An experimental and first-principles study of the effect of B/N doping in TiO₂ thin films for visible light photo-catalysis

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ABSTRACT

Thin films of TiO₂ and boron–nitrogen (B/N) co-doped TiO₂ on glass substrates have been prepared by a simple sol–gel dip coating route. Titanium (IV) isopropoxide, boric acid and urea have been used as titanium, boron and nitrogen sources, respectively. The films were characterized by X-ray diffraction, X-ray photo-electron spectroscopy, scanning electron microscopy, Raman spectroscopy and UV–vis spectroscopy. The TiO₂ thin films with co-doping of different B/N atomic ratios (0.27–20.89) showed better photo-catalytic degradation ability of methylene blue compared to that of bare-TiO₂ under visible light. The TiO₂ film doped with the highest atomic concentration of N showed repeatedly the best photo-catalytic performance. The high activity of co-doped TiO₂ thin films toward organic degradation can be related to the stronger absorption observed in the UV–vis region, red shift in adsorption edges and surface acidity induced by B/N doping. Furthermore, several atomic models for B/N doping have been used to investigate the effect of doping on electronic structure and density of states of TiO₂ through ab-initio density functional theory calculations. The computational study suggested a significant narrowing of the band gap due to the formation of midgap states and the shift of Fermi-level for the interstitial N model supporting the experimental results.

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1. Introduction

The utilization of solar irradiation to supply energy or to initiate chemical reactions is already a well established idea [1]. Anatase phase of titanium dioxide (TiO₂), a non-toxic and biocompatible wide-band gap semiconductor, when irradiated with a suitable wavelength light is known to facilitate chemical processes on its surface including degradation reactions. In addition, TiO₂ is one of the most important and widely investigated photo-catalyst materials [2]. It can be used in decomposition of various environmentally hazardous compounds (organic, inorganic and biological materials) in both gaseous and liquid phases [3].

It is well known that TiO₂ has three polymorphs: brookite, rutile and anatase. Mixed-phase photo-catalysts with rutile and anatase,

e.g. P25 Degussa [4], phases have been reported to exhibit enhanced photo-activity relative to single-phase anatase. However, synthesis of rutile–anatase phase mixture requires a high temperature treatment; heating anatase up to 600–700 °C is needed for the transformation of anatase to rutile [5]. Furthermore, there are still problems in the use of TiO₂ for practical and wide-spread photo-catalytic applications:

- (1) Recycling of nano-particulate TiO₂ requires costly separation/filtering processes.
- (2) TiO₂ photo-catalyst has a wide band gap (3.2 eV, for anatase), and can only be activated by UV radiation ($\lambda < 387$ nm) which constitutes only a small fraction (3–5%) of the solar spectrum. Thus, the use of visible light (400–750 nm, ~45% of the solar spectrum) by anatase should be enabled [6].
- (3) TiO₂ has a relatively low rate of electron transfer to oxygen and a high rate of recombination which results in a low quantum yield rate and also a limited photo-oxidation rate [7].

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There are several approaches proposed and applied for the remediation of the issues listed above. Some of the efforts are listed as accordingly:

- (1) Nano-crystalline TiO_2 thin films have attracted a great deal of attention [8,9] owing to their flexibility in treating wastes, e.g. no separation required and reuse of photo-catalytic products.
- (2) Any red shift in the optical response of TiO_2 from the UV band toward the visible spectrum will have a profound effect on the photo-catalytic efficiency [10,11]. With this view, doping of pure TiO_2 has been undertaken by a number of research groups [12–30] in the last decade. Modification by noble-transition metals has been historically regarded as the first strategy and by nonmetals as the second strategy [12]. However, these metal-doped TiO_2 materials suffered from thermal instability and low-quantum efficiency because of increased carrier trapping after doping [13,14].

In contrast anion doping has shown great potential in introducing bathochromism and intensive efforts have been undertaken to synthesize anion-doped titania toward visible-light-active photocatalysts [15–23], usually by introducing localized states in the band gap. Fittipaldi et al. has critically discussed the limitations and future challenges in the use of electron paramagnetic resonance technique in the investigation of anion doped TiO_2 based photocatalyst [31]. Recent emphasis has been placed on co-doped systems, that is, those involving combinations of cations and anions [24] or two anions together within the oxide lattice, in which a dramatic enhancement of photo-catalytic behavior has been reported [25–28].

