Tailoring the photocatalytic properties of anatase TiO_2 by B-TM (TM = Pt, Ta, V) co-doping

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Abstract

In order to provide insight into the influence of co-doping with boron (B) and transition metals (TM = Pt, Ta, V) on the photoactivity of anatase TiO_2, the electronic, structural and optical characteristics of the mentioned co-doped systems were studied using modified density functional theory calculations. For each transition metal two cases were considered, with B atom either replacing O atom (B-substitutional) or imbedding interstitially (B-interstitial) into TiO_2 lattice. The calculations showed that the co-doping is more favorable for the B-interstitial systems than for the B-substitutional ones and under the O-rich conditions. For the B-substitutional cases a slight decrease of the band gap is observed. In contrast, the results obtained for the B-interstitial systems exhibited no band gap narrowing. However, in these systems, the occurrence of localized states within the band gap is noticed, which could improve visible light absorption through a two-step optical transition.

Keywords: first principles calculations; TiO_2; transition metals; photocatalysis

1. Introduction

Titanium dioxide (TiO_2) is promising photocatalyst for an effective decomposition of organic pollutants and photocatalytic hydrogen production. However, due to its wide band gap (3.2 eV), it mainly absorbs light from the UV region, meaning that only about 5% of the solar spectrum can be utilized for a photocatalytic reaction. The main adopted strategy to overcome this constraint is

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doping with either metal cations or nonmetal anions, which creates additional states into the forbidden gap and/or above the valence band maximum (VBM). However, the monodoped systems are limited by high recombination rate of the photogenerated electron-hole pairs, which is not favorable for the photocatalytic reaction [1]. In recent years, passivated co-doping with nonmetal and metal elements was proposed [2] in order to produce synergistic effect to increase the visible light absorption and at the same time decrease the charge recombination rate. Among nonmetals the most investigated co-dopants are N and C, forming pairs mostly with Cu [3-9], but also with other metals (La, Cr, W, V, Sb, Nb, Sn, Zr, Ta, Sm, Fe, Ni, Pt, Pd) [10-29] and elements [30, 31], while B anion is the least studied element for co-doping with metal cations.

B-Ni co-doped TiO_2 was fabricated by Huang and coworkers [32] and it exhibited superior photocatalytic activity for NO removal in comparison with its monodoped and undoped counterparts. Gong et al. [33] produced B and Ta co-doped TiO_2 samples that showed much better efficiency for photodegradation of methylene blue (MB) solution under solar light irradiation than undoped and monodoped samples. Jaiswal et al. [34] found that the photocatalytic degradation level of aqueous pollutants enhanced remarkably for TiO_2 co-doped with Co and B on substitutional and interstitial sites as compared to single doped and undoped TiO_2. Ibrahim et al. [35] calculated the optical properties of (Cr, B) co-doped anatase TiO_2 and found that its absorption edge extended to the visible light region and the absorption efficiency was enhanced. Azizi et al. [36] produced the carbon/boron co-doped TiO_2 sample which was efficient for the removal of 4-nitrophenol. B-Zr [37, 38], B-Bi [39, 40] and B-La [41] co-doped TiO_2 also showed good photocatalytic properties for the degradation of organic pollutants.

In the present paper, the structural, electronic and optical properties of (B, TM) co-doped (TM = Pt, Ta, V) anatase TiO_2 are explored using the calculations based on modified density functional theory (DFT), in order to provide insight into the synergistic effect of co-doping on the photocatalytic performance of TiO_2. As it was demonstrated earlier that B atoms can be settled at both the interstitial and substitutional sites in TiO_2 [34, 37, 41-43], we considered both possibilities for each co-doped system, i.e., with B atom either replacing O atom (B-substitutional) or incorporating interstitially (B-interstitial) into TiO_2 lattice.

