Enhancing photocatalytic properties of rutile TiO_2 by codoping with N and metals – ab initio study

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Abstract

Substitutional N to O and M to Ti (M = Pt, V, Sb) codoped rutile TiO_2 was investigated using density functional theory (DFT) based calculations with both standard and hybrid exchange-correlation functionals. The band gaps calculated using generalized gradient approximation (GGA) exhibited narrowing compared to the pure rutile TiO_2 in all the investigated cases. In contrast, the results obtained with hybrid exchange-correlation functional showed that there was no band gap narrowing, but doping induced localized states within the band gap just above the valence band, as well as below the conduction band for Pt doped TiO_2. The presence of broad intermediate states (IS) in the band gap could enhance visible light absorption through a two step optical transition from the valence to the conduction band via the IS and at the same time lower recombination of the photogenerated charges.

1. Introduction

The most efficient way of hydrogen production using solar energy is water splitting induced by solar light. In order to achieve it, a photo-semiconductor capable of absorbing solar energy efficiently is needed. Efficient photocatalysts should satisfy several conditions: suitable band gap (about 2-2.2 eV) for visible light absorption and appropriate band edge potentials for water splitting, capability to separate excited electrons and holes, minimal energy losses during charge transport, chemical stability to corrosion, suitable electron transfer properties from photocatalysts' surface to water and low cost [1, 2]. However the applicability of semiconductor photocatalyst is, without any doubt, primarily determined by its electronic structure.

Titanium dioxide TiO_2, in both rutile and anatase form, is one of the most promising photocatalysts. However, the wide energy gaps of pure TiO_2 phases allow efficient absorption of only ultraviolet light and are not suitable for efficient use of solar energy. In this sense, an extensive experimental [3, 4] and theoretical [5-14] work has been carried out in order to shift the TiO_2 absorption edge from the UV to the visible-light region and thus increase its efficiency for solar-driven photocatalysis. For achieving that purpose mostly doping with transition metals was used [15-22]. However, the transition metals as dopants can increase the number of carrier-recombination centers and thus reduce the carrier mobility, causing a decrease in the photocatlytic activity. Doping with nonmetal atoms, such are N, C and S seemed to be more effective [23-38] and recently the donor-acceptor codoping was proposed to improve the photoelectrochemical performance of rutile [39, 41] and anatase TiO_2 [42-57]. Niu et al [41] studied non-metal (N) and non-transition metal (Sb) codoped TiO_2 and found that it has improved photoelectrochemical performance for watter-splitting. Yao et al. [50] investigated photocatalytic activity of anatase TiO_2 codoped with Zr and N and found band gap narrowing by about 0.28 eV. Long and English [47] reported that among the investigated systems (N or C; TM = Ta, Hf, Fe)-codoped anatase TiO_2, only (N, Ta)-codoping case narrows the band gap significantly by about 0.48 eV. Meng et al. [44] indicated that (V, N), (Cr, N) and (Mn, N) codoped anatase TiO_2, which have the impurity energy levels with a significant bandwidth in the band gap, are of great potential as candidates for photovoltaic applications in the visible light range. Long and English [54] used hybrid density functional theory calculations to investigate (N, Si)-codoped TiO_2 and found that codoping produces a larger band gap narrowing compared to monodoping with the same elements. They also found that larger extent of band gap narrowing, with increased N doping concentration, is related to double-hole coupling rather than high doping concentrations. Lin et al [42] upon studying (Sm, N) codoped TiO_2 concluded that this system is a highly active photocatalyst for efficient visible lighte photocatalysis. Recently Dashora et al. [58] reported that (Cu, 2N) – TiO_2, due to the formation of a broad intermediate energy band, improves the photocatalytic water-splitting ability of TiO_2 and allowes charge separation.

The effect expected from some dopant is mainly related to the location of its energy levels with respect to the band structure of the host. In particular, for efficient use of TiO_2 for photocatalytic water splitting, it is necessary to find a dopant pair which narrows the band gap in order to shift the absorption edge to the visible light region, but at the same time does not lower the conduction band minimum, as the reduction potential level of water is just below the CBM of TiO_2 [59]. Therefore, the density functional theory calculations which can provide insight into the electronic structure of the modified semiconductors can guide the selection of the proper dopants to meet the requirements needed for application. In this work, we show that the conduction band and valence band edges of rutile TiO_2 are strongly influenced by codoping with N and various metals (Pt, V, Sb) and that, in all of the investigated cases, some isolated states are introduced in the band gap, resulting in the effective narrowing of the band gap and thus the reduction of the photon absorption energy.

