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Defect pair formation in fluorine and nitrogen codoped TiO₂

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Abstract

Titanium oxide is intensively investigated because of its high chemical stability and its photocatalytic properties, nevertheless, the large band gap limits its activity to a small portion of the solar spectrum. Nitrogen and fluorine codoping is an efficient defect engineering strategy to increase the photocatalytic activity of titanium oxide. In the present study, we apply density functional theory to investigate the interaction of nitrogen with fluorine and the formation of defect pairs. We show that in fluorine and nitrogen codoped titanium oxide the F_iN_i , F_oN_i and F_iN_{Ti} defects can form. Their impact on the electronic structure of titanium oxide is discussed.

1. Introduction

Following the seminal study by Fujishima and Honda¹, titanium oxide (TiO₂) and other metal oxides have been extensively studied because of their interesting catalytic activity, long lifetime of photon generated carriers, and high chemical stability.¹⁻¹⁰ It has been previously established that anatase is the TiO₂ polymorph with the highest photocatalytic activity but its large band gap (3.2 eV) limits its activity to the ultraviolet range, which accounts for about 5% of the solar spectrum.⁷ Ideally, for photocatalysis applications anatase should have a band gap around 2 eV and the positions of the band edges must be compatible with the redox potential of water.¹¹

A way to reduce the band gap is doping, for example nitrogen (N) is a promising dopant as it reduces the band gap enhancing the visible light response.^{3,12,13} Fluorine (F) doping will cause modifications of the electronic structure via the formation of surface oxygen vacancies, nevertheless it does not significantly impact the optical absorption of TiO₂.¹⁴⁻²⁴ Codoping anatase with N and F is beneficial as there is a significant reduction of the band gap, better photocatalytic activity under visible light irradiation and high surface area.¹⁴⁻²⁴ The improvement of the photocatalytic activity is because of the generation of oxygen vacancies by N substitutional atoms and the F atoms that promote the formation of active sites and higher photoelectron mobility.¹⁹ For this reason N and F codoped anatase is considered for numerous applications including self-cleaning applications under visible light.²⁰ In the present study we use electronic structure calculations to investigate F and N codoping in anatase TiO₂. The binding of F and N and the possible formations of clusters at an atomistic level is investigated using density functional theory (DFT). Finally, we consider the density of states (DOS) of the most energetically favourable defects to assess their impact on anatase in view of its photocatalytic application.

2. Methodology

For the calculations we employed the plane wave DFT code CASTEP,^{25,26} with the exchange and correlation interactions modelled using the corrected density functional of Perdew, Burke and Ernzerhof (PBE)²⁷ in the generalized gradient approximation (GGA), with ultrasoft pseudopotentials.²⁸ The kinetic energy cut-off of the plane wave basis is 480 eV, in conjunction with a 2 x 2 x 3 Monkhorst-Pack (MP)²⁹ k-point grid and a 108-atomic site supercell. To consider correlation effects of localized electrons onsite Coulomb repulsions of 8.2 eV is set for the Ti 3d orbitals.³⁰ We have tested this value to establish that the trends are not affected by the specific choice of U-parameter. The calculations were under constant pressure conditions. The binding energies were defined here as the differences in energy between the defect cluster and its constituent defects being as further apart as possible in the supercell. Negative binding energies imply that the cluster is more energetically favourable as compared to its relatively isolated constituent defects. For the DOS calculations, a denser mesh of 7 x 7 x 7 k-points was applied.

3. Results and Discussion

Out of the three polymorphs of TiO₂ (rutile, anatase and brookite), anatase is deemed to have superior photocatalytic properties as it separates more efficiently the photoexcited charge carriers^{31,32}. Anatase is tetragonal with space groups I4/amd respectively.^{33,34} Here we calculate lattice parameters of anatase to be $a = 3.806 \text{ \AA}$ and $c = 9.724 \text{ \AA}$ in very good agreement with the neutron diffraction results ($a = 3.782 \text{ \AA}$ and $c = 9.502 \text{ \AA}$)³³ and previous theoretical results ($a = 3.729\text{-}3.801 \text{ \AA}$ and $c = 9.480\text{-}9.818 \text{ \AA}$).^{34,35}