Thus, many researchers started to investigate anionic nonmetal dopants such as C [32–35], N [34,36–43], S [44,45], and B [46,47] for extending the photo-catalytic activity into the visible-light region because, the related impurity states for such dopants appear near the valence band edge but do not act as charge carriers [34]. Gombac et al. have studied B and N co-doped powdered- TiO_2 , where a significant improvement in activity arises mainly from the red shift in the absorption edge, and also B is reported to inhibit growth thereby resulting in high surface area powders [48]. Especially, surface construction of titania during N-doping has been demonstrated both experimentally and theoretically [37,49]. However N-doping of titania by thermal treatment under an ammonia atmosphere usually leads to very limited visible light activity but greatly impairs the UV activity [11]. Divergent results have been reported for less-studied system involving B-doped TiO_2 [17,46,47]. It is therefore highly important to design and construct effective photocatalyst surface structures with some sorts of co-doping with proper ratio of different anions aiming synergy effects that enhance the separation and transfer of the carriers to develop efficient visible light photocatalysts. However, there is still great debate on the location of the dopants, the synergy effects on photoactivities and the importance of the relative ratios on photoactivities [17,50].

In this work, we focused on the synthesis of B/N co-doped anatase thin films on glass substrates by a simple sol–gel dip coating route. It was our aim to explore possible synergistic advantages arising from the simultaneous presence of B and N as dopants in the TiO_2 structure. As mentioned earlier there are already reports on the photo-catalytic behavior of boron and nitrogen doped TiO_2 nano-powders [51–54] and mesoporous forms [50]. To the best of our knowledge, there is no report on the photo-catalytic activity of boron and nitrogen doped anatase thin films. Detailed structural, compositional and optical characterization of the co-doped titania thin films has been done. Then, these films were employed as photo-catalysts under visible light irradiation in the degradation of aqueous methylene blue (MB), a dye often investigated as

representative of the class of azocompounds [55,56]. A comparative study of the catalytic efficiency was evaluated as a function of the dopant nature and atomic ratio of the dopant.

A variety of internal charge transfers may take place in the doped systems [57]. Co-doping may also be beneficial to reduce the number of intrinsic defects which are supposed to be detrimental in photocatalytic processes since they are considered to favor electron–hole recombination [57]. In order to explain the improvement in the photo-catalytic activity observed for the co-doped films we performed first-principles plane-wave calculations [58] based on the density functional theory (DFT) [59,60] on various atomic models depicting B/N doping in anatase structure. The results of these theoretical works were used to better explain the changes induced in the bonding behavior and the band gap of anatase by doping.

2. Experimental

2.1. Materials

Titanium (IV) isopropoxide (TIP) ($\geq 97.0\%$, Sigma Aldrich) and triethylamine (TA) ($\geq 99\%$, Sigma Aldrich) were used as Ti source and stabilizer, respectively. Microscopic soda lime slide glass was used as substrate. MB was purchased from Merck. Solutions of 1 M HCl and 1 M NaOH were used to adjust the pH of the solution. All reagents were analytical grade and used without further purification.

2.2. Preparation of TiO_2 film

TIP (1.5 ml) was added to anhydrous (Anh.) ethanol (10 ml) under vigorous stirring conditions and then TA (0.35 ml) was added as a stabilizer of the solution and stirred at 200 rpm for 2–3 min under N_2 environment (solution-A). A second solution was prepared separately by mixing hydrochloric acid (0.92 ml), water (0.15 ml) and Anh. ethanol (10 ml) using a magnetic stirrer at 200 rpm (solution-B). The two solutions were then mixed drop wise and stirred vigorously for 60 min under N_2 environment. The formed TiO_2 sol was transparent, quite stable and highly sensitive to the amount of TA and water. Then the sol was aged for 24 h and served for film preparation. The transparent sol was stable for three weeks.