2. Calculation details

The first-principles density functional theory (DFT) calculations were performed with the WIEN2k simulation package [60] based on the full potential (linearized) augmented plane waves method (FP (L)APW). In this method the unit cell is divided into non overlapping muffin-tin spheres around atoms and an interstitial region. In the spheres wave functions, charge density, and potential are expanded in spherical harmonics, while in the interstitial region they are expanded in plane waves. Electronic exchange-correlation energy was treated under both generalized gradient approximation (GGA) parameterized by Perdew-Burke-Ernzerhof (PBE) [61] and hybrid potential with onsite-exact-exchange (GGA exchange-correlation was replaced by exact exchange), as it is well known that GGA approximation underestimates band gap notably [62]. As the first step of structural relaxation, the atomic positions were relaxed according to Hellmann-Feynman forces calculated at the end of each self-consistent cycle, with the force minimization criterion 2 mRy/ a.u. (0.03 eV/a.u.). During this relaxation the cell volumes were fixed to their experimental values. Then the theoretical equilibrium volume was determined by fixing the atomic positions to their optimized values, further keeping the c/a ratio fixed and performing a series of calculations was carried out, changing the volume within ± 5% of its experimental value. The total energies were calculated as a function of volume and fitted to Birch-Murnaghan equation of state [63]. In the last step the c/a ratio was optimized by changing it within ± 2% of its experimental value while keeping the optimized volume fixed.

After obtaining the optimized structure parameters, we have constructed 2 x 2 x 2 supercell (48 atoms), starting from the pure compound unit cell, and replaced one Ti atom with M (M = Pt, V, Sb) and its adjacent O atom with N (figure 1 [64]). We also checked another ’farthest away’ codoped model, in which the N and M dopant atoms were as far apart as possible. The calculation results showed that the formation of an adjacent pair of N and M is energetically favorable by about 0.2 eV than the N-V ’farthest away’ configuration. The cut-off parameter $R_{mt}K_{max}$ for limiting the number of plane waves was set to 7.0, where R_{mt} is the smallest value of all atomic sphere radii and K_{max} is the largest reciprocal lattice vector used in the plane wave expansion. To check the accuracy of the results obtained , we varied this parameter from 7.0 to 8.0. These variations showed that the energy converged within about 0.0006 eV. The Brillouin zone (BZ) integrations within the self-consistency cycles were performed via a tetrahedron method [65], using 18 k points in the irreducible wedge of the Brillouin zone (4 x 4 x 6 mash). The atomic positions were relaxed according to Hellmann – Feynman forces calculated at the end of each self-consistent cycle, with the force minimization criterion 5 mRy / a.u.. In our calculations the self-consistency was achieved by demanding the convergence of the integrated charge difference between last two iterations to be smaller than 10^{-5} electron.

The optimized lattice constants are a = 4.635 Ǻ and c = 2.978 Ǻ for pure TiO_2 rutile, in good agreement with the previously calculated using the same exchange-correlation potential [6, 7]. There is no large difference between the calculated and experimental values (a = 4.594 Ǻ and c =

2.959 Ǻ) [66], especially having in mind the fact that the calculated values correspond to T = 0K, whereas the measurements have been performed at room temperature. The structure parameter of rutile, which determines the position of O atom in the unit cell is u = 0.305.

3. Results and discussion

In the rutile structure each Ti atom is bonded to four nearest and two second nearest oxygen neighbours. The calculated Ti-O bond lengths with the nearest and second nearest oxygen atoms are 1.962 Ǻ and 1.999 Ǻ. Replacing one O atom with N and one Ti atom with M (M = Pt, V, Sb) in the 48-atoms supercell results in local structural changes. For example compared to the Ti-O bond in pure rutile, shortening and degeneration of Ti-O bonds in the doped supercell is observed (the smallest bond lengths are 1.919, 1.922 and 1.931 Ǻ in Pt, Sb and V doped systems, respectively). The shortest bonds between the dopant metals and oxigen vary in the interval from 1.89 Ǻ for V-O to 1.96 Ǻ for Sb-O. We used bond valence method to estimate the oxidation states of constituent atoms in the investigated systems. The bond valence has the property that its sum around each atom in a compound is equal to the oxidation state of that atom. Bond valence sums (BVS) for Pt, Sb and V are 4.92, 6.79 and 4.71, respectively. The last value compares well with the experimental findings [67], that in the (N, V) codoped TiO_2, apart from the V^{4+} ions, V^{5+} ions are also present. The nearest neighbour O atoms have BVS that are very close to a formal 2- state in a ionic picture.