It is calculated using DFT that fluorine can be a substitutional defect occupying oxygen sites (F_O) and also an interstitial defect (F_i). We calculated that F_i resides 1.98 Å from the nearest oxygen atom (refer to Fig. 1 (a)). We thereafter considered the binding of F_i atoms

to form F_iF_i pairs and calculated that F_i interstitials attract each other with -0.10 eV. This is opposite to what is observed in semiconductors such as silicon or germanium where the highly electronegative F interstitials repel each other.³⁶ In Fig. 2(a) the effect of the F_i on the DOS of the supercell is shown. In this case ($Ti_{36}O_{72}F_i$) the F_i gives rise to a mid-gap state at 1.15eV above the valence band maximum (VBM) (mainly due to the Ti p-bands).

Nitrogen was incorporated as an interstitial (N_i , refer to Fig. 1(b)) and it introduces the N 2p states near the valence band (at 0.35 eV from the VBM, refer to Fig. 2(b)). These states reduce the band gap to 2.57 eV (consistently with experiment)²³ and this is positive as it enhances the visible light response of anatase.^{3,12,13}

We consider that in highly N and F codoped anatase there is the possibility that they will interact to form defect clusters consisting of N and F. This is also supported by the low migration energy of F_i , which in turn infers that they will be mobile and it will therefore be very likely for a F_i to encounter a N atom.³⁷ To account for this we performed an extensive search of the different possibilities that the interstitial and/or substitutional F and N defects can associate. Figure 1 (c-e) represents the minimum energy F_iN_i , F_oN_i and F_iN_{Ti} defect pairs. It is calculated that F_iN_i , F_oN_i and F_iN_{Ti} defects form with binding energies of -0.4 eV, -1.6 eV and -0.6 eV respectively. This implies that a F_i would preferably bind to the N_{Ti} (to form F_iN_{Ti}) rather than a N_i (to form F_iN_i) Additionally, a N_i would preferentially bind with F_o (to form F_oN_i) rather than F_i (to form F_iN_i)

To gain an understanding on the impact of the N-F clusters on the electronic structure of anatase we performed density of states calculations (refer to Fig. 2(c)-(e)). It was previously determined that F in TiO_2 can occupy oxygen sites.³⁷ The introduction of F in O lattice sites (i.e. F_o) introduces the formation of Ti^{3+} centers, which localize the extra electron required for charge compensation.³⁷ This is evident in the DOS of the F_oN_i defect pair (refer to Fig. 2(d)) and the Ti^{3+} states are just below the conduction band. The excitation of these

occupied Ti^{3+} states to the conduction band (CB) will result to green colour.¹⁸ Finally, the F_iN_{Ti} defect will induce deep levels in the band gap at 2.03 eV and 2.27 eV below the conduction band (Fig. 2(e)). These will need to be investigated experimentally. In Fig. 2 (f) the DOS of the undoped TiO_2 is also given for reference.

The information presented herein on the energy levels of the interfacial states existent in the bulk F-N codoped anatase can be useful for the interpretation of experimental results or as input to possible Monte Carlo simulations. In general, it is expected that methods to increase the photocatalytic efficiency by doping may be weakened by recombination losses attributed to interface states, dependent on the application. In the present study we considered about 1% nitrogen and/or 1% fluorine. This concentration of nitrogen should be more than sufficient to reduce the band gap and increase the photocatalytic activity of anatase. It is expected that fluorine will mainly saturate dangling bonds. At any rate the optimum concentration of N and F will need to be determined systematically so as to avoid the formation of the deleterious defects proposed here. Finally, experimental work will be required to determine the impact of temperature and other processing conditions on the interactions of N and F in TiO_2 . In that respect thermodynamic modeling and mass action analysis can also be important and act synergetically with DFT and experiment.³⁸⁻⁴⁴

4. Conclusions

In the present study, electronic structure calculations were used to investigate F and N codoped anatase. It is revealed that the F_iN_i , F_oN_i and F_iN_{Ti} defects are bound and it is therefore expected that in codoped anatase there will be a significant concentration of these defects. Considering the impact of these defects on the electronic structure of anatase we examined the DOS. It is shown that for the F_oN_i defect pair Ti^{3+} states are just below the conduction band. Finally, the F_iN_{Ti} defects introduce deep levels. It is therefore proposed here

that anatase without oxygen vacancies and titanium vacancies will be a better material to codope as the deleterious $F_{O}N_{i}$ and $F_{i}N_{Ti}$ will not form.

