

# Synergistic Effects on Band Gap-Narrowing in Titania by Codoping from First-Principles Calculations

Run Long and Niall J. English\*

*The SEC Strategic Research Cluster and the Centre for Synthesis and Chemical Biology, Conway Institute of Biomolecular and Biomedical Research, School of Chemical and Bioprocess Engineering, University College Dublin, Belfield, Dublin 4, Ireland*

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The large intrinsic band gap in TiO<sub>2</sub> has hindered severely its potential application for visible-light irradiation. In this study, we have used a passivated approach to modify the band edges of anatase–TiO<sub>2</sub> by codoping of X (N, C) with transition metals (TM = W, Re, Os) to extend the absorption edge to longer visible-light wavelengths. It was found that all the codoped systems can narrow the band gap significantly; in particular, (N+W)-codoped systems could serve as remarkably better photocatalysts with both narrowing of the band gap and relatively smaller formation energies and larger binding energies than those of (C+TM) and (N+TM)-codoped systems. Our theoretical calculations provide meaningful guides for experiments to develop more powerful visible-light photocatalysts.

## 1. Introduction

Titania (TiO<sub>2</sub>)-based photocatalysts have received intense attention as promising photocatalytic materials for the decomposition of organic pollutants present in water or air.<sup>1</sup> However, their universal use is restricted to ultraviolet light ( $\lambda < 385$  nm) due to the wide band gap of titania ( $\sim 3.2$  eV for anatase). Further, photoexcited electron–hole pairs tend to recombine relatively easily in TiO<sub>2</sub>. Both of these factors limit possible applications in photocatalytic materials design. Therefore, it is highly desirable to extend the optical absorption of TiO<sub>2</sub>-based materials to the visible-light region with a low photogenerated electron–hole recombination rate.

In general, doping is one of the most effective approaches to extend the absorption edge to the visible-light range. For example, N-doped TiO<sub>2</sub> is considered to be a promising photocatalyst, and it has been investigated widely, both by experimental and by theoretical methods.<sup>2</sup> However, as a result of strongly localized N 2p states at the top of valence band,<sup>3</sup> the photocatalytic efficiency of N-doped TiO<sub>2</sub> decreases because isolated empty states trap an appreciable proportion of photoexcited electrons and reduce photogenerated current.<sup>4</sup> Besides N-doped TiO<sub>2</sub>, C-doped TiO<sub>2</sub> also shows photocatalytic activity under visible light.<sup>5</sup> On the other hand, transition metal

doping can also promote photocatalytic efficiency, but this is hindered also by the presence of carrier recombination centers and the formation of strongly localized d states in the band gap, which serve to reduce carrier mobility substantially.<sup>6</sup> Recently, Gai et al.<sup>7</sup> proposed using a passivated codoping approach, consisting of nonmetal and metal elements, to extend the TiO<sub>2</sub> absorption edge into the visible light range. Because defect bands are passivated, it is highly likely that they will be less effective as carrier recombination centers.<sup>8</sup> Recent experiments have reported that the addition of W to N-doped TiO<sub>2</sub> can increase photocatalytic activity under visible-light irradiation significantly.<sup>9,10</sup> Our theoretical calculations on (N+W)-codoped anatase suggest that a continuum band is formed at the top of the valence band, and that W 5d orbitals locate below Ti 3d states at the bottom of conduction band, which narrows significantly the band gap and enhances visible light absorption.<sup>11</sup> To the best of our knowledge, this study<sup>11</sup> was the first theoretical explanation of how (N+W)-codoped anatase possesses such high photocatalytic activity. To find even more effective photocatalyst materials, one may perform further theoretical calculations of codoping with nonmetal and metal elements to guide future experimental work in solar energy materials design.

\*Corresponding author. E-mail: niall.english@ucd.ie.

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In this study, we have used a passivated codoping approach to search for appropriate dopants which do not induce gap states to narrow the band gap of anatase, based on first-principles calculations. This aim is to avoid defect states which act as effective carrier recombination centers. In the analysis of the band structures of codoped anatase, it was found that although (C+TM) (TM = W, Re, Os)-codoped systems narrow the band gap slightly larger than (N+TM)-codoping cases, (N+W)-codoped TiO<sub>2</sub> is the more promising photocatalyst because of the narrowing of its band gap and the relatively small formation energies and large binding energies.

## 2. Methodology

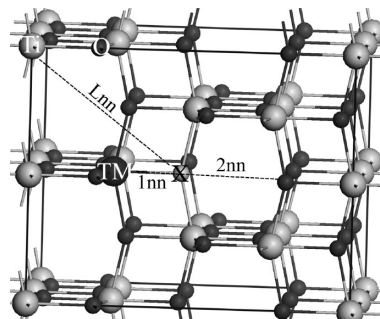
All of the spin-polarized DFT calculations were performed using the projector augmented wave (PAW) pseudopotentials as implemented in the Vienna ab initio Simulation Package (VASP) code.<sup>12,13</sup> The Perdew and Wang parametrization<sup>14</sup> of the generalized gradient approximation (GGA)<sup>15</sup> was adopted for the exchange-correlation potential. The electron wave function was expanded in plane waves up to a cutoff energy of 400 eV and a Monkhorst–Pack  $k$ -point mesh<sup>16</sup> of  $4 \times 4 \times 4$  was used for geometry optimization<sup>17,18</sup> and electronic property calculations. Both the atomic positions and cell parameters were optimized until residual forces were below 0.01 eV/Å. It is well-known that GGA underestimates the band gap of TiO<sub>2</sub> significantly (2.0 eV vs anatase 3.2 eV experimental value). Here, we include the on-site Coulomb correction for the Ti 3d states, the so-called GGA +  $U$  method,<sup>19</sup> which can partially improve the prediction of the band gap. Here,  $U = 5.3$  eV for Ti, which is in agreement with the optimal value ( $5.5 \pm 0.5$  eV);<sup>20,21</sup> using this, the calculated band gap of pure anatase was 3.11 eV, which agrees well with the experimental value of 3.20 eV. A variety of  $U$  values (1.0, 2.0, 3.0, and 4.0 eV) were applied to the dopants. The calculated results for  $U = 1.0$  and 2.0 eV were found to yield a qualitatively wrong metallic ground state as in the standard GGA calculations for W and Os, and the once the  $U$  value was increased to 3.0 eV, the behavior of W- and Os-doped TiO<sub>2</sub> exhibited appropriate semiconductor characteristics. For Re-doped TiO<sub>2</sub>, the band gap is not particularly dependent on the  $U$  value. Therefore, a moderate value of  $U = 3.0$  eV has been applied to TM 5d states, similar to V-doped TiO<sub>2</sub>.<sup>22</sup>

