstitial Boron in TiO₂ Photocatalyst

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Supporting Information

ABSTRACT: Effects of boron doped in TiO₂ at (a) interstitial site (B_{int}), (b) substitutional site (B_{sub}), and (c) combination of both the sites (B_{int+sub}) have been investigated experimentally and theoretically to understand the origin of enhanced photocatalytic activity and stability. B-doped TiO₂ powders were synthesized by sol−gel method with different concentrations of boron. XPS results indicate that boron first prefers B_{sub} site when doped with low concentration (up to 1 at. % B), but as the concentration increases (2 at. % and above) B also occupies substitutional O position in addition to B_{int} to form TiO₂ containing B_{int+sub} (TiO₂−B_{int+sub}). Higher absorption of visible light is achieved for TiO₂−B_{int+sub} due to the presence of two absorption edges (2.4 and 2.2 eV) as observed in the absorption spectra, whereas insignificant narrowing of band gap is observed for TiO₂−B_{int}. Electronic structure calculated by DFT for TiO₂ with B_{int}, B_{sub}, and B_{int+sub} revealed that the two localized deep levels are formed in the mid gap region which are responsible for these optical transitions for TiO₂−B_{int+sub}. Photoluminescence (PL) emission spectra showed that the shallow level (as inferred from the DFT calculations) created below the conduction band is able to decrease the radiative recombination process in TiO₂−B_{int} by trapping electrons and prolonging the lifetime of charge carriers as observed in the time-resolved PL decay curve. Furthermore, lower effective mass ratio of charge carriers calculated using DFT for TiO₂−B_{int} also suggests better charge mobility and low recombination rate. Photocatalytic degradation rate of organic pollutants in water was significantly higher after B-doping with higher performance obtained with TiO₂ containing B_{int} as compared to B_{int+sub}. B_{int} to form TiO₂−B_{int+sub}. Photoluminescence (PL) emission spectra showed that the shallow level (as inferred from the DFT calculations) created below the conduction band is able to decrease the radiative recombination process in TiO₂−B_{int} by trapping electrons and prolonging the lifetime of charge carriers as observed in the time-resolved PL decay curve. Furthermore, lower effective mass ratio of charge carriers calculated using DFT for TiO₂−B_{int} also suggests better charge mobility and low recombination rate. Photocatalytic degradation rate of organic pollutants in water was significantly higher after B-doping with higher performance obtained with TiO₂ containing B_{int} as compared to B_{int+sub}. By imposing the destabilizing circumstances it was established that TiO₂−B_{int} is metastable and collapses under mild conditions, whereas TiO₂−B_{int} is highly stable and retains all its properties. All these unprecedented findings disclose that higher activity of TiO₂−B_{int} as compared to that of TiO₂−B_{int+sub} is mainly because of the delayed recombination processes even though the optical band gap is not significantly varied.

INTRODUCTION

Titanium dioxide (TiO₂) remains the best candidate for the solar-driven photocatalysis reactions owing to its intrinsic properties such as chemical inertness, long-term stability, high resistance against corrosion, nontoxicity, and low cost. It also has possible usage in a large number of applications in environmental purification, energy production, and self-sterilization. However, inability to utilize the visible part of the solar spectrum due to its large band gap and recombination of photogenerated charge carriers are the two main limitations associated with TiO₂ for its practical applications. Doping with foreign elements with appropriate concentration can address both these issues by forming defect levels within the band gap. These levels not only cause intraband transitions for absorption of higher number of photons but also act as the trapping sites for photoexcited charges for its prolonged lifetime.