To investigate the origin of the band structure modifications in the codoped rutile TiO_2 the total and case sensitive bandstructures for all the investigated cases were calculated along the high-symmetry paths in the BZ. The calculated band structure of pure rutile TiO_2 (figure 2) is consistent with previous studies showing a direct energy gap at the Γ point. As can be seen the valence band (VB) is mostly composed of O 2p states while in the conduction band (CB) Ti 3d states dominate. The band gap of pure rutile, calculated at the Γ point using GGA approximation is 1.74 eV, which is consistent with the earlier reported results using the same method [6, 7]. The band gap underestimation of the experimental value (3.0 eV [68]) is due to the well-known shortcoming in DFT; however, comparing the GGA band-gaps is useful given that they provide good trend in general [62].

In the case of (N, Pt) codoped TiO_2 (figure 3) some N p and Pt d states overlap within the band gap, around 0.7 eV above the valence band maximum. The presence of such mid-gap bands divides the gap of the host phase into sub-gaps and intermediate bands can act as stepping stones to relay the valence electrons into the conduction band under the illumination of low energy photons. However it should be mentioned that mid-gap states can also act as recombination centers and the probability for either excitation or recombination is dependent on the corresponding energy gap. Namely if the gap is divided into two sub-gaps, it is preferred to have a lower gap narrower than the upper one. This way, the probability for pumping a valence electron up to the intermediate bands would be larger than the probability for an electron in the conduction band to combine with a hole in the intermediate bands. If that is the case, the intermediate bands can act as an effective stepping stone to assist pumping valence electrons into the conduction band.

In contrast to (N, Pt), (N, V) codoped TiO_2 does not exhibit band-gap states (figure 4), but has a significant band gap narrowing, due to the formation of impurity energy states near both the band edges (V d states at the bottom of the conduction band and N p states at the top of valence band). As spin up and down band structures are evidently different only in the case of (N, Pt), in this figure we present only the spin up cases. Our results are quite similar to those reported by Patel et.al. [67] for V-N-codoped TiO_2 anatase structure. The resulting band gap is about 0.6 eV smaller as compared to the pure TiO_2 rutile, which is a reduction of about 30%. The energy bands around the valence band maximum exhibit significant curvatures, which suggests great hole mobility [69]. The situation is similar for the case of (Sb, N) codoping (figure 4) , but here the band gap narrowing of 0.5 eV mainly originates from the N p states at the edge of the valence band and Sb s states at the bottom of the conduction band.

In order to obtain more accurate results for energy gap and at the same time more realistic picture of electronic structure of the investigated materials, we also did calculations with onsite-exact-exchange, where GGA exchange-correlation was replaced by exact exchange. In this way we obtained the energy gap value of 3.18 eV for pure rutile (figure 5), which differs from the experimental value (3eV [68]) by only 6%.

The total and site-projected densities of states (DOS) obtained in this way are presented in figures 5 and 6. Again, from figure 5 we can observe that the up and down DOS is evidently different only in the case of (N, Pt) codoped TiO_2, meaning that in the other two investigated cases the spin polarization doesn’t play an important role. This observation is also confirmed by the calculated total spin magnetic moment in unit cell, which is significant (1 μ_B), only for the system codoped with Pt, while for the other two systems is almost zero (0.00007μ_B and -0.00088μ_B for V and Sb codoped samples, respectively). Interestingly, the Pt d-states within the gap are present only in one of the spin channels, which was also notable in our GGA calculations (figure 3). This observation illustrates the need of conducting spin-polarized calculations when introducing metal dopants, even though the TiO_2 itself is non-magnetic.

Most important aspect of all the investigated codoped TiO_2 systems is the formation of isolated broad intermediate states (IS) in the band gap region. Hybrid calculations, however, indicate that instead of narrowing, codoping leads to a little broadening of the band gap, similar to the case of N doped rutile TiO_2 [8, 25, 70]. For (N, Pt) codoped rutile, the N 2p states are mostly located about 0.7eV above the valence band maximum in the band gap, again similar to the case of N doped rutile TiO_2. The isolated Pt d states are about 0.5 eV below the conduction band minimum and are now separated from the N p states.