The relaxed ( $2 \times 2 \times 1$ ) 48-atom anatase supercell was used to construct doped systems. Single O and Ti atoms were replaced by single X (N, C) and TM (W, Re, Os) atoms, respectively. The codoped systems were created by simultaneous substitution of

**Table 1. Total Energy Difference of Different Doping Systems (in eV)<sup>a</sup>**

	N+W	N+Re	N+Os	C+W	N+Re	C+Os
1nn	0	0	0	0	0	0
2nn	0.48	0.95	1.0	1.1	0.35	3.1
Lnn	0.57	1.1	1.1	1.3	0.56	3.3

<sup>a</sup> The total energy of nearest-neighbor configuration (1nn) has been set as zero.



**Figure 1.** Supercell model for defective anatase showing the location of the dopants. The ion doping sites are marked with X (C, N) and TM (W, Re, Os). The 1nn, 2nn, and Lnn configurations correspond to the nearest-neighbor, the second nearest-neighbor, and the largest distance between X and TM atoms. The large light spheres and the small dark spheres represent the Ti and O atoms, respectively.

an O atom by an X (N, C) atom and a Ti atom by a TM (W, Re, Os) atom. In principle, the three 5d transition metal elements W, Re, and Os served as n-type dopants and nonmetal elements N and C as p-type dopants. It was found that formation of adjacent metal–nonmetal element pairs is more energetically favorable with respect to other configurations. For clarity, we have listed the total energy differences between X–TM nearest-neighbor (1nn), the second nearest-neighbor (2nn), and the largest distance (Lnn, one dopant in the center of the supercell with the other in a corner) doped systems in Table 1. Here we set the 1nn total energies as 0 eV. It shows that almost all of the energy differences are over 0.5 eV for all systems. We also used a 108-atom supercell to test the energy differences of all the doped systems between 1nn and Lnn, and they confirmed the results from 48-atom calculations. Therefore, we will select the lowest-energy structures to examine their electronic properties. The supercell system and dopant sites are shown in Figure 1.

## 3. Results and Discussion

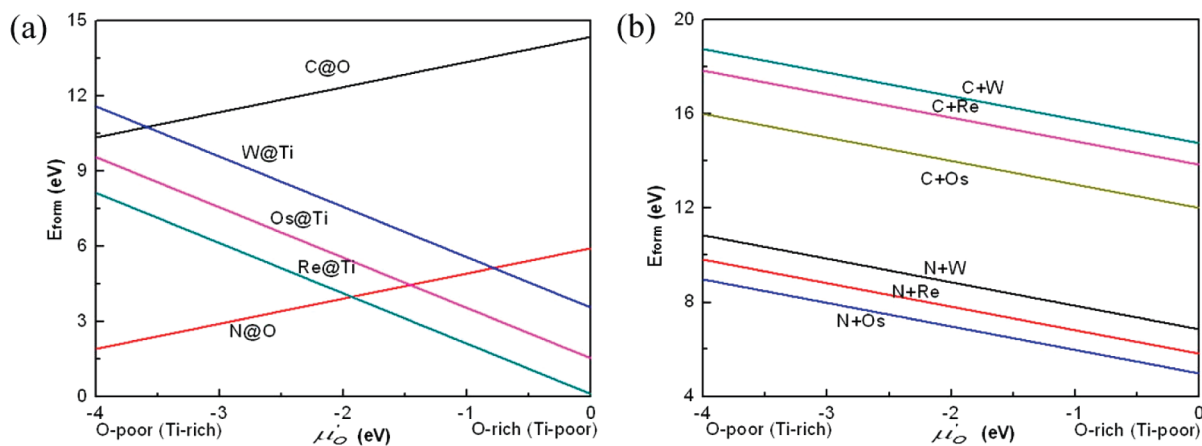
**3.1. Monodoping in Anatase.** In this section, our main concerns are to investigate the relative difficulty for single X (N, C) and TM (W, Re, Os) ions to incorporate into the lattice and how to engineer the band edges appropriately. Hence, we first calculated the dopant formation according to eqs 1 and 2 below:

$$E_{\text{form}} = E(\text{X@O}) - E(\text{TiO}_2) - \mu_{\text{X}} + \mu_{\text{O}} \quad (1)$$

$$E_{\text{form}} = E(\text{TM@Ti}) - E(\text{TiO}_2) - \mu_{\text{TM}} + \mu_{\text{Ti}} \quad (2)$$

where the  $E(\text{X@O})$  and  $E(\text{TM@Ti})$  are the total energies containing impurities ( $\text{X} = \text{N}, \text{C}$ ;  $\text{TM} = \text{W}, \text{Re}, \text{Os}$ ) and  $E(\text{TiO}_2)$  is the total energy of the pure supercell. The formation energies for the different doped systems are considered in this work as a function of the oxygen