TiO_2 thin films were prepared by a dip-coating method. Prior to the coating process, soda-lime-silica glass substrates (microscope slides) with dimension of $10\text{ mm} \times 60\text{ mm} \times 1.5\text{ mm}$ were grinded by a commercial bench grinder (model: ST-150), then cleaned in potassium dichromate and dichloromethane solution. Finally those abrasive substrates were rinsed with alcohol and deionized water and then dried at 100°C in a micro oven. The TiO_2 gel film was obtained by dipping the substrate in the precursor solution bath and pulled upwards with a speed about 4 cm/min. The substrates coated with gel were pretreated in room temperature and then annealed for 20 min using a micro oven at 200°C and finally the film was vapor treated in the vapor of boiling water for 30 s to remove the loosely bonded particles. The coating process was repeated five times for thick film preparation and finally annealed at 500°C for 2 h using a muffle furnace (JSMF-30T, Korea).

B/N doped TiO_2 was synthesized by a similar method where appropriate amounts of boric acid (H_3BO_3) (solution-C) and urea (solution-D) were dissolved separately in Anh. ethanol (5 ml) and rapidly added to the mixture of solution-A and solution-B. A schematic flow chart of the preparation of doped TiO_2 films by sol–gel dip coating is shown in Fig. 1.

Fig. 1. Schematic flow chart of the preparation of doped TiO₂ thin film on glass substrate by sol-gel dip-coating process.

2.3. Film characterization

The surface morphology and the thickness of the films were investigated by scanning electron microscopy (Carl-Zeiss EVO 40 using LaB6 filament). The Raman spectra from the annealed samples were recorded with a Horiba (Jobin-Yvon MicroRaman) spectrometer. XRD patterns were recorded by Rigaku (MiniFlex) using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The Scherrer equation was applied to the anatase (1 0 1) diffraction peak to calculate the average crystalline sizes. XPS in a SPECS PHOIBOS 100 hemispherical electrostatic energy analyzer was used for the checking of atomic percentage of the dopant and others species of the films. The absorption spectra of the bandwidth of the doped and bare (undoped)-TiO₂ films ranging from 300 to 800 nm were investigated by UV-vis spectroscopy (Thermo Scientific: Evolution 160).

2.4. Photo-catalytic studies

Photo-chemical degradation was carried out in an open visible light chamber as shown in Fig. 2. An outer water pump was used to circulate constant temperature water through the system continuously to keep the temperature constant during the degradation study. That chamber consisted of two magnetic stirrers, two cooling fans and a 200 W tungsten lamp. Degradation was carried out under visible light. 50 ml $1 \times 10^{-5} \text{ M}$ MB solution was taken and two catalyst films were used for degradation study. The surface area of each film was 6 cm^2 . Change in the concentration of MB solution during photo-catalytic degradation at different time intervals was monitored by UV-vis spectroscopy (Simadju 1800). The absorption spectra were recorded and rate of decolorization of

MB was observed in terms of change in the intensity at λ_{max} of the dye. The decolorization efficiency (%) has been calculated as: efficiency (%) = $((A_0 - A_t)/A_0) \times 100$, where A_0 is the light absorbance of MB before the treatment and A_t is that of after treatment at time t . Before taking the samples under visible light irradiation, the solution of MB was treated with coated films for 30 min in the dark to get adsorption and desorption equilibrium.

2.5. Computational details

We have performed the first principles plane-wave calculations [58] based on DFT [59,60] using the projector-augmented-wave (PAW) potentials [61,62] implemented in Vienna ab-initio simulation package (VASP) program [61–65]. The exchange-correlation potential was expressed in terms of the generalized gradient approximation (GGA) (Perdew–Wang 91 type) [66]. A plane-wave cut-off energy of 500 eV was used in all calculations to achieve the desired accuracy. The variable-cell structural optimization was performed for doped models in such a way that the external pressure was less than 1.0 Kbar and maximum force magnitude remained on each atom was set at most to 0.05 eV/Å. We used $2 \times 2 \times 2$ cell for which the pure anatase cell contains 48 ions in total. $7 \times 7 \times 7$ Monkhorst–Pack (MP) [67] mesh was used for k-point sampling in the Brillouin zone. The partial occupancy around the Fermi level was treated by Gaussian smearing with a smearing parameter of 0.05 eV. Spin polarization was included and the total energy was minimized up to 10^{-5} eV accuracy for all calculations. During the optimizations no symmetry constraints were imposed in order to avoid entrapment in local minimum configurations for doped models.