2. Calculation details

The full potential augmented plane waves plus local orbitals method within the WIEN2k code [44] was employed for the calculations. The co-doped structures were constructed from the relaxed 2 x 2 x 1 (48 atoms) anatase supercell, by replacing one O atom with B and one neighboring Ti atom with transition metal (TM = Pt, Ta, V). We also simulated systems where one B atom, instead of replacing O, was embedded interstitially into the supercell. The k-points mesh was created by tetrahedron method [45] with 726 and 54 k points in the irreducible wedge of the Brillouin zone for pure TiO_2 and co-doped systems, respectively. The limiting parameter for the number of plane waves, $R_{MT}K_{max}$, was 7 and the parameter for Fourier expansion of charge, G_{max}, was 16. All the structures were relaxed using the PBE-GGA [46] exchange-correlation functional til the forces on each atom were smaller than 5 mRy / a.u. and then modified Becke-Johnson (mBJ) potential [47] was applied to calculate the band structures and densities of states (DOS) of the relaxed systems. The mBJ potential has been proved to give good agreement between the measured band gaps and the calculated ones with less computational cost than hybrid potentials and the GW method, except in the case of strongly localized systems with f states [48, 49].

3. Results and discussion

3.1. Dopant formation energies

To study the relative difficulty of doping of B and TM atoms into the TiO_2 lattice under diverse growth conditions, we computed the co-doping formation energies for all investigated systems using the general formula:

$E_{form} = E_{doped} – E_{pure} – m\mu_B - n\mu_{TM} + x\mu_O + y\mu_{Ti}$,

Where E_{doped} is the total energy of the co-doped TiO_2 supercell, E_{pure} is the total energy of the TiO_2 supercell without the dopant atoms, m and n are the numbers of B and TM atoms doped into the TiO_2 supercell, x and y are the numbers of O and Ti atoms replaced by impurity atoms and μ are the chemical potentials of the corresponding atoms. In our case, the formula comes down to

$E_{form} = E_{doped} – E_{pure} – \mu_B - \mu_{TM} + \mu_O + \mu_{Ti}$,

when B is embedded substitutionally and

$E_{form} = E_{doped} – E_{pure} – \mu_B - \mu_{TM} + \mu_{Ti}$,

when B is embedded interstitially.

The chemical potentials of transition metals μ_{TM} are given as the total energies of corresponding bulk materials, while μ_B is the energy of a B atom calculated from the formula

$\mu_B = ½ E_{B2H6} – 3/2 E_{H2}$,

where B_2H_6 has structure with $P2_1/n$ space group. The dopant formation energies computed under Ti-rich (μ_{Ti} is the total energy of bulk Ti, while $\mu_O = ½ (\mu_{TiO2} - \mu_{Ti})$) and O-rich ($\mu_O$ is half the energy of the ground state of O_2 molecule, while $\mu_{Ti} = \mu_{TiO2} – 2 \mu_O$) growth conditions are given in table 1. It can be observed that the co-doping is less favorable under the Ti-rich than under the O-rich growth conditions. The co-doped samples with Ta and V have similar formation energies, which are much smaller than the formation energy of the system co-doped with Pt, regardless of the growth conditions. The calculations show that the co-doping with interstitial boron is preferred, similarly as for the boron-doped anatase [43]. The formation energies for substitutionally (B, Pt) co-doped anatase are high, indicating that this system is not stable under normal conditions.

Table 1: Dopant formation energies of the investigated systems

B-substitutional	O – rich [eV]	Ti – rich [eV]
Pt	6.9	12.0
Ta	1.1	6.1
V	1.2	6.2
B-interstitial		
Pt	-2.4	7.7
Ta	-8.9	1.1
V	-8.6	1.4

3.2. Charge distribution analysis

We used the Bader's atoms in molecule theory [50], as embedded in the Critic2 code [51] to calculate the charge distribution between the atoms. The calculated results are given in Table 2.

Table 2: Bader charges of Ti, O, B and TM atoms,expressed in electrons

	Ti	O	B	TM
B-substitutional				
Pt	2.41	-1.17	1.09	0.44
Ta	2.09	-1.32	2.02	2.99
V	2.32	-1.27	2.36	2.02
B-interstitial				
Pt	2.57	-1.64	2.71	1.86
Ta	2.55	-1.69	2.71	3.45
V	2.60	-1.72	2.30	1.90

We can see that in all studied cases, the O atom gets part of the charge at the expense of other atoms, as a consequence of its electronegativity being larger than all the other atoms involved. The ratio of the charge transferred from transition metal to oxygen atom is aligned with their electronegativity (Ta atom has the largest, while Pt atom has the smallest quantity of charge transferred).