In the case of (N, V) codoped rutile TiO_2 the valence band is similar to the previous case, with N p states in the gap above the valence band maximum. However, unlike Pt d states, the V d states are not in the gap, but at the bottom of the conduction band, causing a large downward shift of the conduction band compared to the pure TiO_2 rutile. The overall energy gap is increased by 0.08 eV compared to the pure TiO_2 rutile, again similar to the N doped rutile TiO_2 [8, 70]. The presence of the intermediate N p states separates the energy gap into a narrower lower part (0.3 eV) and a significantly wider upper part (2.58 eV), which contributes to visible light absorption through a two step transition. The latter value is in excellent agreement with the measured band gap of 2.52 eV for the N-V-codoped TiO_2 sample with the predominant fraction of the rutile phase [67], indicating that the excitations from these (occuppied) N p states to the conduction band occur. Bearing in mind the previously mentioned criterion, it seems that the N p states in this case are ideally positioned to support easier transition from VB to CB. In addition, these states are quite broad (≈ 0.3 eV) with respect to the highly localized levels created by monodoping, which is important because the charge carriers have higher mobility in the broader IS, so the recombination problem is reduced.

The situation is similar for (N, Sb) codoped rutile, but here there is no major variation in the position of the CBM of TiO_2, as only a small portion of Sb s states is present at the CBM. The overall gap is little lower (3.21 eV) and the distance from the isolated N p states within the gap to the conduction band is also lower (2.45 eV). The formation of IS, while leaving the conduction band almost unchanged, qualify this system to be an efficient material for the photocatalytic water splitting, similar as in the case of (Cu, N) codoped TiO_2, for which the photocatalytic efficiency was experimentaly verified [45]. Nevertheless, experimental evidence is necessary to prove the ability of this system to be used as efficient photocatalyst.

In order to investigate the optical properties, we address the absorption spectra for all studied systems. On the basis of the computed band structure, we calculated the imaginary part of the dielectric tensor $\varepsilon_i(\omega)$ for all the investigated cases and then, using the Kramers-Kroning relation, [71] the real parts of the dielectric tensor $\varepsilon_r(\omega)$ were evaluated. The absorption spectra were calculated from the relation

$$\alpha(\omega) = \sqrt{2\left[\sqrt{\varepsilon_1{}^2(\omega) + \varepsilon_2{}^2(\omega)} - \varepsilon_1(\omega)\right]}$$

where $\alpha(\omega)$ is the absorption coefficient. As the calculated optical spectra depend strongly on the Brillouin zone sampling, we used a sufficiently dense k-mesh of 90 k points in the ireducible BZ.

The calculated absorption spectra as a function of the photon wavelength for pure rutile TiO_2 and codoped TiO_2 systems are presented in figure 7. It can be seen that the codoped systems have better visible light absorption, as compared to the pure TiO_2 rutile. Although the tails of the absorption edges of (M, N) codoped systems slightly extend up to the visible light region, the main absorption peaks, which originate mainly from the direct transition between O 2p and Ti 3d states, still occur in the the UV range. The red-shift in absorption edge is only found for (N, V) codoped system, while for the other two investigated systems minor variations are observed. The absorption tail for the (N, V) case extends up to around 470 nm (≈ 2.6 eV), due to the two-step optical transition between VB and CB through the intermediate Np states. This result is consistent with the experimentally obtained absorbance for the N-V-codoped TiO_2 sample with the predominant fraction of the rutile phase [67]. Among the investigated systems, (N,Pt) gives the best visible light absorption and the longest extension of the absorption tail into the visible light region, probably due to the existence of the additional intraband transition between the Pt d states in the gap and the Ti d states in the conduction band.

4. Conclusion

We have performed electronic structure calculations for TiO_2 rutile codoped with N and various metal dopants. We have addressed the properties of interest for the photocatalytical application of rutile TiO2, namely the band gap and absorption coefficients. We observe significant changes of the band gap in all studied cases. Our results support the assumption that the improved visible light photcatalytic activity can be caused by the presence of isolated band gap states which reduce the transition energy of the photon, rather than a band gap narrowing. We have outlined the need for conducting the spin-polarized calculations when introducing metal dopants, even though the TiO_2 itself is non-magnetic, as the pronounced spin polarization has been observed for the (N, Pt) codoped TiO_2. The calculated absorption spectra indicate that the codoping with N and one of the metals (Pt, V, Sb) should be effective for enhancing the absorption in the visible light region, but further modifications are needed in order to achieve a significant use of solar irradiation in this region. The results of this DFT research prove that codoping might be a good starting point for the tuning properties of semiconductor materials in such a way as to provide a suitable path from widely used and economical materials, such as rutile TiO_2, to efficient semiconductors for photocatalytical water splitting.