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**Figure 2.** Formation energies (eV)  $E_{\text{form}}$  as a function of the oxygen chemical potential for (a) monodoped (C, N, W, Re, Os) and (b) codoped (N + W, N + Re, N + Os, C + W, C + Re, C + Os) anatase.

chemical potential ( $\mu_{\text{O}}$ ), which is a parameter that characterizes the oxygen environment during synthesis.<sup>23–25</sup> The environment acts as a reservoir, which can give or take any amount of oxygen without changing its temperature and pressure.<sup>26</sup> Low values of  $\mu_{\text{O}}$  correspond to O-poor conditions while high values of  $\mu_{\text{O}}$  correspond to O-rich conditions. By referencing  $\mu_{\text{O}}$  to the energy of an O atom in the  $\text{O}_2$  molecule ( $\mu_{\text{O}} = \frac{1}{2}\mu(\text{O}_2) + \mu'_{\text{O}}$ ), here we take  $-4 \text{ eV} \leq \mu'_{\text{O}} \leq 0 \text{ eV}$ , where the value  $\mu'_{\text{O}} = 0$  corresponds to the O-rich limit whereas  $\mu'_{\text{O}} = -4 \text{ eV}$  is approximately half of the enthalpy of formation of anatase  $\text{TiO}_2$  (our calculated value is 9.98 eV in comparison to an experimental value of 9.8 eV).<sup>27</sup> The chemical potential of a Ti atom,  $\mu_{\text{Ti}}$ , is calculated from  $\mu_{\text{Ti}} = \mu(\text{TiO}_2) - 2\mu_{\text{O}}$ . For C and N, we used fixed values of the chemical potentials  $\mu_{\text{C}}$  and  $\mu_{\text{N}}$  and calculated these from the formulas  $\mu_{\text{C}} = \mu(\text{CO}_2) - \mu(\text{O}_2)$  and  $\mu_{\text{N}} = \frac{1}{2}\mu(\text{N}_2)$ . Here, the molecular species were contained in periodic cells large enough to avoid molecule–molecule interactions. Although a variety of N dopant sources have been used in different experiments, such as  $\text{NH}_4\text{Cl}$ ,<sup>28</sup>  $(\text{NH}_2)_2\text{CO}$ ,<sup>29</sup> and N ions,<sup>30</sup> it is commonly accepted practice in theoretical calculations to use the chemically stable configuration of  $\text{N}_2$  to calculate nitrogen's chemical potential by many authors.<sup>25,31</sup> Furthermore, this avoids the introduction of any other impurity atoms into the  $\text{TiO}_2$  lattice besides the dopant sources themselves. On the other hand,  $\text{CO}_2$  has usually been used to estimate carbon's chemical potential.<sup>24</sup> Similarly, the chemical potentials for W ( $\mu_{\text{W}}$ ), Re ( $\mu_{\text{Re}}$ ), and Os ( $\mu_{\text{Os}}$ ) were also fixed and

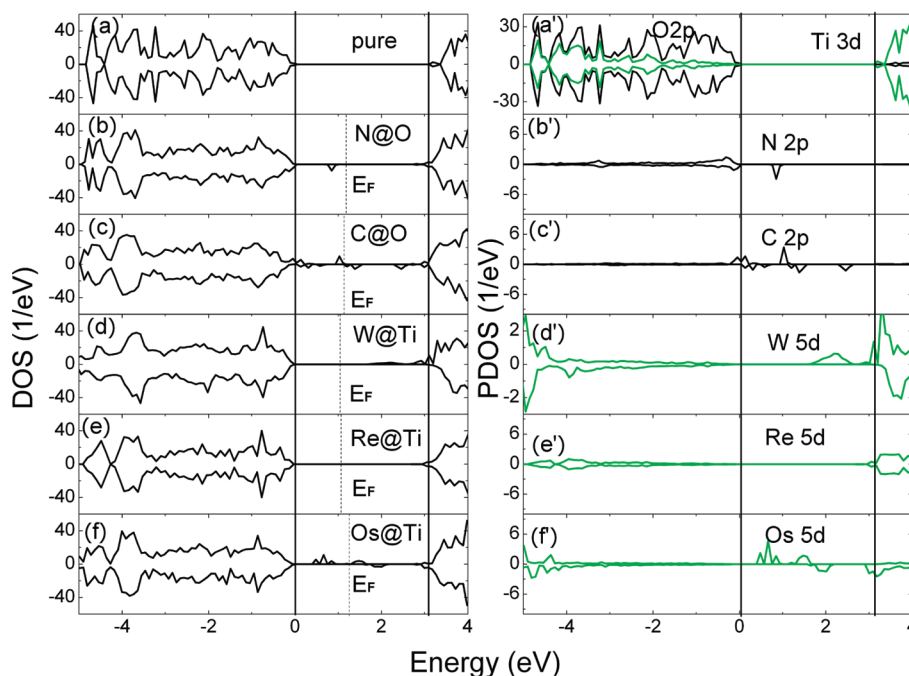
calculated from the formulas  $\mu_{\text{W}} = \mu(\text{WO}_3) - \frac{3}{2}\mu(\text{O}_2)$ ,  $\mu_{\text{Re}} = \mu(\text{ReO}_2) - \mu(\text{O}_2)$  and  $\mu_{\text{Os}} = \mu(\text{OsO}_2) - \mu(\text{O}_2)$ , respectively. The stability diagram for single N-, C-, and TM- (W, Re, Os) doped  $\text{TiO}_2$  is reported in Figure 2. For N- and C-doped  $\text{TiO}_2$ , the values of formation energies agree well with previous theoretical work,<sup>24,25</sup> indicating that our calculation method is reasonable. Figure 2a suggests that (1) X (N, C) occupies the O site preferentially under Ti-rich conditions while possessing a high formation energy under O-rich conditions and (2) TM (W, Re, Os) may be substituted relatively easily under O-rich conditions, but it is more difficult under Ti-rich conditions.