Metal ion doping significantly improves the light absorption ability by forming a deep level in the band gap but at the same time introduces recombination centers which affect the charge transfer toward the surface for photocatalytic reaction. On the other hand, with the introduction of shallow levels, nonmetal or anion dopants do not cause major narrowing of the band gap, yet these impurity states participate in trapping the charges to cause improvement in the photocatalytic activity. Among the various anions (N, C, S, F, B) doping in TiO₂, boron is very efficient in band gap narrowing and in decreasing the recombination of charges. However, it is not well-understood which of these factors is more effective for photocatalytic...
activity. Chen et al.\textsuperscript{6} observed blue shift in the band edge of TiO\textsubscript{2} after boron doping in interstitial site due to quantization effects which improve the photocatalytic activity by intense absorption in the UV range. It was also tentatively suggested that boron in interstitial site reduces Ti\textsuperscript{4+} to Ti\textsuperscript{3+} to facilitate separation of photoexcited electron and hole pairs and slow down their recombination.\textsuperscript{6} In et al.\textsuperscript{7} were able to decrease the band gap by substitutionally replacing oxygen with boron in the TiO\textsubscript{2} lattice to enhance the visible light photoactivity. The electronic variation upon B-doping was theoretically studied by Yang et al.\textsuperscript{8} and Geng et al.\textsuperscript{9} Using density functional theory (DFT) calculations, they showed that boron in the substitutional site of oxygen can create midgap states and eventually cause the red shift in the absorption edge, while interstitial occupancy of B does not cause any significant variation in the band gap. By similar type of calculations Finazzi and co-worker\textsuperscript{10} suggested that substitutional B is a metastable species and decomposes into interstitial boron or B\textsubscript{2}O\textsubscript{3} by forming oxygen vacancy. They also predicted that interstitial boron is the preferred site in TiO\textsubscript{2}. The experimental evidence for the stability of these boron species was provided by Artiglia et al.\textsuperscript{11} using different synthesizing techniques to produce four components: substitutional B with Ti (Ti−B), substitutional B with O (Ti−B−O), interstitial B (Ti−O−B), and B\textsubscript{2}O\textsubscript{3}. On annealing both the substitutional sites of B disappear to form B\textsubscript{2}O\textsubscript{3} while the interstitial B is highly stable at all temperatures. However, the effect of these sites of B on its photocatalytic activity was not studied. Various techniques were adopted by Zaleska et al.\textsuperscript{12,13} to dope B in TiO\textsubscript{2} and it was observed that activity depends on the preparation conditions, method, and type of TiO\textsubscript{2} used; however, they have failed to explain the role of B in improvement in the photocatalytic activity. Boron presence simultaneously at both the interstitial and substitutional locations was first reported by Xue et al.\textsuperscript{14} and was later also confirmed by Wu et al.\textsuperscript{15} The optical properties studied by the latter group\textsuperscript{15} using theoretical calculation showed the presence of midgap states at different locations than that found in TiO\textsubscript{2} doped with substitutional boron. These states are formed by the charge balancing due to the interaction between interstitial and substitutional boron. Coexistence of both these B-species shifts the ability of H\textsubscript{2} generation found in pure TiO\textsubscript{2} to O\textsubscript{2} generation in the photocatalytic water splitting.\textsuperscript{16} Few attempts were carried out to codope B with N,\textsuperscript{18} Ag,\textsuperscript{17} and Ni\textsubscript{2}O\textsubscript{3}\textsuperscript{19} to improve the visible light photocatalytic activity.

From the above studies it is still not clear if B in a substitutional site (B\textsubscript{sub}), creating band gap narrowing, is more catalytically active than B in an interstitial site (B\textsubscript{int}) assisting in charge separation, or if the combination of both these positions provides a synergic effect in increasing photoactivity. Although theoretically the variation in the band gap is well-studied with respect to boron position in TiO\textsubscript{2}, experimentally reproducing these band structures has not been reported until now. Speculation about better charge separation is reported for TiO\textsubscript{2}−B\textsubscript{int} due to Ti\textsuperscript{3+} formation, but no experimental or theoretical proof has been presented for the reduced recombination rate in TiO\textsubscript{2}−B\textsubscript{int} or TiO\textsubscript{2}−B\textsubscript{sub}. Doping concentration playing the central role in controlling the photocatalytic activity is also under studied. In et al.\textsuperscript{12} and Zaleska et al.\textsuperscript{13} found a discrepancy in the photocatalytic performance upon varying the boron concentration but failed to explain the physical reasoning behind it. Although the metastable nature of TiO\textsubscript{2}−B\textsubscript{sub} is known, the consequence upon destabilizing TiO\textsubscript{2}−B\textsubscript{sub} has not been experimentally reported yet. Understanding these factors will provide pathways for tuning this material for the optimum photocatalytic activity. Thus, the present work focuses on the experimental and theoretical studies of TiO\textsubscript{2}−B\textsubscript{int} and TiO\textsubscript{2}−B\textsubscript{int+sub} for determining the origin of enhanced photocatalytic activity and the stability of doped TiO\textsubscript{2}.

\section{EXPERIMENTAL AND THEORETICAL SECTION}

\textbf{Photocatalyst Preparation.} Pure TiO\textsubscript{2} and boron-doped TiO\textsubscript{2} were synthesized by a sol−gel method by using titanium butoxide [Ti(OC\textsubscript{4}H\textsubscript{9})\textsubscript{4}] and boric acid (H\textsubscript{3}BO\textsubscript{3}) as precursors for TiO\textsubscript{2} and B doping, respectively. During the synthesis of pure TiO\textsubscript{2} the solution mixture of deionized water, ethanol, and HNO\textsubscript{3} (used as catalyst) was added dropwise to the homogeneous mixture of ethanol and titanium butoxide under constant stirring. The resultant solution was further stirred for 1 h to increase the homogeneity of the mixture. Molar ratio of Ti(OC\textsubscript{4}H\textsubscript{9})\textsubscript{4}/H\textsubscript{2}O/ethanol/HNO\textsubscript{3} was kept constant at 1/30/20/0.1. In the case of B-doped TiO\textsubscript{2} boric acid was added to the acidic solution before adding it to the Ti precursor solution. The concentration of boron was varied from 1 to 4 at. % by varying the amount of boric acid. Gelation of the final mixture was performed overnight at room temperature, followed by drying at 100 °C for 3 h to remove the excess solvent. Subsequent calcination was performed at 400 °C for 2 h for crystallization of the TiO\textsubscript{2} powders.