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References

[1] Rufino Manuel Navarro Yerga, María Consuelo Alvarez-Galván, Fernando Vaquero, Javier Arenales, José Luis García Fierro, Hydrogen Production from Water Splitting Using Photo-Semiconductor Catalysts, in: Luis M. Gandia, Gurutze Arzamendi and Pedro M. Dieguez (Eds.),Renewable Hydrogen Technologies, *Elsevier B.V. 2013, pp. 43-61.*

[2] M. Carmo, D. L. Fritz, J. Mergel, D. Stolten, A comprehensive review on PEM water electrolysis, International Journal of Hydrogen Energy 38 (2013) 4901-4934.

[3] H. Luo, T. Takata, Y. Lee, J. Zhao, K. Domen, Y. Yan, Photocatalytic Activity Enhancing for Titanium Dioxide by Co-doping with Bromine and Chlorine, Chem. Mater. 16 (2004) 846-849.

[4] J. Navas, A. Sanchez-Coronilla, T. Aguilar, N. C. Hernandez, D. M. de los Santos, J. Sanchez-Marquez, D. Zorrilla, C. Fernandez-Lorenzo, R. Alcantara, J. Martin-Calleja, Experimental and theoretical study of the electronic properties of Cu-doped anatase TiO_2, Physical Chemistry Chemical Physics 16 (2014) 3835-3845.

[5] J. He, Q. Liu, Z. Sun, W. Yan, G. Zhang, Z. Qi, P. Xu, Z. Wu, S. Wei, High Photocatalytic Activity of Rutile TiO_2 Induced by Iodine Doping, J. Phys. Chem. C 114 (2010) 6035-6038.

[6] R. Shirley, M. Kraft, O. R. Inderwildi, Electronic and optical properties of aluminium-doped anatase and rutile TiO_2 from *ab initio* calculations, Physical Review B 81 (2010) 075111

[7] R. Long, Y. Dai, B. Huang, Structural and electronic properties of iodine-doped anatase and rutile TiO_2, Computational Materials Science 45 (2009) 223-228.

[8] C. Di Valentin, G. Pacchioni, A. Selloni, Origin of the different photoactivity of N-doped anatase and rutile TiO_2, Physical Review B 70 (2004) 085116

[9] A. Shin Hwa Lee, K. Li, Y. W. Zhang, Z. D. Sha, H. Pan, *Ab initio* study on the effects of dopant-defect cluster on the electronic properties of TiO_2-based photocatalysts, International Journal of Hydrogen Energy 39 (2014) 2049-2055.

[10] R. Long, Y. Dai, G. Meng, B. Huang, Energetic and electronic properties of X- (Si, Ge, Sn, Pb) doped TiO_2 from first-principles, Physical Chemistry Chemical Physics 11 (2009) 8165-8172.

[11] X. Yu, C. Li, H. Tang, Y. Ling, T. A. Tang, Q. Wu, J. Kong, First principles study on electronic structures and properties of Sn-doped rutile TiO_2, Computational Materials Science 49 (2010) 430-434.

[12] C. Fu, T. Li, J. Qi, J. Pan, S. Chen, C. Cheng, Theoretical study on the electronic and optical properties of Ce^{3+} -doped TiO_2, Chemical Physics Letters 494 (2010) 117-122.

[13] K. Yang, Y. Dai, B. Huang, M. H. Whangbo, Density Functional Characterization of the Band Edges , the Band Gap States, and the Preferred Doping Sites of Halogen-Doped TiO_2, Chem. Mater. 20 (2008) 6528-6534.

[14] S. K. Zheng, G. Wu, L. Liu, First-principles calculations on Hg-doped anatase TiO_2 with and without O vacancy, Solid State Communications 165 (2013) 15-18.

[15] K. Song, X. Han, G. Shao, Electronic properties of rutile TiO_2 doped with 4d transition metals: First-principles study, Journal of Alloys and Compounds 551 (2013) 118-124.

[16] G. Shao, Electronic Structures of Manganese-Doped Rutile TiO_2 from First Principles, J. Phys. Chem. C 112 (2008) 18677-18685.

[17] G. Y. Gao, K. L. Yao, Z. L. Liu, J. Zhang, X. L. Li, J. Q. Zhang, N. Liu, Magnetism and electronic structure of Cr-doped rutile TiO_2 from first-principles calculations, Journal of Magnetism and Magnetic Materials 313 (2007) 210-213.