3.3. Electronic properties

In order to explore variations in the band gap for various co-doped anatase systems, the corresponding band structures were calculated. Our calculations showed that pure anatase TiO_2 has an indirect band gap between X and Γ points with a value of 3.13 eV, which is in agreement with the experimental value (3.2 eV) [52]. In the case of substitutionally doped boron (figure 1), B and Pt co-incorporation leads to a reduction of the band gap by about 15%, to 2.64 eV, while for the (B, Ta) and (B, V) co-doped systems, the band gaps are only slightly narrowed (3.05 eV and 3.10 eV, respectively) as compared to the pure TiO_2. However, two isolated energy states are formed in the middle of the band gap region, which can serve as stepping stones for electron transition, but at the same time as electron-hole recombination centers. The calculated band gap reduction for (B, Ta) co-doped anatase of 0.08 eV, compares well with the value of 0.11 eV, measured in paper by Gong et al. [33].

To further understand the effect of (B, TM) co-doping on anatase TiO_2, the total and projected densities of states of pure and co-doped systems were calculated (figures 2 and 3). As expected, in pure anatase TiO_2 the valence band is principally composed of the O 2p states, while the conduction band is dominated by Ti 3d states. For (B, Pt) co-doped TiO_2, an upward shift of the valence band maximum (VBM), caused primarily by the Pt d states is observed. The conduction band, in contrast, remains almost unchanged, which in the aggregate leads to the band gap narrowing by 0.49 eV. In the case of (B, Ta) co-doping, two peaks corresponding to the impurity states can be clearly seen between VBM and conduction band minimum (CBM), close to the Fermi level. These states are mostly of B p character and are located at 1.24 eV and 2.1 eV above the VBM in the band gap and are divided by 0.5 eV. For (B, V) co-doped TiO_2 the situation is similar, except that the states within the band gap are closer to VBM (0.94 eV and 1.65 eV) and that the upper state consists of the hybridized V d and B p states.