Fig. 2. Experimental setup for photo-catalytic reactions.

3. Results and discussion

3.1. Morphology and structure

In order to investigate the morphology of the obtained samples, a comparison between the SEM images of the 500 °C for 2 h annealed samples were made; bare-TiO₂ and different co-doped TiO₂ films is illustrated in Fig. 3(a)–(d). Top and bottom images of those figures showed low and high magnification of the images, respectively. Fig. 3(e) shows a typical cross section view taken from sample 'b'. As estimated from the Fig. 3(e), the thickness of the films was approximately 4 μm. Significant cracking was observed on the surface of all films. The films morphology are comparable to those of Fe³⁺ and W⁶⁺ doped TiO₂ films prepared on ceramic and Ti substrate, respectively by Yao et al. [68].

Fig. 4 shows the Raman spectra of the standard TiO₂ (anatase) and the samples with different B/N ratios. Comparison with the Raman spectrum of pure anatase TiO₂ (curve d), which shows band at 143, 196, 396, 515, and 638 cm⁻¹, demonstrates that the surface layer is mainly constituted by anatase. Conversely, Raman spectrum of the samples with N and B doping show a strong sharp band at 140.7 cm⁻¹ (*E_g*), three mid-intensity bands at 393 (*B_{1g}*), 513.5 (*A_{1g}* and *B_{1g}*) and 634.8 cm⁻¹ (*E_g*), and a very weak band at ~200 cm⁻¹ (*E_g*). Those bands have been ascribed for anatase TiO₂ [69–71]. The intensities of various TiO₂ features have been clearly decreased with B/N doping with respect to that of bare TiO₂ [69]. Since change in the particle sizes with respect to B/N content is not so significant for our samples (have been explained in XRD part) compare to those shown in Ref. [69], there is not very clear picture of intensity changes of different anatase features with in different

Fig. 3. SEM images of the B/N co-doped and bare-TiO₂ films obtained on glass substrates and annealed at 500 °C for 2 h where atomic ratio of each doping is given at the bottom of each pair.

Fig. 4. Raman spectra of different TiO₂ thin films. The modes of symmetry of the anatase are indicated.

B/N doping films. It is useful to underline that the Raman peaks of the B/N doped TiO₂ are broader than those of the pure anatase. In particular, particles having small dimension and low crystallinity are characterized by Raman peak broadening. The shifts (5 cm⁻¹) in the Raman bands compare to the references [69] might be due to the N doping and difference in particle size phonon confinement and oxygen deficiency.

XRD patterns of doped and bare-TiO₂ thin films annealed at 500 °C for 2 h are shown in Fig. 5. It is identified that all the diffraction peaks can be indexed to the anatase phase of TiO₂ (101), (004), (200), (105), (211), (204), (116) and (215) planes [JCPDS: 00-002-0406] and no other phase can be detected. No B- and N- derived peaks due to other oxides and nitrides have also been detected in all the patterns, indicating that B and N as dopant in TiO₂ exhibit no tendency to segregate and/or precipitate in different phases during the synthetic process [72]. The B and N in the matrix are assumed to be either interstitial or systematically substitute Ti or O without changing the host TiO₂ matrix. It can be found that the XRD peak positions of doped samples are in good agreement with those reference anatase phase of TiO₂ [48JCPDS:00-002-0406].

Fig. 5. XRD patterns of the thin films of co-doped TiO₂: (a) B/N: 0.27, (b) B/N: 3.83, (c) B/N: 20.89 and (d) bare-TiO₂.

Fig. 6. Typical XPS survey scans of bare-TiO₂ and B/N: 20.89 doped TiO₂ films.