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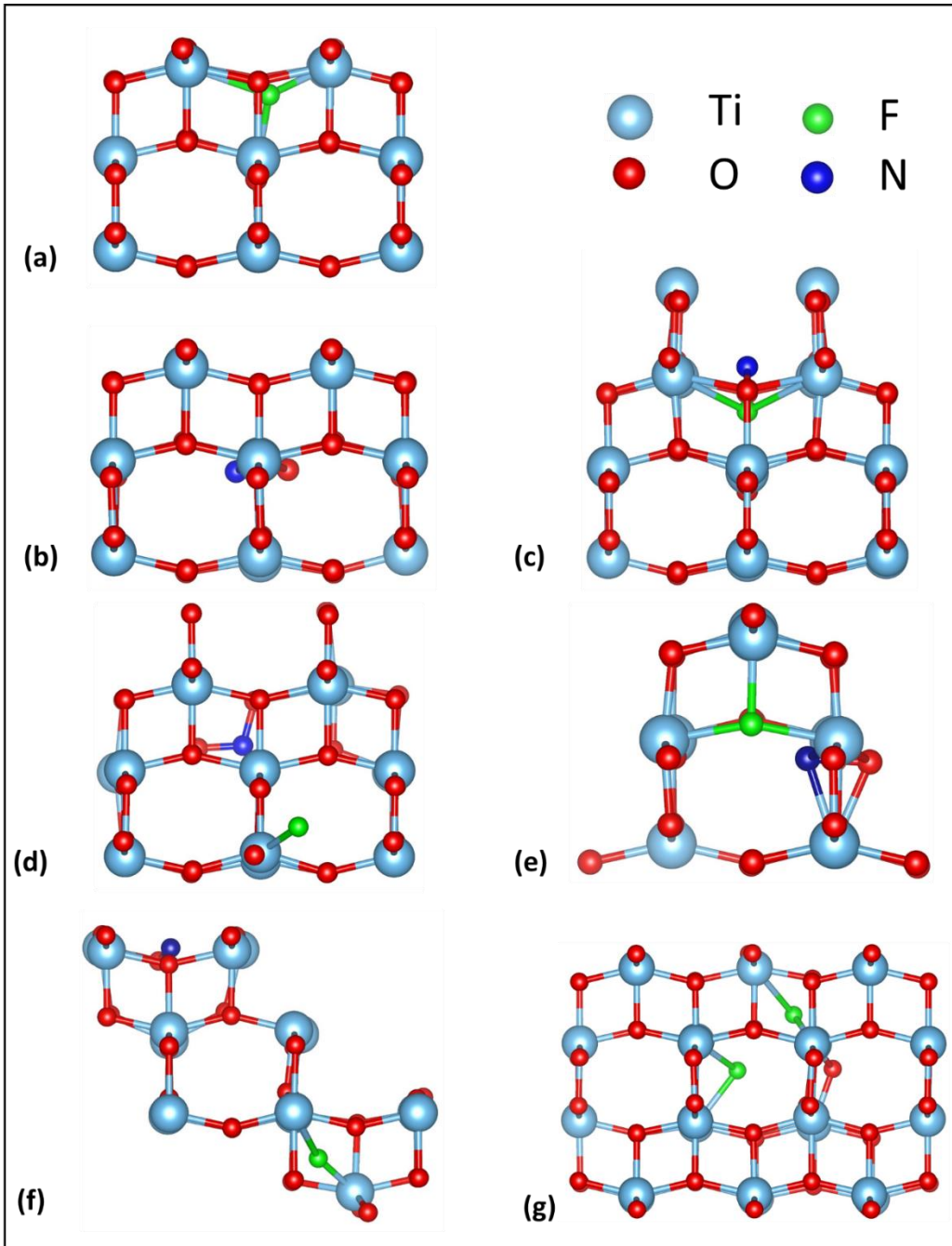


Figure 1. The structure of minimum energy fluorine-nitrogen defects in anatase. The (a) F_i , (b) the N_i , (c) F_iN_i (d) F_oN_i (e) F_iN_{Ti} (f) $F_iN_i_{away}$ and (g) F_iF_i defects.