\textbf{Characterizations.} Scanning electron microscope (SEM−FEG, JSM 7001F, JEOL) equipped with energy-dispersive spectroscopy analysis (EDS, INCA PentaFET-x3) was used to study the surface morphology and composition of all the samples. The structural characterization was performed by X-ray diffraction (XRD) using Cu K\textalpha\ radiation (\(\lambda = 1.5414\) A) and by Raman spectroscopy using Renishaw micro-Raman spectrometer (RE-04) using solid state laser with the diode pumped at 514 nm. The band gap of the doped TiO\textsubscript{2} was determined by measuring diffuse reflectance absorption spectra, using a Cary 500 UV−vis−NIR spectrophotometer, in the range 200−800 nm. The surface composition and chemical states of each element in the samples were examined by X-ray photoelectron spectra (XPS) using a PHI 5000 VersaProbe II instrument equipped with a monochromatic Al K\textalpha (1486.6 eV) X-ray source and a hemispherical analyzer. Appropriate electrical charge compensation was employed to perform the analysis and binding energy was referenced to the C 1s peak. Photoluminescence (PL) emission spectra were collected, by exciting the photocatalyst with wavelength of 385 nm, using a fluorescence spectrophotometer (Varian, Cary Eclipse). Time-resolved photoluminescence spectroscopy was performed using ISS Chronos BH fluorometer. For excitation, pulse diode laser (Hamamatsu) of wavelength 405 nm with pulse width of 70 ps operating with a peak power of 100 mW was used. Both normal and time-resolved PL spectra were acquired by dispersing 3 mg of powder photocatalyst in aqueous medium of fixed amount and transferred into 1 cm × 1 cm cuvette for the measurement. BET surface area of the powder photocatalysts was determined by nitrogen absorption at 77 K (Smart SORB 93) after degassing at 120 °C for 2 h.

\textbf{Photocatalytic Activity Measurement.} The photocatalytic activity of all the samples was evaluated by photodegradation of p-nitrophenol (p-NP) aqueous solution (10 ppm) and methylene blue (MB) dye (0.01 mM) solution under light irradiation. For the source of light, 150 W xenon lamp (Philips) was used having a spectrum nearly similar to the
solar spectrum. A 20 mg portion of photocatalyst was dispersed in 50 mL of aqueous p-NP or MB solution for each photocatalytic degradation experiment. The powder suspension was first stirred for 30 min in the dark to attain adsorption—desorption equilibrium of the molecules in the solution. The distance between the beaker and the light source was kept constant at 47 cm. For given time intervals, 1 mL of p-NP or MB aqueous solution was filtered out from the reactor vessel and transferred to the 1 cm × 1 cm quartz cuvette. The photocatalytic activity was determined by measuring the normalized intensity of the absorption band of p-NP at 320 nm and of MB at 665 nm using a spectrophotometer, and plotting it as a function of irradiation time. All the photocatalysis experiments were performed at room temperature, and the pH of the solution was maintained neutral during all the photocatalytic measurements.

**Theoretical Calculations.** To understand the effects of B doping in TiO$_2$, we have performed the first-principles calculations. For this purpose we have used a full-potential linearized augmented plane wave (FP-LAPW) method within the DFT as implemented in WIEN2k code.$^{19}$ In the FP-LAPW prescription, wave functions, charge density, and potential are expanded in spherical harmonics within nonoverlapping muffin-tin (MT) spheres, while plane waves are used in the remaining interstitial region of the unit cell. Core and valence states are, respectively, treated within a multiconfigurational relativistic Dirac–Fock approach and scalar relativistically. Different from the previous theoretical studies,$^{8–10}$ the exchange and correlation of PBE-sol given by Perdew et al.$^{20}$ within the generalized gradient approximation with modified Backe–Johnson (mBJ)$^{21}$ correction were used for the present computations. For pure anatase TiO$_2$, lattice parameters were considered as $a = 3.838$ Å and $c = 9.642$ Å as optimized by Rubio-Ponce et al.$^{12}$ using FP-LAPW scheme.