[18] X. Yu, C. Li, Y. Ling, T. A. Tang, Q. Wu, J. Kong, First principles calculations of electronic and optical properties of Mo-doped rutile TiO_2, Journal of Alloys and Compounds 507 (2010) 33-37.

[19] B. D. Mukri, U. V. Waghmare, M. S. Hedge, Platinum Ion-Doped TiO_2: High Catalytic Acytivity of Pt^{2+} with Oxide Ion Vacancy in $Ti^{4+}{}_{1-x}Pt^{2+}{}_{x}O_{2-x}$ Compared to Pt^{4+} WITHOUT Oxide Ion Vacancy in $Ti^{4+}{}_{1-x}Pt^{4+}{}_{x}O_2$, Chemistry of Materials 25 (2013) 3822-3833.

[20] M. Khan, W. Cao, N. Chen, Z. Usman, D. F. Khan, A. M. Toufiq, M. A. Khaskheli, Influence of tungsten doping concentration on the electronic and optical properties of anatase TiO_2, Current Applied Physics 13 (2013) 1376-1382.

[21] Y. Wang, D. J. Loren, Electronic structures of V-doped anatase TiO_2, Solid State Communications 136 (2005) 142-146.

[22] R. Long, N. J. English, First-principles calculation of electronic structure of V-doped anatase TiO_2, ChemPhysChem 11 (2010) 2606-2611.

[23] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Visible-light photocatalysis in nitrogen-doped titanium oxides, Science 293 (2001) 269-271.

[24] K. Yang, Y. Dai, B. Huang, Understanding Photocatalytic Activity of S- and P-Doped TiO_2 under Visible Light from First-Principles, J. Phys. Chem. C 111 (2007) 18985-18994.

[25] K. Yang, Y. Dai, B. Huang, S. Han, Theoretical Study of N-Doped TiO_2 Rutile Crystals, J. Phys. Chem. B 110 (2006) 24011-24014.

[26] T. Yamamoto, F. Yamashita, I. Tanaka, E. Matsubara, A. Muramatsu, Electronic States of Sulfur Doped TiO_2 by First Principles Calculations, Materials Transactions 45 (2004) 1987-1990.

[27] C. Sun, D. J. Searles, Origin of the Visible Light Absorption of Boron/Nitrogen Co-doped Anatase TiO_2, J. Phys. Chem. C 117 (2013) 26454-26459.

[28] Y. Lin, S. Zhu, Z. Jiang, X. Hu, X. Zhang, H. Zhu, J. Fan, T. Mei, G. Zhang, Electronic and optical properties of S/I-codoped anatase TiO_2, Solid State Communications 171 (2013) 17-21.

[29] J. Yu, P. Zhou, Q. Li, New insight into the enhanced visible-light photocatalytic activities of B-, C- and B/C-doped anatase TiO_2 by first-principles, Physical Chemistry Chemical Physics 15 (2013) 12040-12047.

[30] M. Harb, P. Sautet, P. Raybaud, Anionic or Cationic S-Doping in Bulk Anatase TiO_2: Insights on Optical Absorption from First Principles Calculations, J. Phys. Chem. C 117 (2013) 8892-8902.

[31] M. L. Guo, X. D. Zhang, C. T. Liang, Concentration-dependent electronic structure and optical absorption properties of B-doped anatase TiO_2, Physica B 406 (2011) 3354-3358.

[32] K. Yang, Y. Dai, B. Huang, Density Functional Study of Boron-Doped Anatase TiO_2, J. Phys. Chem. C 114 (2010) 19830-19834.

[33] H. Gao, C. Ding, D. Dai, Density functional characterization of C-doped anatase TiO_2 with different oxidation state, Journal of Molecular Structure: THEOCHEM 944 (2010) 156-162.

[34] E. Finazzi, C. Di Valentin, G. Pacchioni, Boron-Doped Anatase TiO_2: Pure and Hybrid DFT Calculations, J. Phys. Chem. C 113 (2009) 220-228.

[35] K. Yang, Y. Dai, B. Huang, Study of the Nitrogen Concentration Influence on N-Doped TiO_2 Anatase from First-Principles Calculations, J. Phys. Chem. C 111 (2007) 12086-12090.

[36] S. Matsushima, K. Takehara, H. Yamane, K. Yamada, H. Nakamura, M. Arai, K. Kobayashi, First-principles energy band calculation for undoped and S-doped TiO_2 with anatase structure, Journal of Physics and Chemistry of Solids 68 (2007) 206-210.