Second, we investigated how to modify the band gap of  $\text{TiO}_2$ . Therefore, a knowledge of the characteristics of band edges in pure  $\text{TiO}_2$  is needed. The density of states (DOS) and projected DOS (PDOS) of pure anatase are plotted in Figure 3a,a'. It shows that the top of the valence band is composed mainly of O 2p states and the bottom of the conduction band is dominated by Ti 3d states. Therefore, to modify the valence band edge (i.e., p-type doping), one should choose a different p orbital energy relative to the O atom, and to modify the conduction band edge (n-type doping), different d orbital energies relative to the Ti atom should be selected.

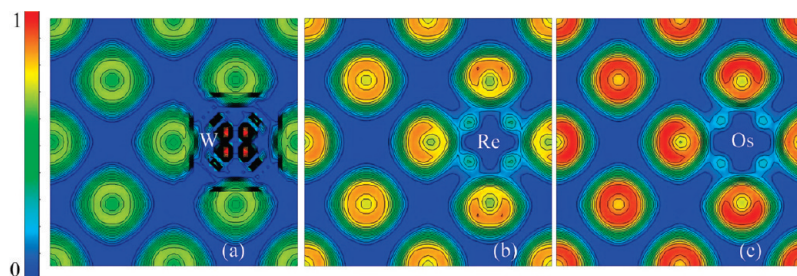
For N and C dopants, these introduce acceptor states above the VBM, as one might expect. Further, C 2p acceptor states [cf. Figure 3b,b'] lie deeper inside the gap than those of N 2p acceptor states [cf. Figure 3c,c'] because the C 2p orbital energy is higher than that of N 2p. Replacement of Ti atoms by transition metals, W, Re, and Os, results in the largest influence occurring at the conduction band edge and gap states, respectively. The position of the donor state near the CBM depends on the d orbital energy of the dopants. Our calculated results show that W@Ti and Re@Ti substitution creates shallow levels below the Ti 3d states while Os@Ti substitution induces deep levels in the gap. Certainly, when Ti is replaced by W and Re, the impurity levels resonate with the conduction band. However, these monodoped systems either create impurity states (for C and Os) which may act as recombination centers, thereby reduce photoefficiency, or narrow slightly the band gap of  $\text{TiO}_2$  (for W and Re),

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**Figure 3.** DOS for monodoped anatase compared with pure anatase and PDOS for impurity and host atoms (black for p orbital and green for d orbital). The top of the valence band for pure anatase is taken as the reference level. The dashed lines represent the Fermi level,  $E_F$ .



**Figure 4.** Electron localization function contour plots (ELF) on the (100) surface of bulk materials for (a) W-, (b) Re-, and (c) Os-doped anatase.

which extends the visible-light absorption edge marginally. To investigate if the differences in electronic properties between Re- and Os-doped  $\text{TiO}_2$  may be rationalized from the bond characteristics, we plotted the electron localization function (ELF) in Figure 4 at the (100) surface of bulk anatase for these three doped systems. The ELF is a scalar continuous function bounded between 0 and 1, and the value of 1 indicates that electrons are fully localized and 0 implies that electrons are fully delocalized or that there is no electron in that place. So a value between 0 and 1 indicates the probability of the formation of an electron-gas-like pair.<sup>32</sup> Figure 4 shows that the degree of electron localization is in the order  $W > \text{Re} > \text{Os}$ , which implies that Os–O covalent bonds [cf. Figure 4c] are stronger than W–O ionic bonds [cf. Figure 4a] and Re–O covalent bonds [cf. Figure 4b] so that the extent of hybridization is in the order  $\text{O} - \text{W} < \text{O} - \text{Re} < \text{O} - \text{Os}$ , which coincides with characteristics evident in the DOS.

**3.2. Synergistic Effects of Codoping in Anatase.** We propose to codope anatase with donor–acceptor pairs to reduce the formation energy and to narrow the band gap

further. Therefore, we calculated the formation energy for the (X+TM)-codoped system, that is, (N+W), (N+Re), (N+Os), (C+W), (C+Re), and (C+Os), according to eq 3:

$$E_{\text{form}} = E(\text{TM@Ti} + \text{X@O}) - E(\text{TiO}_2) - \mu_{\text{X}} - \mu_{\text{TM}} + \mu_{\text{O}} + \mu_{\text{Ti}} \quad (3)$$

where  $E(\text{TM@Ti} + \text{X@O})$  is the total energy of the codoped system. The formation energies are also plotted in Figure 2(b). The results show that codoping of X (N, C) with TM (W, Re, Os) reduces the formation energies significantly with respect to N and C monodoping under O-rich conditions, which corresponds to the usual growth conditions for synthesis samples in experiments. This indicates that codoping is beneficial for C or N introduction into the titania lattice. Hence, one could select W, Re, and Os to act as the codopants with N or C to favor the incorporation of N or C into the titania lattice in experiments. Furthermore, (N+TM)-codoped systems have lower formation energies than (C+TM)-doped  $\text{TiO}_2$ , which means that synthesis of the (N+TM) samples is relatively easier than the (C+TM) case.