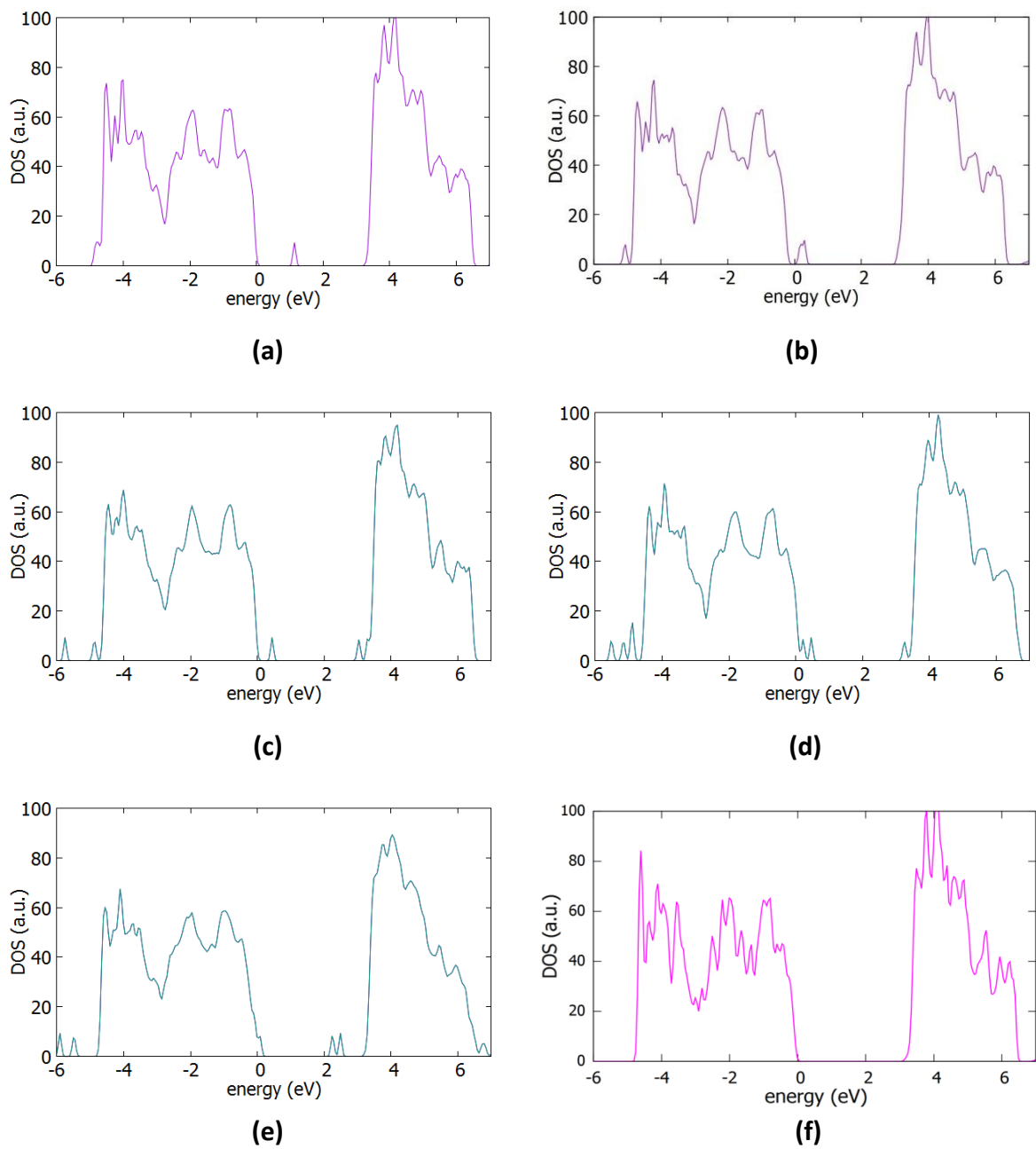


Figure 2. Densities of states of defective supercells containing the (a) F_i , (b) the N_i , (c) F_iN_i (d) F_oN_i and (e) F_iN_{Ti} defects and (f) the non defective supercell of anatase TiO_2