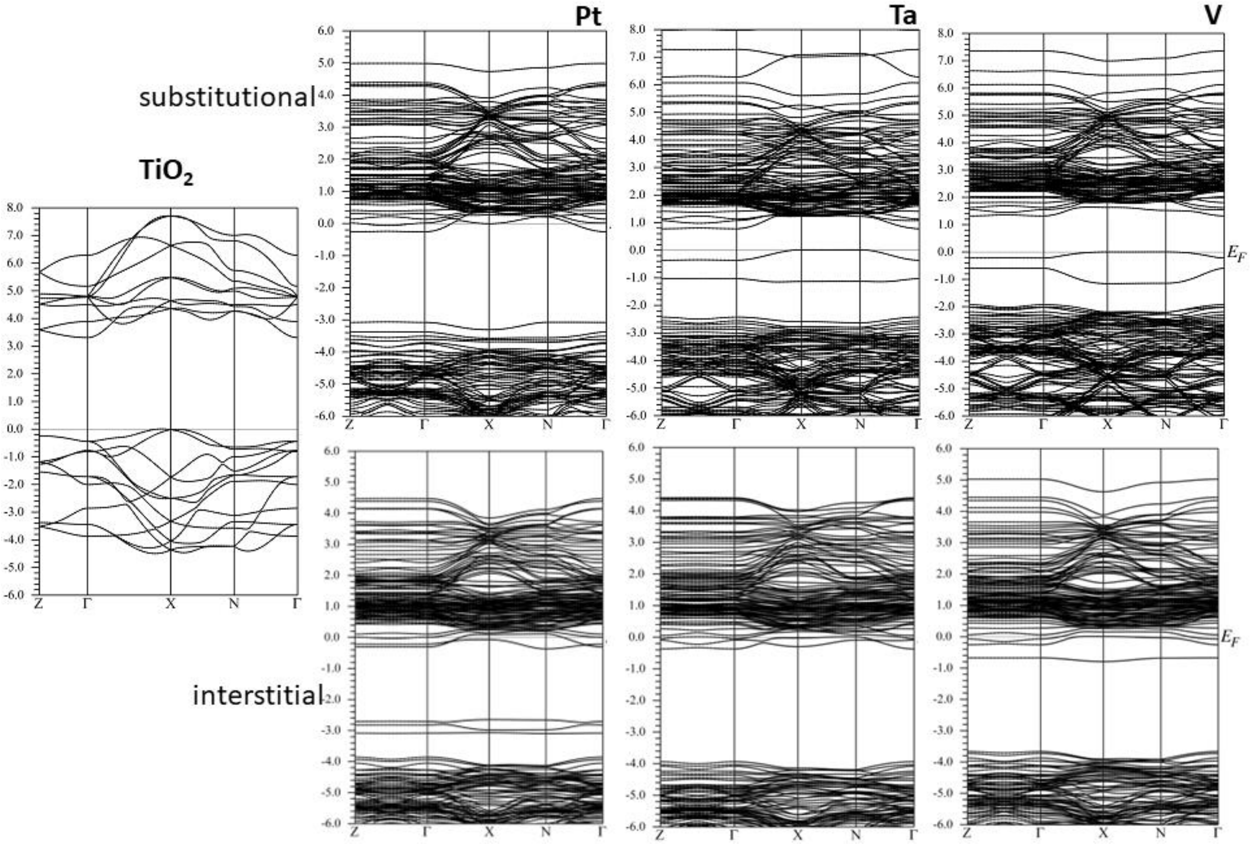

Figure 1: Band structures for pure and (B-substitutional or interstitial, TM = Pt, Ta, V) co-doped anatase TiO_2

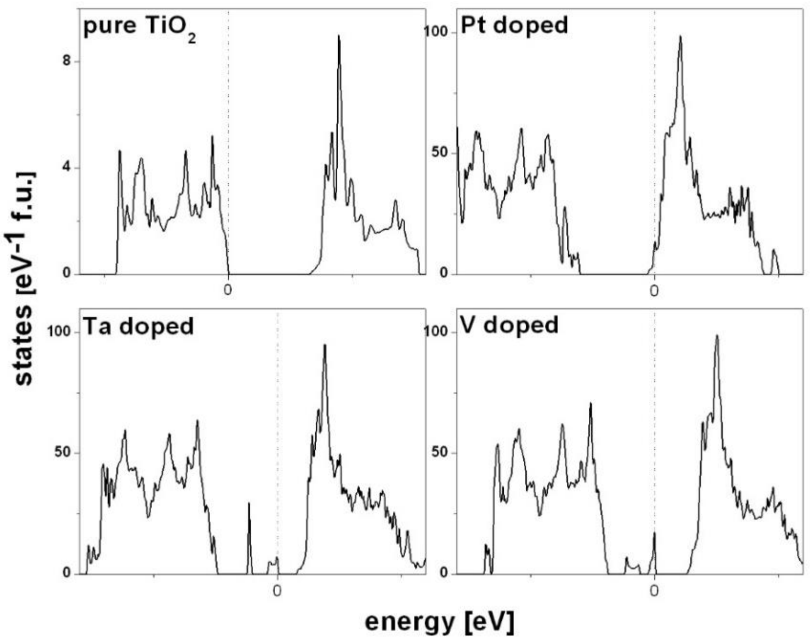

Figure 2: Total densities of states for pure and (B-substitutional, TM = Pt, Ta, V) co-doped anatase TiO_2