As suggested in the existing literature,$^{6–10}$ that B atom in the TiO$_2$ lattice occupies various positions, in the present study, we have considered the B atom at interstitial site and substitutional at O site henceforth referred as $\text{B}_{\text{int}}$ and $\text{B}_{\text{sub}}$, respectively. There are various possible sites for interstitial B as suggested by Finazzi et al.$^{10}$ Authors$^{10}$ have considered three different interstitial sites and finally concluded that the electronic structure of all the interstitial B-doped TiO$_2$ samples changes in the same way and introduces the same kind of defects. Therefore, we have considered a single interstitial doping of B in TiO$_2$. For this we have constructed a $2 \times 2 \times 2$ supercell of TiO$_2$, which generates 48 atoms in the supercell. We have added 1 interstitial or 1 substitutional B (substituted at O site) in the supercell. With increasing B concentration, we have also studied the effect of both interstitial and substitutional doping of B simultaneously in the TiO$_2$ lattice, referred as $\text{B}_{\text{int}}+\text{B}_{\text{sub}}$.

For the present computations, radii for MT spheres were selected as 1.92 au for Ti, 1.74 au for O, and 1.62 au for B atom. The $k$-point sampling of the Brillouin zone (BZ) was set $14 \times 14 \times 14$ and $5 \times 5 \times 5$ for pure TiO$_2$ and other studied compounds, respectively. Other computational parameters were set as $R^\text{MT}K_{\text{max}} = 71, l_{\text{max}} = 10,$ and $G_{\text{max}} = 12.$ Finally, all the structures were fully relaxed for atomic forces until the forces on each atom reach value less than 5 mRy per au. To ensure sufficient accuracy in convergence, total energy of all the studied compounds was converged to 0.01 mRy.

### RESULTS AND DISCUSSION

XRD (Figure 1a) and Raman spectroscopy (Figure 1b) were used to study the structural modification induced both at the surface and in the bulk of TiO$_2$ after boron doping, respectively. All the major peaks assigned to the anatase phase are clearly visible in pure TiO$_2$. In addition to the anatase phase, the peaks due to rutile (27.4°, 36°, 41.1°, 56.5°) and brookite (30.8°) are also observed after boron doping in TiO$_2$. The sharpness and intensity of peaks due to rutile increase with the doping concentration, while those of brookite remain unchanged. Most importantly, the main diffraction peak of anatase at 25.3° shifts to the lower angle (inset of Figure 1a) indicating the expansion of the TiO$_2$ lattice by introduction of B. In the case of boron substitutionally replacing O, the unit cell volume is expected to decrease since the radius of B$^{3+}$ (0.023 nm) is smaller than O$^{2-}$ (0.132 nm) while the occupancy of the interstitial position will induce the lattice expansion to shift the diffraction to the lower angle. This result shows that boron is dominantly present in the interstitial sites rather than in substitutional position. However, $\text{B}_{\text{sub}}$ cannot be neglected because of the existence of rutile phase formed by rearrangement of atoms caused by oxygen deficiency created by the occupancy of boron atom through oxygen substitution. In agreement with XRD, Raman spectra (Figure 1b) also show the mode of vibrations of only the anatase phase for pure TiO$_2$. On the other hand, B-doped TiO$_2$ shows the mixture of anatase, rutile, and brookite phases with a major contribution from anatase phase. No signal due to boron or...
boron oxide (B₂O₃) is detected in the XRD pattern and Raman spectra. The average crystal size measured through the width of XRD peaks is in the range 6–9 nm for all the samples. This value is consistent with the particle size measured using SEM images (Figure S1 of Supporting Information). However, the nanoparticles are in agglomerated state with lower surface area than that expected from the nanoparticles below 10 nm size. No major variation is detected after B-doping in the BET surface area (Table S1) which is in the range 50–80 m²/g for all samples.

UV−vis absorption spectra were measured for pure and B-doped TiO₂ in diffuse reflectance mode and are reported in Figure 2a. Irrespective of boron concentration the absorption edge is red-shifted for B-doped TiO₂ as compared to pure anatase TiO₂. The shift is small in the case of 1 at. % B-doped TiO₂ while the maximum narrowing of the band gap is obtained with 2 at. % B. Further increase in concentration (3 at. % and 4 at. %) causes the absorption edge to shift to lower wavelength. Tauc plot (Figure 2b) was used to determine the band gap of these samples (Table S1). At low concentration of B-doping (1 at. %), a minor decrease in band gap is observed, reducing from 3.15 eV for pure TiO₂ to 3.0 eV. However, in the case of 2 at. % B-doping the presence of two absorption edges (2.4 and 2.2 eV) is clearly evident from the Tauc plot thus suggesting the possible existence of a localized state deep in the band gap causing a two-step transition. At higher concentrations (3 at. % and 4 at. %), a similar characteristic of the absorption edge is observed but with higher energy transition. These new energetic features in the band gap at higher B concentration are mainly due to the possibility of different B-doping sites (Bint or Bsub or Bint+sub) in TiO₂ and the interaction of B atoms with the host elements in the TiO₂ lattice which will be discussed in the next section.