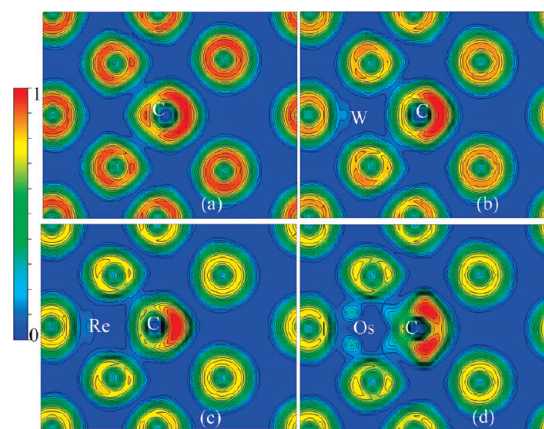
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Before we study the passivation effect on the band gap of  $\text{TiO}_2$  via X-TM codoping, one needs to consider the stability of defect pairs. Therefore, we calculated the defect pair binding energy<sup>33</sup> according to eqs 4 and 5:

$$E_b = E(\text{TM@Ti}) + E(\text{C@O}) - E(\text{TM@Ti} + \text{C@O}) - E(\text{TiO}_2) \quad (4)$$

$$E_b = E(\text{TM@Ti}) + E(\text{N@O}) - E(\text{TM@Ti} + \text{N@O}) - E(\text{TiO}_2) \quad (5)$$

Positive  $E_b$  values indicate that the defect pairs tend to bind to each other and are stable. The calculated binding energies for the (C+W), (C+Re), (C+Os), (N+W), (N+Re), and (N+Os) pairs are 3.15, 0.65, 3.94, 2.64, 0.23, and 2.54 eV, respectively, indicating that C-W, C-Os, N-W, and N-Os impurity pairs are significantly stable relative to the isolated dopants. Furthermore, these binding energies are comparable with the reported results of Gai et al.<sup>7</sup> However, the values of binding energy for C-Re and N-Re impurity pairs are not large enough and may possibly be broken up at high temperatures during the synthesis process. To confirm this, we also calculated the binding energies with a 108-atom supercell using a  $2 \times 2 \times 2$   $k$ -mesh. The corresponding values are 2.84, 0.50, 4.56, 2.28, 0.20, and 2.55 eV, respectively, indicating that the binding energies from the 48-atom system are reasonable. The large binding energy results arise from charge transfer from donor to acceptor, and the strong associated Coulomb interaction is due to interactions between positively charged donors and negatively charged acceptors. The ELF is plotted in Figure 5 at the (100) surface of bulk anatase for these three doped systems, and the Bader charges are summarized in Tables 2 and 3.<sup>34,35</sup> Here, the partial optimized geometries are presented in Figure 6 to compare with Tables 2 and 3. Figure 5 shows that C-W and C-Re bonds exhibit ionic behavior while C-Os shows covalent characteristics. Table 2 shows that the C ion has a charge of  $-1.20$  |e| for C@O monodoping, while it is  $-2.60$  |e| for (C+W)-codoping, with more electrons transferring from the W and adjacent Ti atoms to the C ion. The bond length of C-W is 1.868 Å, which is shorter than that of the C-Ti length of 2.196 Å for C@O doping, indicating further that a strong C-W bond forms. For (C+Re), the optimized C-Re bond length is only 1.624 Å, shorter than that of C-W and significantly shorter than that of C-Ti. Therefore, a much stronger interaction between the C and Re ion takes place. For the (C+Os) system, the C-Os bond behavior is different from C-W and C-Re (cf. Figure 5) such that the formation of a covalent C-Os bond takes place through sharing of electrons between Os and C. The Bader charges



**Figure 5.** Electron localization function contour plots (ELF) on the (100) surface of bulk materials for (a) C-, (b) (C+W)-, (c) (C+Re)-, and (d) (C+Os)-doped anatase.

**Table 2. Average Bader Charges (|e|) on Dopant Atoms and Their Adjacent Atoms in C- and (C+W)-, (C+Re)-, and (C+Os)-doped  $\text{TiO}_2$ <sup>a</sup>**

	C-doped	(C+W)-doped	(C+Re)-doped	(C+Os)-doped
C	-1.20	-2.60	-2.60	-1.74
TM		4.82	2.94	0.97
O		-1.52(5)	-1.29(5)	-1.31(5)
Ti	2.69(3)	2.65(2)	2.58(2)	2.71(2)
bond length (Å)	2.196	1.868	1.624	1.743

<sup>a</sup> Bond lengths of C-Ti, C-W, C-Re, and C-Os are also reported. The number in parentheses denotes the number of nearest-neighbor atoms around a dopant.