[37] F. H. Tian, C. B. Liu, DFT Description on Electronic Structure and Optical Absorption Properties of Anionic S-Doped Anatase TiO_2, J. Phys. Chem. B 110 (2006) 17866-17871.

[38] H. Geng, S. Yin, X. Yang, Z. Shuai, B. Liu, Geometric and electronic structures of the boron-doped photocatalyst TiO_2, J. Phys. Condens. Matter 18 (2006) 87-96.

[39] Y. Fang, D. Cheng, M. Niu, Y. Yi, W. Wu, Tailoring the electronic and optical properties of rutile TiO_2 by (Nb + Sb, C) codoping from DFT + U calculations, Chemical Physics Letters 567 (2013) 34-38.

[40] J. Atanelov, C. Gruber, P. Mohn, The electronic and magnetic structure of p-element (C, N) doped rutile-TiO_2; a hybrid DFT study, Computational Materials Science 98 (2015) 42-50.

[41] M. Niu, W. Xu, X. Shao, D. Cheng, Enhanced photoelectrochemical performance of rutile TiO_2 by Sb-N donor-acceptor coincorporation from first principles calculations, Applied Physics Letters 99 (2011) 203111.

[42] Y. Lin, Z. Jiang, R. Zhang, C. Zhu, X. Hu, X. Zhang, H. Zhu, The structure, electronic, and optical properties of (Sm, N)-codoped anatase TiO_2 photocatalyst: A density functional study, Journal of Catalysis 309 (2014) 115-120.

[43] V. Celik, E. Mete, Electronic and optical properties of Cr and Cr-N doped anatase TiO_2 from screened Coulomb hybrid calculations, J. Phys. Condens. Matter 25 (2013) 365502

[44] Q. Meng, T. Wang, E. Liu, X. Ma, Q. Ge, J. Gong,Understanding electronic and optical properties of anatase TiO_2 photocatalysts co-doped with nitrogen and transition metals, Physical Chemistry Chemical Physics 15 (2013) 9549-9561.

[45] R. Jaiswal, J. Bharambe, N. Patel, A. Dashora, D.C. Kothari, A. Miotello, Copper and Nitrogen co-doped TiO_2 photocatalyst with enhanced optical absorption and catalytic activity, Applied Catalysis B: Environmental 168-169 (2015) 333-341.

[46] J. Gong, C. Yang, J. Zhang, W. Pu, Origin of photocatalytic activity of W/N-codoped TiO_2: H_2 production and DFT calculation with GGA+U, Applied Catalysis B: Environmental 152-153 (2014) 73-81.

[47] R. Long, N. J. English, Band gap engineering of (N, Ta)-codoped TiO_2: A first-principles calculation, Chemical Physics Letters 478 (2009) 175-179.

[48] R. Long, N. J. English, Synergistic Effects of Bi/S Codoping on Visible Light-Activated Anatase TiO_2 Photocatalysts from First Principles, J. Phys. Chem. C 113 (2009) 8373-8377.

[49] D. E. Gu, B. C. Yang, Y. D. Hu, V and N co-doped nanocrystal anatase TiO_2 photocatalysts with enhanced photocatalytic activity under visible light irradiation, Catalysis Communications 9 (2008) 1472-1476.

[50] X. Yao, X. Wang, L. Su, H. Yan, M. Yao, Band structure and photocatalytic properties of N/Zr co-doped anatase TiO_2 from first-principles study, Journal of Molecular Catalysis A: Chemical 351 (2011) 11-16.

[51] K. Zakrzewska, K. Kollbek, M. Sikora, Cz. Kapusta, J. Szlachetko, M. Sitarz, M. Ziabka, M. Radecka, Importance of the electronic structure of modified TiO_2 in the photoelectrochemical processes of hydrogen generation, International Journal of Hydrogen Energy 40 (2015) 815-824.

[52] L. Ping Peng, L. Xu, Z. Cai Xia, Study the high photocatalytic activity of vanadium and phosphorus co-doped TiO_2 from experiment and DFT calculations, Computational Materials Science 83 (2014) 309-317.

[53] R. Long, N. J. English, Band gap engineering of double-cation-impurity-doped anatase-titania for visible-light photocatalysts: a hybrid density functional theory approach, Physical Chemistry Chemical Physics 13 (2011) 13698-13703.

[54] R. Long, N. J. English, Band gap engineering of (N, Si)-codoped TiO_2 from hybrid density functional theory calculations, New Journal of Physics 14 (2012) 053007.