The crystal sizes of all the samples are estimated using the Scherrer equation:

$$B(2\theta) = \frac{K\lambda}{L \cos \theta}$$

where L is the full width at half maxima (FWHM) of the diffraction peak of anatase, $K=0.89$ is the shape factor, θ is the diffraction angle and λ is the X-ray wavelength corresponding to the Cu K α irradiation. Considering peak of (101) planes in account, the average crystalline sizes of the sample 'a', 'b', 'c' and 'd' are 13.43, 11.67, 12.99 and 13.43 nm, respectively. It suggested that the change in particle size with respect to B/N content is not significant. In addition, there is no change in the d spacing value; 3.5 Å, which implies that B/N modification in co-doping samples do not change the average unit cell dimension. For our samples the average lattice parameters are as follows: $a=3.78$ Å, $c=9.44$ Å and unit cell volume = 134.52 Å³.

3.2. XPS study

XPS studies using mono-chromated Al K α X-ray source were performed to check the atomic percentage of different doping elements within the annealed films and bonding environment among Ti, O and dopant. Atomic percentages of different elements were calculated from the XPS narrow scan peak intensity considering the relative sensitivity factor of each element. The atomic ratios of boron to nitrogen (B/N) for different samples are as follows; 0.27 (a), 3.83 (b) and 20.89 (c). Fig. 6 shows the typical XPS spectrum of the B/N: 20.89 co-doped TiO₂ film. The spectrum from bare-TiO₂ sample is also shown in that figure for comparison. XPS peaks showed that the doped samples contained Ti, O, C, Si elements with B and N as dopant. The presence of carbon could be ascribed to the residual carbon from the precursor's solution. Fig. 7(i) shows the B1s XPS spectrum for the sample 'c' which contains highest atomic percentage of B. It shows single peak centered at binding energy (BE) of 192.1 eV. Referring to the standard BE of B1s in B₂O₃ (193.1 eV, B–O bond) [73] and TiB₂ (187.5 eV, B–Ti bond) [74], it is speculated that boron atom might probably be incorporated into TiO₂ matrix and form Ti–O–B or Ti–B–O or O–Ti–B bond [52,75]. Hence peak at 192.1 eV have been assigned to Ti–O–B or Ti–B–O or O–Ti–B bond. Fig. 7(ii) shows the N1s XPS spectrum for the sample 'a' which contains highest atomic percentage of N. Considering significant asymmetry, N1s peak has been deconvoluted with in two peaks at

Fig. 7. XPS narrow scan of B1s and N1s of doped-TiO₂ thin films with B/N: 20.89 and 0.27, respectively.

398.5 and 400.0 eV. The peak at 398.5 eV may be because of anionic N incorporated in TiO₂ in O–Ti–N linkages [22,76], which might be responsible for visible light photo-catalysis. The higher binding energy peak at 400.0 eV are attributed to oxidized nitrogen in the form of Ti–O–N or Ti–N–O linkages [22,76]. The absence of a peak at or near 396 eV for the N1s core level implied that the TiN phase or chemisorbed nitrogen is not formed in the nano materials [77].

3.3. UV–vis absorption spectra

Fig. 8 compares the UV–vis absorption spectra of thin films of bare- and B/N co-doped TiO₂ with different atomic ratios. After B/N co-doping to the TiO₂, the absorptions of catalysts increased significantly in the range of wavelengths from 400 to 800 nm. This clear red-shift in UV–vis spectra reveals the visible light absorption with B/N co-doped TiO₂ [52,78–81]. The red-shift within the absorption edges follows an increasing order as (a) > (b) > (c) >> (d). It implies that as atomic percentage of N is higher in B/N co-doping case, the red shift in the absorption edge is higher which is in good agreement with the result in reference [52]. Moreover the red shift observed in the co-doping cases are significantly higher compare to that of bare-TiO₂ case.

Fig. 8. UV–vis absorption spectra of co-doped and bare-TiO₂ thin films.