**Table 3. Average Bader Charges (|e|) on Dopant Atoms and Their Adjacent Atoms in N- and (N+W)-, (N+Re)-, and (N+Os)-doped  $\text{TiO}_2$ <sup>a</sup>**

	N-doped	(N+W)-doped	(N+Re)-doped	(N+Os)-doped
N	-1.41	-2.02	-1.94	-0.74
TM		4.22	2.68	2.55
O		-1.47(5)	-1.31(5)	-1.31(5)
Ti	2.74(3)	2.72(2)	2.59(2)	2.75(2)
Bond length (Å)	2.026	1.851	1.717	1.798

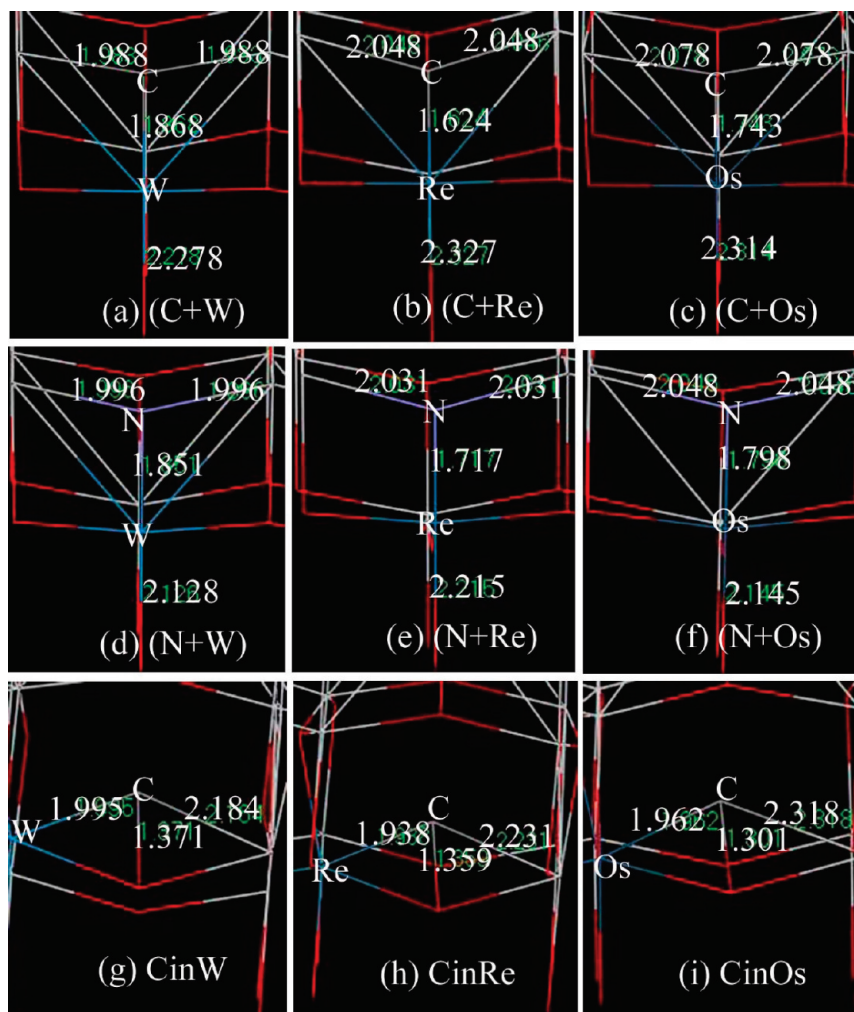
<sup>a</sup> Bond lengths of N-Ti, N-W, N-Re, and N-Os are also specified. The number in parentheses denotes the number of nearest-neighbor atoms around a dopant.

also confirm this result, in which the C ion has a charge of  $-2.74$  |e|. This method could be also employed to analyze the (N+TM) system.

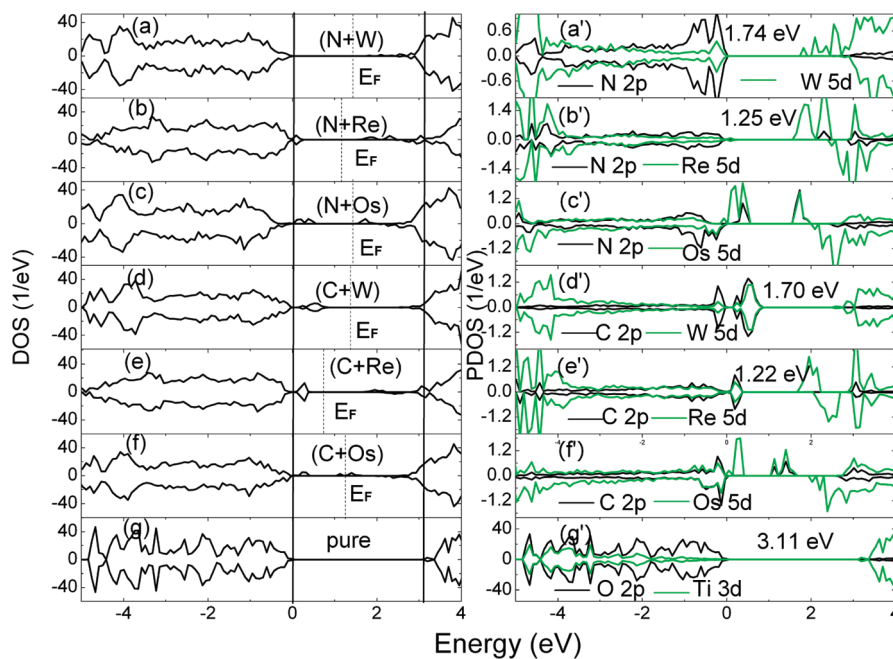
Second, we have examined synergistic effects on narrowing the band gap of  $\text{TiO}_2$  by codoping X (N, C) with TM (W, Re, Os). Hence, the calculated DOS and PDOS for these six systems, compared to the results with that of pure  $\text{TiO}_2$ , are shown in Figure 7. It may be seen that the reduction in band gap caused by codoping is very significant with respect to that observed in the corresponding X (N, C) and TM (W, Re, Os) monodoped cases, leading to a large reduction of the band gap in these doped systems.