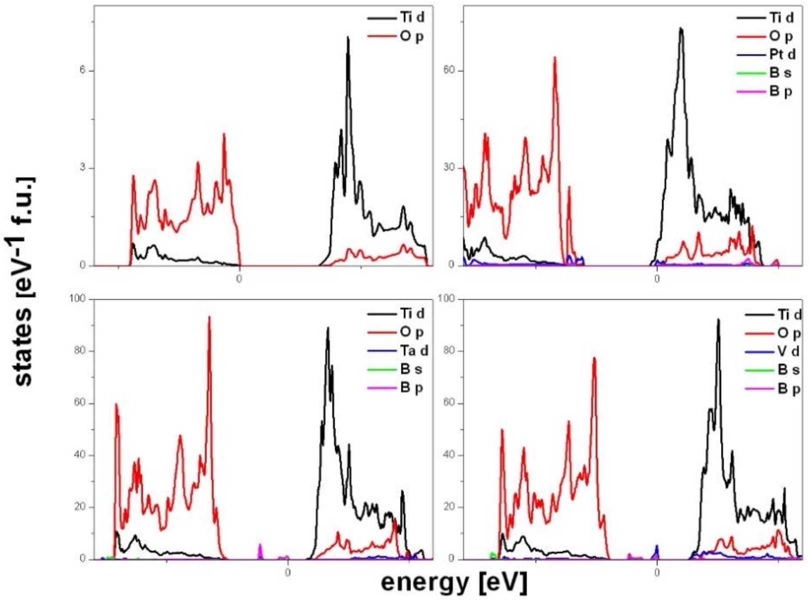

Figure 3: Partial densities of states for pure and (B-substitutional, TM = Pt, Ta, V) co-doped anatase TiO_2

When it comes to the systems with interstitially doped boron (figures 1 and 4), they all have similar, slightly increased band gap (3.40 eV for V, 3.43 eV for Pt, and 3.48 eV for Ta). However, for (B, Pt) co-doped case, the presence of the broad intermediate Pt d states near the middle of the band gap and about 2.1 eV below the CBM, could serve as an intermediate step and perhaps improve the absorption of lower-energy photons.

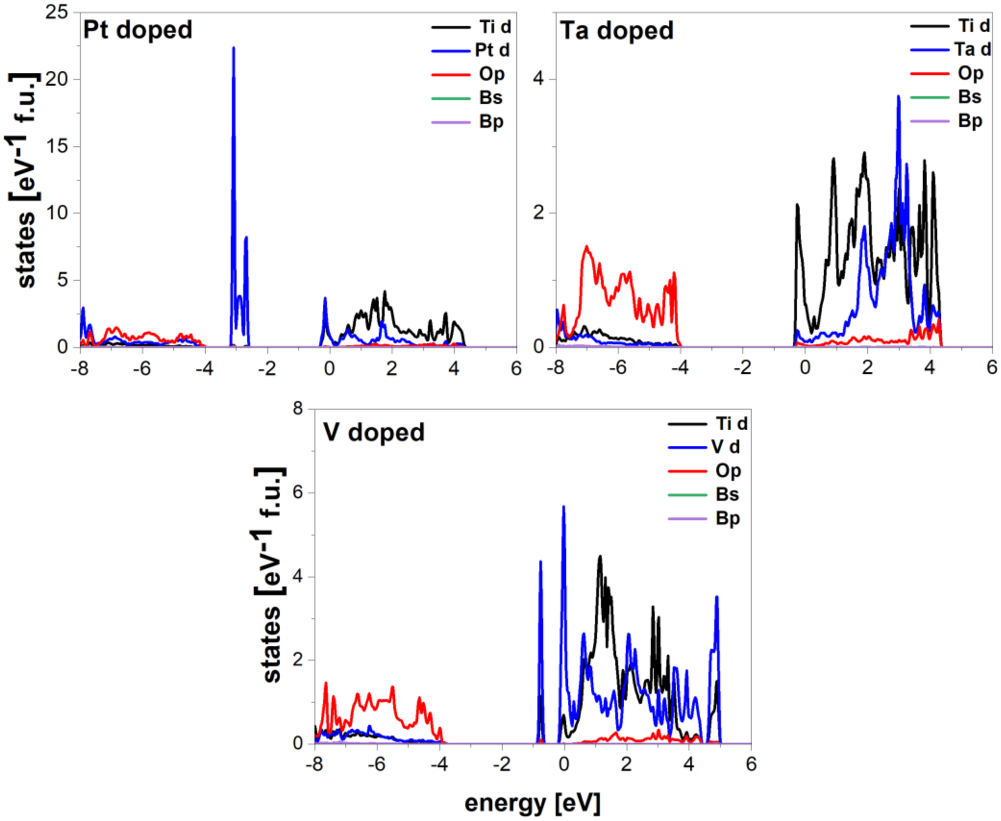

Figure 4: Partial densities of states for (B-interstitial, TM = Pt, Ta, V) co-doped anatase TiO_2