3.4. Evaluation of photo-catalytic activity

The photo-catalytic activity of bare- and B/N co-doped TiO₂ has been examined by photo-catalytic degradation of MB. Fig. 9 shows the percentage of degradation efficiency for the same films in (i) cycle number 1 (1st cycle), (ii) cycle number 2 (2nd cycle) and (iii) cycle number 3 (3rd cycle). Data clearly shows that the degradation efficiency increases continuously during the process of degradation for all cycles. However the rate of degradation is clearly differed from bare- to co-doped TiO₂ films. The doped TiO₂ films with B/N atomic ratios: 0.27, 3.83 and 20.89 showed higher degradation performance, up to 70%, whereas bare-TiO₂ films showed that of 30%. The photo-catalytic performance within the co-doped films were increased with N contents and decreased with B contents. However all co-doped films showed significantly better activity under visible range light compare to bare-TiO₂ films. For 1st cycle, degradation performance for co-doped films and bare-TiO₂ films are 51–63% and 28%, respectively.

One of the main problems in the use of TiO₂-based photo-catalysts is the deactivation; mostly attributed to blockage of the active sites on the surface, loss of coating material from the surface due to erosion or etc [82,83]. To evaluate the possibility of catalyst recovery and re-use, successive photo-catalytic MB degradation was performed for all of the doped and bare-films. After each cycle, films were annealed for 1 h at 500 °C and then re-used. Fig. 9(ii) shows that successive utilization for 2nd cycle induced even better performance for all the films (a), (b), (c) and (d). For 2nd and 3rd cycles the efficiency increased to 62–69% for co-doped films whereas that increased to 32–34% for bare-films. The increasing of efficiency for 2nd and 3rd cycles might be (i) due to the surface chemistry changing at each time heat treatment after each degradation study and/or (ii) the nitrogen concentration within the structure might be increased for the MB solution adsorption on the film. It is still in great debate of the synergy effects on photoactivities and the importance of the relative ratios on photoactivities [17,50]. Further work is ongoing to understand this behavior.

3.5. Theoretical results

We have also performed DFT calculations for bulk anatase, single doped B- to O- and N- to O- and co-doped BN- or NB- to TiO- cases where a titanium atom was replaced with B or N and an oxygen atom was replaced by N or B, respectively. We have investigated various single doped cases (e.g. B and N substitution on Ti site and

Fig. 9. Percentage of degradation efficiency of films (i) in cycle number 1 (1st cycle), (ii) in cycle number 2 (2nd cycle) and (iii) in cycle number 3 (3rd cycle).

on O site, and interstitial of B and N) and co-doped cases (e.g. substitution of B and N on different sites, and for different separations between B and N). We are presenting the most relevant cases for the experimental situations. The lattice parameters of bulk anatase were found to be 3.81 Å and 9.72 Å (*a* and *c*), and *c/a* ratio was 2.55 which are close to our experimental values (*a* = 3.78 Å, *c* = 9.44 Å and *c/a* = 2.50). Contrary to the earlier report claiming large volume expansion, which has significant effect on the electronic band structures, upon doping [84], the volume change is less than 1.5% for all of the doped structures in our calculations.

Fig. 10 displays the structural models and the total (DOS) and partial density of states (PDOS) of pure TiO₂, single doped B- or N- to O- site and interstitial N. The band gap of anatase is 2.04 eV, lower than experimental value; 3.2 eV [85] but consistent with the previous theoretical studies [39,86] underestimation of band gap is a well-known deficiency of DFT calculations. A correction can be made using hybrid functional, self-interaction correction or 'DFT+U' methods, but in this study our primary purpose is to understand the changes induced by the dopants on the electronic structures of bulk anatase, not the exact value of the band gap. PDOS analysis shows that the top most valence bands are formed mainly from O2p states while the conduction bands minimum are formed from Ti3d states. For the case of B substituting O atom (Fig. 10(b)), the hybridization of B2p, Ti3d and O2p orbitals gives rise to gap states appearing at 0.27 eV below the conduction band for B- doped O- model. In this structure, B atom makes a strong bonding with one of the neighbor O atoms with bond length as 1.36 Å. B–Ti bond distance is 2.11 Å which is even larger than Ti–O bond distance of pure anatase (1.95 Å). The systematic investigation of non-metal doping