XPS was used to investigate the chemical state of boron in TiO₂ (Figure 3). For both pure TiO₂ and 1 at. % B-doped TiO₂, two peaks centered at 458.4 and 464.1 eV, assigned to Ti 2p₁/₂ and Ti 2p₃/₂ of Ti⁴⁺ states, are observed in Ti 2p core level. Similar peaks were detected for TiO₂ doped with higher boron concentrations (2 at. %, 3 at. %, and 4 at. %) but with a positive shift in binding energy by 0.2 eV as compared to those of pure TiO₂. This signifies that boron is present in the TiO₂ lattice, in agreement with the XRD data, to influence the local chemical states of Ti⁴⁺ ion. The signal of Ti⁵⁺ was detected on the surface only for the 1 at. % B-doped TiO₂ which is in the form of shoulder at around 456.8 eV. In the oxygen 1s core level, a single peak centered at 529.8 eV is displayed in the spectra of all the samples. However, in B-doped TiO₂, after deconvolution, an extra peak at 530.7 eV attributed to B−O bond is present in addition to the major peak at 529.8 eV related to oxygen bonded in TiO₂. For 1 at. % B-doped TiO₂, a broad signal in the B 1s level was deconvoluted into two peaks with binding energy of 191.7 and 193.0 eV. The former peak with major contribution (95%) in overall signal is attributed to the interstitial boron while the latter peak is due to the presence of the B−O bond of the boron oxide (B₂O₃). Besides these two peaks, a small peak centered at 189.0 eV assigned to substitutional B at oxygen site was clearly observed for B-doping above 1 at. %. The contribution due to Bsub is about 20% in overall boron signal with major signal recorded from Bint (above 75%) and the rest (about 5%) from B₂O₃. By increasing the concentration of boron content an increase of the signal due to B₂O₃ is observed while no change in the intensity ratio of Bint/Bsub was detected. This XPS result shows that boron is mainly present at an interstitial site forming a B−O−Ti bond when doped with low concentrations (1 at. %). In this chemical bond, the boron atom reduces Ti⁴⁺ in the lattice to form B³⁺ and 3Ti³⁺, thus explaining the presence of Ti³⁺ species in 1 at. % B-doped TiO₂. Such ionization is compensated by forming bonds between B and neighboring O to obtain B−O−Ti species. As concentration increases to 2 at. %, boron is present not only at the interstitial site but also occupies a substitutional site by replacing an oxygen atom in the lattice forming B−Ti−O bonds. At higher concentrations, saturating the interstitial and substitutional sites, the extra boron might contribute in forming B₂O₃ species. Further evidence of boron present at a substitutional site along with the interstitial site (for B concentration 2 at. % and above) is provided by the positive shift of the Ti⁴⁺ peak. Boron is more electronegative than the Ti atom, so the presence of boron in the substitutional site will cause electron transfer from Ti to B to create a positive shift of Ti₂p binding energy. In addition, the separation between the B 1s peak of Bsub and Bint is about 2.7 eV which is in good agreement with that reported by the calculations (2.6 eV) performed by Finazzi et al.¹⁰

To further understand the effect of B doping at various sites (Bint or Bsub or Bint+sub) on the electronic structure of TiO₂, theoretical simulations were performed using DFT with mBJ potential. Boron replacing Ti is energetically less favorable and not stable; thus, the calculations were performed (a) by substitutionally replacing one O atom with B atom (Bsub), (b)
by placing boron in the interstitial position (B_{int}), and (c) by introducing boron at both substitutional as well as interstitial sites (B_{int+sub}). The selected interstitial site is the most stable site according to the calculations performed by Finazzi et al.\textsuperscript{10} and the electronic properties of B-doped TiO$_2$ at different interstitial sites remain unchanged.

In Figure 4a–d, we have presented the total density of states (TDOS, left panel) and crystal structure (right panel) of TiO$_2$, TiO$_2$–B$_{int}$, TiO$_2$–B$_{sub}$ and TiO$_2$–B$_{int+sub}$.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4}
\caption{Total density of states (TDOS, left panel) and crystal structure (right panel) of TiO$_2$, TiO$_2$–B$_{int}$, TiO$_2$–B$_{sub}$ and TiO$_2$–B$_{int+sub}$.}
\end{figure}