3.4. Optical absorption

On the basis of calculated band structures, we firstly computed the imaginary parts of the dielectric tensor $\varepsilon_i(\omega)$ and then employed the Kramers-Kroning relation [53] to get the real ones $\varepsilon_r(\omega)$. Finally we computed the absorption spectra using the formula:

$$\alpha(\omega) = \sqrt{2\left[\sqrt{\varepsilon_i{}^2(\omega) + \varepsilon_r{}^2(\omega)} - \varepsilon_i(\omega)\right]}$$

and they are presented in Figure 5, as a function of the photon wavelength.

Both a redshift and a blueshift of the absorption edge were observed experimentally in interstitially B doped TiO_2, which was explained by the fact [42] that boron can occupy different interstitial positions in anatase. Yang et al. [54] suggested, based on their calculations, that substitutional B doping causes a redshift of the absorption edge and band gap reduction, whereas interstitial B doping results in a blueshift, which is consistent with the experimental work of Huang et al. [32]. However, Lan et al. [41] noticed a small redshift of absorption edge in their B-doped TiO_2 sample with dominant B interstitials.

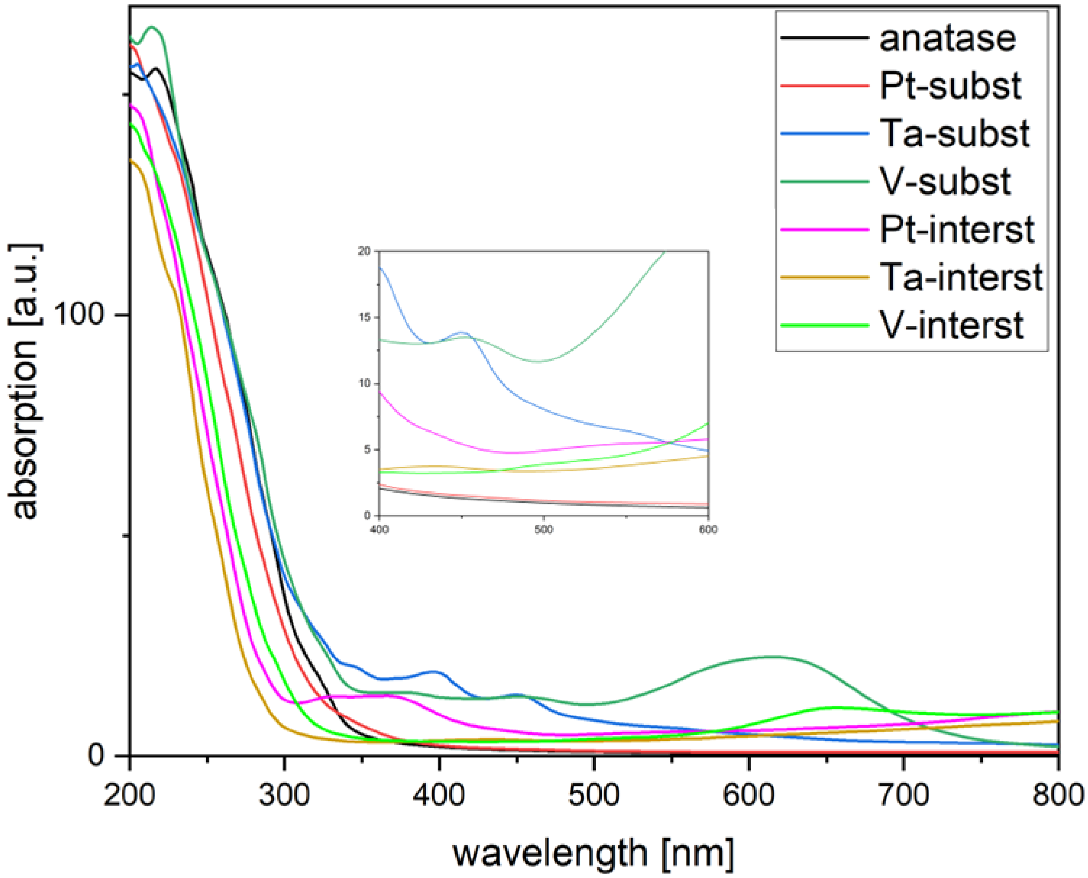

Figure 5: Optical absorption spectra of pure and co-doped anatase TiO_2, with the inserted enlarged visible light region

Figure 5 shows that for undoped anatase no absorption is observed in the visible light range. However, after co-doping the absorption in this region increases for most of the co-doped systems. The increase is particularly pronounced for substitutionally (B, V) and (B, Ta) co-doped anatase, due to the generation of broad intermediate bands (IB), which gives the possibility of two-step transition between VB and CB through IB.