For the (N+W)-codoped system (cf. Figure 7a,a'), identifying the formation of a continuous band of hybridized N2p-O2p states, which consists of the valence band edge and W5d orbitals dominating the conduction band edge, leads to a significant band gap reduction of about 1.37 eV.<sup>11</sup>

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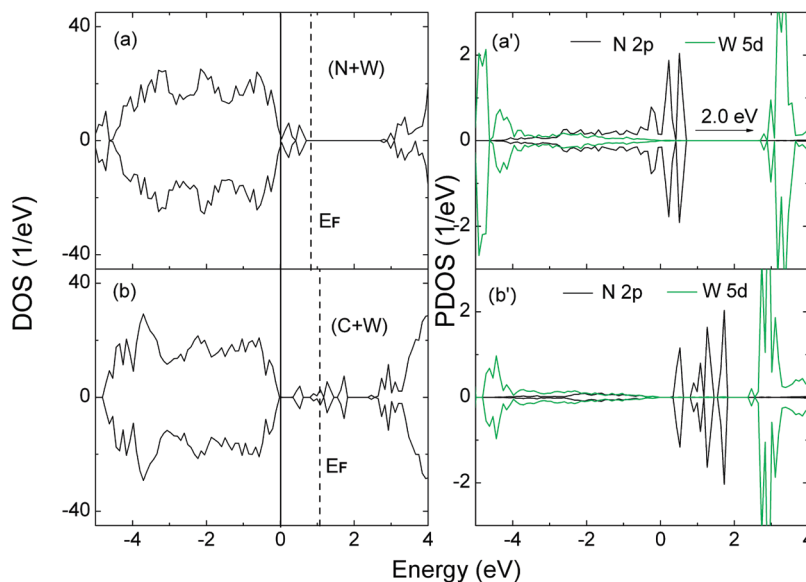


**Figure 6.** Geometry-optimized structures for (a) (C + W)-, (b) (C + Re)-, (c) (C + Os)-, (d) (N + W)-, (e) (N + Re)-, (f) (N + Os)-, (g) C in W-, (h) C in Re-, and (i) C in Os-doped anatase. The bond length unit is Å.



**Figure 7.** DOS of undoped anatase and (C + W), (C + Re), (C + Os), (N + W), (N + Re), and (N + Os)-codoped anatase and PDOS for impurity atoms (black for p orbital and green for d orbital) with 48-atom supercell. The top of the valence band of pure anatase is taken as the reference level. The dashed lines represent the Fermi level,  $E_F$ .





**Figure 8.** DOS for (N + W)- and (C + W)-codoped anatase compared with pure anatase and PDOS for impurity and host atoms using a 108-atom supercell (black for p orbital and green for d orbital). The top of the valence band for pure anatase is taken as the reference level. The dashed lines represent the Fermi level,  $E_F$ .

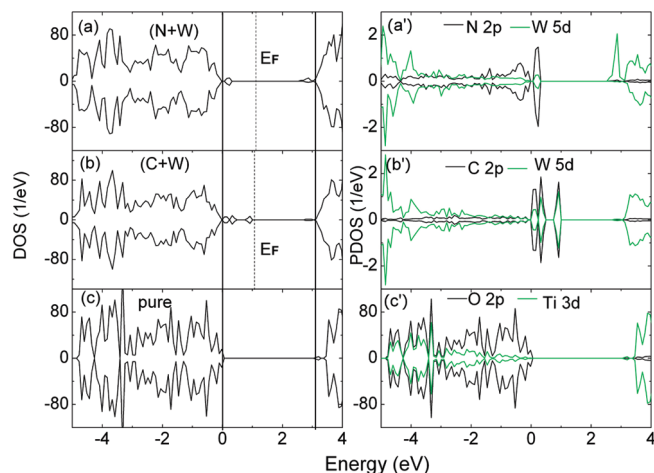
This means (N+W)-codoped  $\text{TiO}_2$  is an effective photocatalyst for absorption of visible light. Examining the other two (N+TM)-codoped systems, (N+Re) (cf. Figure 7b,b') and (N+Os) (cf. Figure 7c,c') possess much smaller band gaps than those of both pure anatase and the (N+W) system. However, they exhibit shortcomings. First, the binding energy of the (N+Re) system is so small that it may easily depart the titania during the synthesis process. Second, some empty states located in the band gap of the (N+Os) system can act as recombination centers and reduce phonon absorption efficiency. Although these two codoped systems extend substantially the absorption edge to longer visible-light ranges, it is expected they are not effective as applied photocatalysts because of either instability or low efficiency.

Compared to (N+TM)-codoped systems, (C+TM) exhibits much better effects on band gap narrowing, which may be due to deeper C acceptor energy levels than those of N and a much stronger interaction between C and TM atoms. For the (C+W)-codoped system (cf. Figure 7d,d'), the band gap is reduced by about 1.41 eV with the formation of the isolated band above VBM with a value of 0.83 eV and CBM down-shifting by about 0.37 eV, which is different from the (N+W) system. Like (N+W)-codoped titania,<sup>11</sup> a C2p-W5d hybridized band is formed, which renders the hybridization between C 2p and O 2p stronger than C monodoping, giving rise to a fully occupied band above the top of the valence band edge. At the same time, partial W 5d states are located at the edge of the conduction band, and importantly, the isolated states disappear and a continuum-like band is formed. This finding is very similar to our previous work on (N+Ta)-codoped  $\text{TiO}_2$ .<sup>36</sup> Obviously, incorporation of W into C-doped  $\text{TiO}_2$  changes the character of C 2p orbitals from isolated midgap states to C 2p states mixed

with O 2p states above the top of the valence band and conduction band edge consisting of W 5d itself. However, its formation energy is nearly double that of the (N+W) case and therefore it would not be easily synthesized experimentally under either O-rich or Ti-rich conditions.