of species of B, C, N and F for substitutional and interstitial cases has been carried by Valentin and Pacchioni [57]. The gap states are expected for substitutional non-metal doping and the positions of these states are mainly depend on the nuclear effective charge of the dopant. For lighter elements, the 2p states in the gap appear higher in the gap that is close to the conduction band minimum (CBM). Our results for B substitution to O case are in good agreement with this observation. However, the states in the gap also contain Ti3d states. The typical position of Ti³⁺ states is just below the CBM. This situation can also be addressed to low electronegativity of B atom compared to O and less charge transfer from Ti to B. We can conclude that substitution of B to O site produces states in the gap, which provides the absorption of visible light, as well as Ti³⁺ ions which act like electron–hole recombination centers and therefore diminish the photocatalytic activity. Moreover, a high frequency electron paramagnetic resonance (HF-EPR) measurements on B doped anatase [51] observed some spin density on B, Ti and O atoms which might be explained as the formation of substitution of B to O site. The valence electrons from B might be transferred to lattice Ti ions (Ti⁴⁺) producing Ti³⁺ ions and it is well-known that the presence of Ti³⁺ ions produce midgap states [85].

For the case of N substituting O atom (Fig. 10(c)), N2p defect states are located at the top of the valance band maximum. The position of these states might be related with the effective nuclear charge of N atom [57], that is the N2p states appear low compared to that of B2p in the forbidden region due to high effective nuclear charge of N atom compared to B atom. The N2p states are localized at the defect site and the position of N2p states. Along with this,

Fig. 10. Relaxed structures and partial density of states (PDOS) of (a) pure anatase, (b) B- doped O-, (c) N- doped O- and (d) N interstitial models. Energies are shifted such that Fermi levels are matched with zero of energy. The bond lengths between doped atoms and first neighbors are indicated. Solid lines, gray shaded, green shaded and blue shaded areas represent the total DOS, PDOS of Ti3d, O2p and N2p states, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

the EPR measurements also indicate the localization of unpaired electron on N dopant [37]. The visible light absorption might be enhanced by the substitution of N atom to O site due localized states in the gap region. Due to these defect states, band gap is reduced to 1.66 eV and 1.87 eV for down and up spin states, respectively. Nitrogen atom has five electrons in the valence shell therefore the structure is paramagnetic and an acceptor state appears just above the Fermi level.

For the interstitial N model (Fig. 10(d)), there will be a strong N–O bonding with a bond length of 1.34 Å. Since the electronegativity of O is higher, N tends to donate electrons to O and N–O–Ti configuration is formed at the defect region. These excess electrons behave in the same manner of B- to O- model (Fig. 10(b)) resulting the formation of midgap states [37]. However, in this case, in

addition to the un-occupied state formed at the edge of conduction band, extra midgap states appear below the Fermi level.

In order to understand the effect of co-doping in anatase we substituted B and N atoms for various positions of Ti and O sites. Fig. 11 displays the relaxed structures and PDOS for BN- and NB- doping to TiO- positions as well as the bond lengths to nearest atoms of doped species is indicated. For BN-doped to TiO- model, B atom transfers its electrons to O atoms and reaches closed-shell configuration which prevents BN bonding. The interaction of N atom with its surrounding atoms produces midgap bands which behave as acceptor states and a localized nitrogen state appears at the top of the valence band. Thus, N–Ti–O type of hybridization produces midgap states. PDOS analysis indicates that there is no boron contribution to DOS around Fermi level but band gap of this case is

Fig. 11. Co-doping of anatase: (a) B atom replaced with Ti and N atom replaced with O and (b) N atom replaced with Ti, and B atom replaced with O. Solid lines, gray shaded, green shaded and blue shaded areas represent the total DOS, PDOS of Ti3d, O2p and N2p states, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Fig. 12. Formation energy as a function of chemical potential of oxygen for the doped structures.

found to be 1.76 eV for the spin up states and 1.2 eV for spin down states. Compared to single-doped models, this is a relatively larger narrowing in the band gap. Thus, co-doping of anatase with B/N can be expected to improve photo-degradation with respect to single-doped cases via band gap narrowing.