TiO$_2$–B$_{int}$, TiO$_2$–B$_{sub}$ and TiO$_2$–B$_{int+sub}$. In Figure 4a, zero energy represents the Fermi level ($E_F$) for pure TiO$_2$. Band gap of 2.9 eV was observed for pure TiO$_2$ (Figure 4a) which is within 10\% of the experimental band gap (3.2 eV) (DFT with mBJ potential produces results within 10\% of experimental value). In Figure 4b–d, the zero energy has been shifted to the valence band maxima (VBM) of TiO$_2$, and $E_F$ is marked by a dotted line. Figure 4b presents TDOS and crystal structure (right panel in the figure) of $B_{int}$ located in the center of an anatase cell where B forms a bond with the surrounding Ti and O atoms.\textsuperscript{3} The present theoretical result for $B_{int}$ is in good agreement with the earlier reported data.\textsuperscript{24} The impurity bands are formed below the conduction band (CB) of TiO$_2$ and reduce the band gap of TiO$_2$ with $E_F$ shifted toward the CB. In TDOS TiO$_2$–B$_{sub}$ (Figure 4c), the B atom forms impurity states around 1 eV above the VBM in the band gap of TiO$_2$, and again the $E_F$ is shifted toward the CB. Figure 4d shows the TDOS and crystal structure of $B_{int+sub}$ in which the concentration of B is double than that in $B_{int}$ and $B_{sub}$. In the crystal structure (right panel), the B interstitial and substitutional sites are similar as considered in the case of $B_{sub}$ and $B_{int}$ respectively. The localized impurity states of $B_{int+sub}$ are formed below the conduction band minima (CBM), and these states are not identical to the impurity states in $B_{sub}$ and $B_{int}$. $E_F$ is shifted toward CB even in this case. A minor change in the band edges of TiO$_2$ is observed on B doping while impurity states of B are formed in the band gap of TiO$_2$.\textsuperscript{25}
Figure 5a–c presents the energy bands (left panel) and PDOS (right panel) of $B_{\text{int}}, B_{\text{sub}},$ and $B_{\text{int+sub}}$ with $E_F$ at 0.0 eV.

Impurity states by $B_{\text{int}}$ doping (Figure 5a) are formed just below the CBM to reduce the band gap to 2.7 eV from 2.9 eV as seen in pure TiO$_2$. This value of band gap reconciles well with the UV–vis spectra of 1% B-doping where B in the interstitial position, as confirmed by XPS, is able to reduce the gap by $\sim$0.15 eV. This shallow level (Figure 5a) is formed by strong hybridization of Ti, O, and B states as observed from the overlapping of the Ti, O, and B orbitals (in antibonding state) in PDOS which is also seen as B–O–Ti bond in the XPS results. In $B_{\text{sub}}$ (Figure 5b), a localized state is formed deep in the band gap located at 0.96 eV (1.86 eV) above (below) the VB (CB) of TiO$_2$. Unlike $B_{\text{int}}$, solely the $B_{\text{sub}}$ orbital is responsible for the formation of this intermediate level. Small contribution of B states is also found around $E_F$ and in the CB region. In Figure 5c, where B atoms are placed at both interstitial and substitutional sites, the impurity states generated by B in the mid gap region are located at different positions than those created by $B_{\text{int}}$ or $B_{\text{sub}}$. Two localized impurity states separated by 0.33 eV at $\Gamma$ position of BZ (mainly due to $B_{\text{sub}}$) are observed in the band gap placed at about 2.24 and 2.57 eV above the VBM (at $\Gamma$ position of BZ). This new electronic configuration is able to create two additional optical transitions by absorbing visible light as confirmed by UV–vis spectra of 2% B-doped TiO$_2$ in which $B_{\text{int+sub}}$ is present as suggested by the XPS spectra. The overlapping of B orbitals at interstitial and substitutional sites is also observed around $E_F$. The absence of a shallow level in $B_{\text{int+sub}}$ near the CBM due to $B_{\text{int}}$ is mainly attributed to the interaction between the $B_{\text{int}}$ and $B_{\text{sub}}$ as indicated by the overlapping of B orbitals. Thus, the theoretical results are in good agreement with the experimental results and show that for $B_{\text{int}}$ a small narrowing of the band gap is due to the formation of shallow level formed below the CBM due to B–O–Ti bond as in case of 1 at. % B. However, when $B_{\text{int+sub}}$ is present, two extra optical transitions, occurring within the band gap, due to the formation of two localized states, are responsible for high visible light absorption for 2 at. % B-doped TiO$_2$. As the concentration of B increases above 2 at. %, the increase in formation of B$_2$O$_3$ is also observed which will contribute to the absorption edge of TiO$_2$. The band gap of B$_2$O$_3$ (6.2 eV) is higher than that of TiO$_2$, so as the concentration of B increases the absorption edge is blue-shifted for B-doped TiO$_2$ at 3 at. % and 4 at. %.

The recombination process of photogenerated electron and hole pair is as important as the absorption of photon to determine the photocatalytic performance. Photoinduced charges can recombine by either radiative transition or by nonradiative phonon generation. To study the radiative transition, PL spectra acquired by exciting the samples with wavelength of 385 nm (matching the band edge of the TiO$_2$) are reported in Figure 6a for pure and doped TiO$_2$. Three distinct emission peaks at 425, 486, and 527 nm are recorded in the visible range. The first emission peak (425 nm) in the visible range arises by relaxation of a self-trapped exciton localized on TiO$_6$ octahedral while the other two emission peaks (486 and 527 nm) are due to the intraband transitions within the energy levels due to traps or surface defects related to oxygen vacancies. All three peaks are associated with the recombination of charges either at shallow trap level (425 nm) or deep trap levels (486 and 527 nm). The intensities of these peaks are either unchanged or increased nominally by boron doping except for 1 at. % B-doping where the peak at shallow trap level blue-shifted for B-doped TiO$_2$. As the concentration of B increases above 1 at. %, the increase in formation of B$_2$O$_3$ is also observed which will contribute to the absorption edge of TiO$_2$.