The (C+Re)-codoped system (cf. Figure 7e,e') reduces the band gap significantly by about 1.89 eV, with the formation of a fully occupied band above the VBM of about 0.4 eV and the CBM down-shifting by 1.43 eV, which is different from the (C+Os)-codoped cases (cf. Figure 7f,f'). The band gap of the (C+Os) case narrows less than (C+Re) but produces gap states, which are partially occupied. This implies that the (C+Os)-codoped system is not as promising as a possible photocatalytic material due to the existence of recombination centers. Moreover, the small binding energy of (C+Re)-codoped anatase would also lead this system to be unstable at high temperatures.

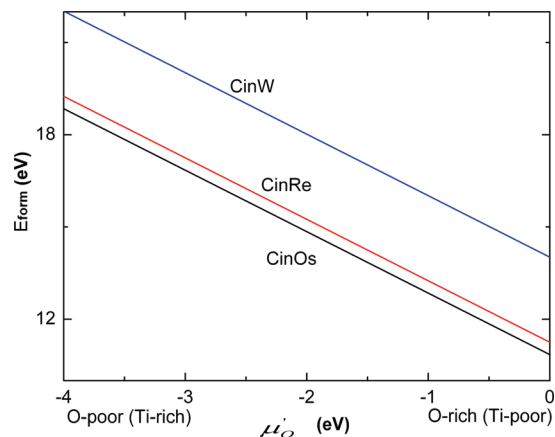
Briefly, considering the findings for band gap narrowing, formation energies, and binding energies, it seems that (N+W) and (C+W) should be promising candidates for photocatalytic materials under visible light irradiation. Therefore, we have plotted the DOS and PDOS for these doping cases (N, C, and W as far apart as possible, i.e., the Lnn configuration) in Figure 8. For the (N+W) system (cf. Figure 8a,a'), the value of the band gap narrowing is about 1.11 eV, which is smaller than that of 1.37 eV with the formation of an N–W pair. Furthermore, the impurity band locates about the VBM, which is very different from Figure 7a due to no passivation effect. On the other hand, the (C+W) system (cf. Figure 8b,b') exhibits some unoccupied states located at the band gap acting as recombination centers. This is quite different behavior from Figure 7d, in which there are no such unoccupied states which may serve to accommodate recombination centers.



**Figure 9.** DOS for (N + W)- and (C + W)-codoped anatase (black for p orbital and green for d orbital). The top of the valence band for pure anatase is taken as the reference level (not shown here). The dashed lines represent the Fermi level,  $E_F$ .

To compare different dopant concentration effects on the electronic structure, we selected the best (N+W)- and (C+W)-codoped systems and calculated their DOS and PDOS using the GGA+U method with a 108-atom supercell, as shown in Figure 9. For comparison, we have also presented the DOS and PDOS of the pure 108-atom anatase supercell. The electronic structures of the (N+W)-codoped case (cf. Figure 9a,a') exhibit two obvious different characteristics compared with the 48-atom supercell (cf. Figure 7a,a'). First, the gap narrowed less. Second, there is the formation of a fully occupied continuum-like band above the VBM. Nevertheless, this still shows excellent potential band gap behavior to absorb more visible light. On the other hand, (C+W)-codoped  $\text{TiO}_2$  (cf. Figure 9b,b') has similar electronic properties with respect to its 48-atom supercell analogue, except for a comparatively smaller band gap reduction due to the lower doping concentration. Therefore, this also serves as a promising photocatalytic material under visible-light irradiation independent of consideration of formation energy.

C may also certainly occupy interstitial sites, in particular, under O-rich conditions.<sup>21</sup> Therefore, we consider three configurations of C locating at interstitial sites and TM (W, Re, Os) locating at Ti sites. Partial views of the geometry-optimized structures are shown in Figure 6g–i; the C–W, C–Re, and C–Os bond lengths were 1.995,



**Figure 10.** Formation energies (eV)  $E_{\text{form}}$  as a function of the oxygen chemical potential for (a) C in W, (b) C in Re, and (c) C in Os-doped  $\text{TiO}_2$ .

1.938, and 1.962 Å, respectively. The formation energies were calculated from eq 6:

$$E_{\text{form}} = E(\text{TM@Ti} + \text{C}_{\text{in}}) - E(\text{TiO}_2) - \mu_{\text{X}} - \mu_{\text{TM}} + \mu_{\text{Ti}} \quad (6)$$

Here,  $E(\text{TM@Ti} + \text{C}_{\text{in}})$  represents the total energies of the defective systems. The formation energies are plotted in Figure 10. It shows that the values of formation energies are always high regardless of whether growth conditions are O- or Ti-rich. Therefore, it is more difficult to fabricate these codoped systems.

In conclusion, based on first-principles calculations and analysis of electronic structures, we find that although (C+TM) (TM = W, Re, Os)-codoped systems narrow the band gap to a slightly larger extent than those of (N+TM) systems, (N+TM) has more medium formation energies, which is of greater convenience for synthesis. Band gap narrowing is a highly important contribution to the enhancement of optical absorption under visible light irradiation. The calculated results suggest that codoping of N or C with TM can effectively reduce the formation energy relative to N and C monodoping and enhance the N or C concentration. The results indicate that (N+W)-codoped anatase may serve as a very promising photocatalytic material because of its relatively small formation energy and large binding energy.

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