In contrast with the previous co-doping case, for the NB-doped TiO- model, there is a bonding between B and N atoms with bond-length of 1.617 Å. Similar to the B- to O- case, the Fermi level is also pinned for this model to the bottom of the conduction band causing a conductor like band structure, which obviously does not contribute in the photo-catalytic activity of TiO₂.

In summary, band gap narrowing leads to the red shift of the absorbance spectra to the visible light region. Meanwhile, the appearance of midgap states could be responsible for the enhancement of the photo-catalytic activity either by improving the absorbance or avoiding the recombination of electron-hole pairs [87].

XPS results of the doped films suggested the formation of N–Ti–O configuration upon the examination of the N1s and Ti2p spectra (Section 3.2). As shown in Fig. 10(c) and (d), N–Ti–O configuration can be formed in both N- to O- and N interstitial cases. Therefore, in order to understand the energetically more stable structures, we have compared the formation energies of doped models using the following formalism:

$$E_{\text{form}} = E\left(\text{TiO}_2 + \frac{B}{N}\right) - E(\text{TiO}_2) - k\mu_B - l\mu_N + m\mu_O + n\mu_{\text{Ti}}$$

where $E(\text{TiO}_2 + B/N)$ and $E(\text{TiO}_2)$ are the total energies of doped structure and pure anatase, respectively and μ 's are the chemical potentials of corresponding species. Chemical potentials of N and B are calculated from gaseous phase of N₂ and α -boron phase, respectively. μ_O is set as the chemical potential of the gas state of O₂ for the case of O rich environment. On the other hand, μ_{Ti} is set from metallic Ti phase for the case of O poor (Ti rich) environment. Furthermore we imposed the constraint as $\mu_{\text{Ti}} + 2\mu_O = \mu_{\text{TiO}_2}$ in order to ensure the equilibrium of bulk anatase phase. Integers m and n are the numbers of O and Ti vacancies, respectively while k and l are the numbers of doped B and N atoms (if any), respectively. Fig. 12 displays the formation energy of the different doped models as a function of the chemical potential of oxygen with respect to the value of gas phase ($\Delta\mu_O$). Variation of oxygen chemical potential indicates the relative abundance of oxygen in the synthesis medium within two limiting cases; O₂-rich and O₂-poor environments. Two limits in the figure represent the environments; $\Delta\mu_O = 0$ eV for the

O₂-rich and $\Delta\mu_O = -4.7$ eV for the O₂-poor or Ti-rich. As depicted in Fig. 12, N- doped O- case is energetically the most favorable doping model in the O poor environment, while BN- doped TiO- is the stable one in the O rich environment. There is a cross over between these two models at $\Delta\mu_O = -2.3$ eV. However N interstitial case might be stabilized in O rich environment within the single doped models. This might be the reason for the formation of N–O–Ti or/and N–Ti–O bonding in the case of our experiment.

4. Conclusions

An experimental and theoretical study has been performed to realize the synergistic effect of non metal doping in TiO₂ for photo-catalytic degradation. Co-doped TiO₂ thin films with boron and nitrogen have been successfully synthesized by simple sol-gel dip coating method. The B/N co-doped TiO₂ films demonstrated up to 40% higher photo-catalytic activities than bare-TiO₂ films under visible light irradiation. The absorption edges for the doped films were found to be shifted toward the visible region, while the overall absorption remarkably increased for doped films. The film with the B/N atomic ratio of 0.27 displayed the highest degradation rate among all doped films. The doped films retained their superior catalytic activity for extended periods. Computational studies were conducted on several atomic models describing various doping schemes. The results showed that doping with B and/or N induced (a) band gap narrowing (red shift of the absorbance spectra to the visible light region) and (b) formation of midgap states especially in case of N interstitial model. These results also supported the observed synergistic effects of B/N doping for higher photo-degradation activity. These computational findings supported our experimental data by indicating the possible routes that can be responsible for the improvement of the photo-catalytic activity in TiO₂ due to B and N doping. It is revealed that B/N doped TiO₂ films could be a potential candidate for scaling up for industrial applications.

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