The average lifetime, obtained by fitting the decay curve, is about 1.39 ± 0.07 ns for pure TiO$_2$. In the case of B-doped TiO$_2$, the average lifetime is increased to 1.68 ± 0.08 ns for low concentration B-doping (1 at. %), showing a prolonged time period of the charge carriers as...
At higher concentrations of B-doping, the lifetime reduces to the value below that of pure TiO$_2$, while the phenomenon is reversed for higher boron concentrations. The reduced PL intensity with longer lifetime for 1 at. % B-doped TiO$_2$ (1.17 ± 0.06 ns). The reduced PL intensity with longer lifetime for 1 at. % B-doped TiO$_2$ suggests the decrease in radiative recombination of charge carriers in comparison to that for pure TiO$_2$. The reduced PL intensity with longer lifetime for 1 at. % B-doped TiO$_2$ shows low recombination rates of the charge carriers which is in agreement with the above PL results. The effect of boron doping on the photacatalytic performance was investigated by degrading organic pollutants such as P-nitrophenol (p-NP) and methylene blue (MB) dye. The catalytic activity for degradation was determined by examining the characteristic absorption peak of these organic pollutants as a function of time (Figure 7). In absence of photocatalyst, a negligible amount of self-degradation of p-NP and MB dye was observed under the light irradiation after 4 h. In contrast to pure TiO$_2$, the boron-doped TiO$_2$ showed significantly improved degradation rate for both the pollutants. Among the B-doped TiO$_2$, 1 at. % B-doped TiO$_2$ showed the highest photocatalytic activity with 75% and 65% degradation achieved in 4 h for p-NP and MB dye in comparison to 20% and 25% obtained with pure TiO$_2$, respectively. The data points in Figure 7 were fitted linearly to calculate the apparent rate constant and the p-NP and MB degradation rates per gram of the photocatalyst (Table S2). Low concentration (1 at %) boron-doped TiO$_2$ is able to degrade p-NP and MB dye with the rate 4 and 2.5 times higher than that with pure TiO$_2$, respectively. However, as the concentration of boron increases structure in improving the charge separation. Defect centers introduced by the dopant species can play a huge role in trapping the charges depending upon the location of these centers in the band gap. For 1 at. % B-doped TiO$_2$, boron is mainly positioned at the interstitial site forming a shallow level below the CBM due to B–O– Ti bond. This shallow level containing Ti$^{3+}$ seems to act as the trapping site for the photogenerated electrons to increase the lifetime and decrease the recombination process. Nevertheless, at higher concentrations the boron is present at interstitial as well as substitutional sites with the latter forming the defect level deep in the gap. From the PL results, the presence of these deep levels acts as the recombination centers to produce the emission peak intensity and lifetime of the boron doped at higher concentration nearly similar to that of pure TiO$_2$. Similar findings were reported by Chaudary et al. for Cu-doped TiO$_2$, in which shallow trap centers due to oxygen defects are able to capture photoexcited electrons. These trap centers transfer the electron to the surface to enhance the photocatalytic activity. On the contrary, the deep trap formed by Cu d-states was not suitable for photocatalytic applications due to the increase in recombination as indicated by the increase in emission intensity. 

To check the charge carrier mobility and separation using first-principles calculations we have calculated the relative effective mass ratio of electron and hole. The effective mass of charge carriers is calculated by taking the coefficient of second-order term in a quadratic fit of energy band diagrams (Figure S5a–c, left panel) at the edges of VB, CB, and intermediate bands. A lower charge carrier effective mass corresponds to a higher charge carrier mobility, and the large value of the ratio of electron to hole effective mass ($m_e^*/m_h^*$) suggests a lower recombination rate of the electron–hole pair. The energy bands at VBM, CBM, and intermediate bands at various k-points of BZ (mainly, Γ, H, and K points) were fitted to calculate the effective masses of electrons and holes for all the B-doped samples and finally to take the average of the ratio of effective masses of electron to hole at the same k-point. The average values of the ratio of effective masses of electron to hole are obtained as 3.2 ± 0.16, 2.1 ± 0.11, and 2.7 ± 0.14 for $B_{\text{sub}}$, $B_{\text{int}}$, and $B_{\text{int+sub}}$, respectively. High value of $m_e^*/m_h^*$ for $B_{\text{int}}$ shows low recombination rates of the charge carriers which is in good agreement with the above PL results.
higher concentrations interstitial boron is also present, it is however not able to form a shallow level due to the interaction with substitutional boron. This shows that interstitial boron is far more active than the boron present in both the sites (B_{int+sub}). The present results highlight the importance of the recombination of photogenerated charges over light absorption ability in photocatalytic processes.

