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**University College Cork, Ireland**  
Coláiste na hOllscoile Corcaigh

**A First Principles Investigation of Bi<sub>2</sub>O<sub>3</sub>-Modified TiO<sub>2</sub> for Visible Light  
Activated Photocatalysis: the Role of TiO<sub>2</sub> Crystal Form and the Bi<sup>3+</sup>  
Stereochemical Lone Pair**

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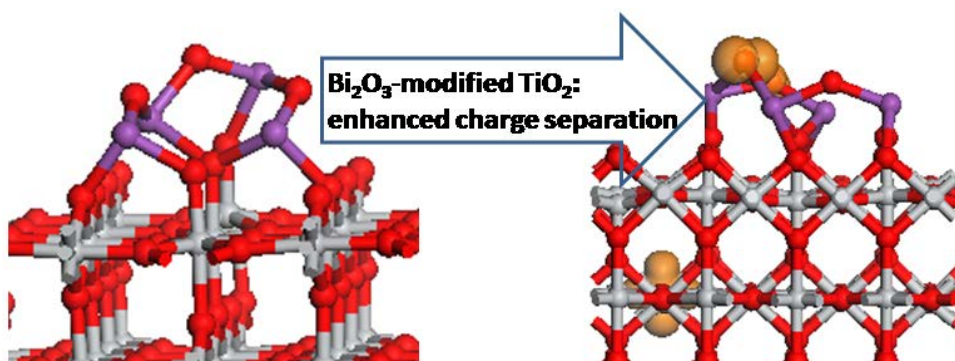
## Highlights

- First principles simulations of  $\text{TiO}_2$  rutile (110), anatase (101) and anatase (001) surfaces modified with  $\text{Bi}_2\text{O}_3$  nanoclusters as potential visible light active photocatalyst
- A reduction in the energy gap over  $\text{TiO}_2$  is predicted for  $\text{Bi}_2\text{O}_3$ -modified rutile (110).
- Enhanced charge separation after photoexcitation is predicted, with holes localised on  $\text{Bi}_2\text{O}_3$  and electrons on  $\text{TiO}_2$ .
- There is little change in the energy gap for  $\text{Bi}_2\text{O}_3$ -modified anatase and electrons and holes reside on anatase.
- The effect of the  $\text{Bi}^{3+}$  lone pair is much reduced compared to  $\text{Sn}^{2+}$

**Abstract.**

Modification of  $\text{TiO}_2$  with metal oxide nanoclusters is a novel strategy for the design of new photocatalysts with visible light activity. This paper presents a first principles density functional theory (DFT) analysis of the effect of modifying  $\text{TiO}_2$  rutile (110) and anatase (101) and (001) surfaces with  $\text{Bi}_2\text{O}_3$  nanoclusters on the band gap and the nature of the photoexcited state. We show that band gap modifications over unmodified  $\text{TiO}_2$  depend on the crystal form: modifying rutile (110) results in new  $\text{Bi}_2\text{O}_3$  derived states that shift the valence band upwards. On anatase surfaces, there is little effect due to modification with  $\text{Bi}_2\text{O}_3$  nanoclusters, but an enhanced UV activity would be expected. Analysis of electron and hole localisation in a model photoexcited state shows enhanced charge separation in  $\text{Bi}_2\text{O}_3$ -modified rutile (110) but not in  $\text{Bi}_2\text{O}_3$ -modified anatase. The effect of the  $\text{Bi}^{3+}$  lone-pair on the properties of  $\text{Bi}_2\text{O}_3$ -modified  $\text{TiO}_2$  contrasts with  $\text{SnO}$ -modified  $\text{TiO}_2$ , consistent with the weaker lone pair in  $\text{Bi}_2\text{O}_3$  compared with  $\text{SnO}$ .