3.5. Edge positions

To study the photocatalytic activity of the investigated co-doped systems, we computed their band edges positions, as they have the major influence on the ability of a semiconductor to absorb species on its surface. That is to say, the acceptor absorbed on the semiconductor surface, can be reduced by the electrons if its potential is lower than the CB potential of the semiconductor and the donor absorbed on the semiconductor surface, can be oxidized by the holes if its potential is higher than the VB potential of the semiconductor. The CB and VB edge positions of a semiconductor can be obtained from the formulas

$E_{CB} = X - E^{e} - 0.5E_{g}$, and $E_{VB} = E_{CB} + E_{g}$, where E_{CB} represents the CB edge potential, X is the semiconductor's electronegativity obtained as the geometric mean of the electronegativities of the constituent atoms, E^{e} is the energy of free electrons on the hydrogen scale (~ 4.5 eV), E_{g} is the semiconductor's band gap, and E_{VB} is the VB edge potential.

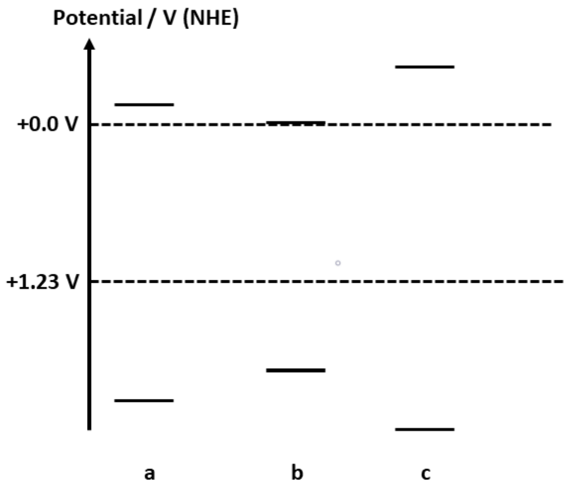

Figure 6: Band level diagram for (a) pure, (b) (B-substitutional, Pt) and (c) (B-interstitial, Ta) co-doped anatase TiO_2

Our calculated conduction band edge potential of TiO_2 is -0.253 eV, which is more negative than the hydrogen reduction potential (0 eV), while VB edge potential is 2.877 eV, which is more positive than oxygen evolution (1.23 eV) and standard redox potential of OH/OH^- (1.99 eV), meaning that TiO_2 can be used for these reactions. (B-interstitial, Ta) co-doped TiO_2 has calculated CB edge of -0.444 eV and VB edge of 3.036 eV, which means that both its oxidation and reduction abilities are slightly increased. In contrast, (B- substitutional, Pt) co-doped TiO_2 is poorly suitable for hydrogen evolution, as it has CB edge of -0.0189 eV, but with VB edge of 2.62 eV it can safely be used for oxygen evolution.

4. Conclusion

Using the augmented plane waves plus local orbitals method and the modified Becke-Johnson correction for the band gap, as implemented in WIEN2k simulation package, we have conducted a series of calculations of anatase TiO_2 co-doped with boron and various transition metals, in order to investigate their properties of interest for photocatalytic applications. We have calculated band gaps, densities of states, absorption coefficients and band level arrangements of TiO_2 substitutionally and interstitially co-doped with B and Pt, Ta, and V. The calculations showed that although the co-doping is more energetically favorable for the interstitially co-doped cases, the band gap reduction and the improvement of the absorption in the visible light region occurs for the substitutionally doped ones.

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Data availability

The raw/processed data required to reproduce these findings can be obtained from the authors upon reasonable request.

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