To check the relative stability of B-doped TiO$_2$ with B at various sites, we have computed the formation energies of all the studied compounds (equations used to formulate the formation energies are reported in the Supporting Information). The values of formation energy per unit cell are calculated as 2.7±0.13, 4.7±0.23, and 3.2±0.16 eV for TiO$_2$ containing B_{int}, B_{sub}, and B_{int+sub} respectively. These values suggest that B_{int} is the highly preferred B-doping site in TiO$_2$, while B_{sub} is difficult to obtain experimentally because of the high formation energy. The formation energy value of TiO$_2$−B_{sub+int} is in between that of TiO$_2$−B_{int} and TiO$_2$−B_{sub}; thus signifying that as the doping concentration increases B will occupy substitutional sites but only after the interstitial sites are saturated, to produce a mixture of both the sites at the same time.

According to the calculated formation energy, TiO$_2$−B_{int} is more stable than TiO$_2$−B_{sub}. Finazzi et al. also showed through DFT calculations that TiO$_2$−B_{int} is preferred over TiO$_2$−B_{sub} and that the latter is a metastable structure. In order to verify this finding experimentally, 1 at. % and 2 at. % B-doped TiO$_2$ samples containing B_{int} and B_{int+sub} respectively, were treated thermally and mechanically in order to destabilize the structure. The former treatment was done by calcinating the finally prepared samples for 4 h at 450 °C (the temperature selected is higher than that used for as-prepared sample) and later was achieved by ball milling for 6 h at 500 rpm. No major variation in structural, optical, and chemical states of boron was observed in 1 at. % B-doped TiO$_2$ as confirmed by XRD pattern, UV−vis and XPS spectra, respectively. On the contrary, for 2 at. % B-doped TiO$_2$ the peak due to substitutional boron at 189 eV completely disappeared from the XPS spectra (Figure 8a) after both the treatment conditions. The absorption edge was also relocated near that of pure TiO$_2$, indicating the disappearance of deep levels within the band gap which were responsible for higher light absorption in the untreated sample (Figure 8b). Even visually the color of 2 at. % B-doped TiO$_2$ was transformed from dark yellow to white, like pure TiO$_2$, after both treatment conditions. All these results suggest that substitutional boron is not stable and collapses upon mild destabilizing conditions. As suggest by Finazzi et al., the B_{sub} can convert into B_{int} and form an oxygen vacancy. By analyzing the Ti core level, the ball milled sample showed the presence of small peak at 456.5 eV attributed to Ti$^{3+}$ species formed by oxygen vacancy, while this peak is not observed in the thermally treated sample. Ball milling is performed at room temperature in the closed chamber while the thermal treatment is carried out in open air at high temperature. Thus, even if the oxygen vacancies are formed upon B_{sub} moving to B_{int} the oxygen from the air can refill the vacancy at high temperature which is not possible during the ball milling process. Photocatalytic degradation of MB dye performed using these treated samples (Figure S2) shows reduction in the activity in relation to the as-prepared 2 at. % B-doped TiO$_2$. Lack of visible light absorption due to disappearance of deep levels within the band gap was mainly responsible for detrimental photocatalytic performance.

Figure 7. Comparison of photocatalytic degradation of (a) p-nitrophenol and (b) methylene blue dye under light irradiation in the presence of pure and B-doped TiO$_2$ powders with different dopant concentrations, plotted in terms of the normalized intensity of the UV−vis measurements vs irradiation time (lines are drawn to guide the eye).

to 2% the rate decreases but is still higher than that of pure TiO$_2$ with values nearly constant for further increase in doping concentrations. Photogenerated holes oxidize the absorbed H$_2$O on the surface of TiO$_2$ to produce a strong oxidizing agent in the form of OH$^+$ radicals which participate in the degradation of organic pollutants like p-NP and MB dye. This process is mainly affected by the surface area of the photocatalyst, light absorption capability, and charge separation and transfer. The surface area of all the photocatalysts is approximately the same, so it cannot be responsible for the significant difference in photocatalytic activity. The enhanced activity of 1 at. % B-doped TiO$_2$ is mainly attributed to the reduced recombination processes. The boron located in the interstitial site develops a shallow level, below CBM due to the formation of the B−O−Ti bond. This level hardly affects the band gap but plays a major role in trapping the photogenerated electrons, due to the presence of Ti$^{3+}$, to prolong the time for the hole to travel to the surface and form OH$^+$ radical. On the contrary, for higher doping of boron (2 at. %, 3 at. %, and 4 at. %) the increase in the degradation rate is related to the enhanced light absorption achieved by the deep levels formed within the band gap by B_{sub}. These deep levels do not participate in charge separation by trapping. Although at these
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REFERENCES