[55] R. Long, N. J. English, New insights into the band-gap narrowing of (N, P) codoped TiO_2 from hybrid density functional theory calculations, ChemPhysChem 12 (2011) 2604-2608.

[56] Y. Gai, J. Li, S. S. Li, J. B. Xia, S. H. Wei, Design of Narrow-Gap TiO_2: A Passivated Codoping Approach for Enhanced Photoelectrochemical Activity, Physical Review Letters 102 (2009) 036402.

[57] .W. J. Yin, H. W. Tang, S. H. Wei, M. M. Al-Jassim, J. Turner, Y. Yan, Band structure engineering of semiconductors for enhanced photoelectrochemical water splitting: The case of TiO_2, Physical Review B 82 (2010) 045106.

[58] A. Dashora, N. Patel, D.C. Kothari, B. L. Ahuja, A. Miotello, Formation of an intermediate band in the energy gap of TiO_2 by Cu-N-codoping: First principles study and experimental evidence, Solar Energy Materials & Solar Cells 125 (2014) 120-126.

[59] K. Maeda, K. Domen, New Non-Oxide Photocatalysts Designed for Overall Water Splitting under Visible Light, J. Phys. Chem. C 111 (2007) 7851-7861.

[60] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, J. Luitz, WIEN 2k an Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties, Vienna University of Technology, Vienna, Austria, 2001.

[61] J. P. Perdew, K. Burke, M. Ernzerhof, Generalized Gradient Approximation Made Simple, Physical Review Letters 77 (1996) 3865-3868.

[62] W. Li, C. F. J. Walther, A. Kuc, T. Heine, Density Functional Theory and Beyond for Band-Gap Screening: Performance for Transition-Metal Oxides and Dichalcogenides, Journal of Chemical Theory and Computation 9 (2013) 2950-2958.

[63] F. Birch, The effect of pressure upon the elastic parameters of isotropic solids, according to Murnaghan's theory of finite strain, Journal of Applied Physics 9 (1938) 279-288.

[64] A. Kokalj, J. Mol. Graphics Modelling 17 (1999) 176-179.

[65] P. E. Blochl, O. Jepsen, O. K. Andersen, Improved tetrahedron method for Brillouin-zone integrations, Physical Review B 49 (1994) 16223-16233.

[66] C. J. Howard, T. M. Sabine, F. Dickson, Structural and thermal parameters for rutile and anatase, Acta Crystallogr. B: Struct. Sci. 47 (1991) 462-468.

[67] N. Patel, R. Jaiswal, T. Warang, G. Scarduelli, A. Dashora, B. L. Ahuja, D.C. Kothari, A. Miotello, Efficient photocatalytic degradation of organic water pollutants using V-N-codoped TiO_2 thin films, Applied Catalysis B: Environmental 150-151 (2014) 74-81.

[68] A. Amtout, R. Leonelli, Optical properties of rutile near its fundamental band gap, Physical Review B 51 (1995) 6842-6851.

[69] M. Long, L. Tang, D. Wang, Y. Li, Z. Shuai, Electronic Structure and Carrier Mobility in Graphdiyne Sheet and Nanoribbons: Theoretical Predictions, ACS Nano 5 (2011) 2593-2600.

[70] M. Batzill, E. H. Morales, U. Diebold, Influence of Nitrogen Doping on the Defect Formation and Surface Properties of TiO_2 Rutile and Anatase, Physical Review Letters 96 (2006) 026103-1 – 026103-4.

[71] D. B. Melrose, R. J. Stoneham, Generalised Kramers-Kronig formula for spatially dispersive media, J. Phys. A: Math. Gen. 10 (1977) L17

Table 1: Comparison between tha calculated and measured structural data for TiO_2 rutile. The distances are in Å.

	Experimental results [66, 68]	WIEN 2k
A	4.594	4.635
c	2.959	2.978
u	0.30478	0.305
Ti – O (1)	1.949	1.962
Ti – O (1)	1.980	1.999
E_g (eV)	3.0	3.18

Figure captions:

Figure 1: Model of supercell used in this study

Figure 2: Calculated band structure for pure rutile TiO_2

Figure 3: Calculated band structure for (N, Pt) codoped rutile TiO_2

Figure 4: Calculated band structure for (N, V) and (N, Sb) codoped rutile TiO_2. For the sake of clarity only the band structures for spin up cases are shown.

Figure 5: Total densities of states for pure and codoped rutile TiO_2

Figure 6: Partial densities of states for codoped rutile TiO_2

Figure 7: Optical absorption spectra of pure and codoped TiO_2. The enlarged segment represents the visible range.