## Graphical Abstract



The effect of modifying TiO<sub>2</sub> with Bi<sub>2</sub>O<sub>3</sub> nanoclusters depends on the crystal form of TiO<sub>2</sub>

**Keywords:** Photocatalysis,  $\text{TiO}_2$ ,  $\text{Bi}_2\text{O}_3$ , Lone Pair, Density functional theory, Energy gap

## 1. Introduction

With the problems of diminishing fossil fuel supply, global warming and CO<sub>2</sub> emissions, as well as widespread environmental pollution, solar energy driven photocatalysis for fuel production or pollution remediation is of great interest and TiO<sub>2</sub> based photocatalysts receive a significant level of attention [1-6]. As a photocatalyst, TiO<sub>2</sub> is a very good candidate, with low cost, good availability, stability and non-toxicity. However the main drawback is that the band gap of TiO<sub>2</sub> means it absorbs in the UV region of the electromagnetic spectrum, which makes up around only 5 % of the visible solar spectrum. The ability to modify TiO<sub>2</sub> for visible light absorption brings with it the possibility for solar driven photocatalysis in areas such as water splitting, environmental remediation and bacterial removal.

There have been many attempts to reduce the band gap of TiO<sub>2</sub> to enable visible light absorption and photocatalytic activity [7-]. The primary approach in band gap engineering has been either metal doping at Ti sites [7 – 13] or non-metal doping at O sites [14 – 20] of TiO<sub>2</sub>. More recently, so-called “co-doping” of a metal and non-metal at the Ti and O sites is receiving some attention [21,22]. It is usually concluded that the visible light absorption originates from the formation of new dopant-derived defect states formed in the energy gap of TiO<sub>2</sub>. These states are supposed to facilitate electronic transitions from filled dopant states to empty conduction band states of TiO<sub>2</sub> or from filled valence band of TiO<sub>2</sub> to empty dopant states and these transitions have energies in the visible region.

However, the formation of these localised defect states will, unfortunately, reduce photocatalytic efficiency by acting as recombination centres, trapping electrons or holes. This was shown recently by Hermann for Cr-doped TiO<sub>2</sub> [XX]. Simultaneous metal-non metal co-doping of TiO<sub>2</sub> is proposed as an alternative so long as the dopants charge compensate each other and remove the localised defect states [21], and has been demonstrated experimentally for, e.g. C/Mo co-doped TiO<sub>2</sub> [22].



A different approach to designing effective photocatalysts is to fabricate heterostructures composed from rutile-anatase composites or modification with another metal oxide [23-31]. The formation of the interface between the two phases in composites or  $\text{TiO}_2$  and the modifier can change the electronic structure to introduce visible light absorption and enhance charge carrier separation [23-31]. Iron oxide nanoclusters have been deposited onto anatase  $\text{TiO}_2$  using atomic layer deposition of iron oxide by Libera et al. [23] and by chemisorption-calcination-cycling (CCC) deposition of transition metal oxide nanoclusters by Tada and co-workers [24, 25, 29, 32]. These experiments have reported band gap reduction, predominantly from an upwards shift in the valence band edge as determined by X-ray photoelectron spectra and a reduction in electron/hole recombination from photoluminescence spectroscopy [23, 25, 29]. Enhanced visible and UV photocatalytic activity for oxidation of organic molecules over unmodified  $\text{TiO}_2$  has also been demonstrated [23 - 25, 29, 32]. Accompanying theoretical work from our group using density functional theory (DFT) studies has shown that  $\text{TiO}_2$  modified with  $\text{TiO}_2$  [30],  $\text{FeOx}$  [27],  $\text{Ga}_2\text{O}_3$  [31] and  $\text{NiO}$  [32] nanoclusters will lead to a band gap reduction over unmodified  $\text{TiO}_2$  and we have discussed the enhanced charge carrier separation and electron and hole polaronic localisation.

We have also discovered that the stereochemical lone pair in  $\text{SnO}$  can give rise to a notable difference between  $\text{SnO}$  and  $\text{SnO}_2$  modified  $\text{TiO}_2$  [29, 33], which was also found for  $\text{SnO}/\text{SnO}_2$  modified  $\text{ZnGa}_2\text{O}_4$  [34], although in the latter paper, this difference was not discussed. Briefly, the lone pair present in  $\text{SnO}$  [35] results in new  $\text{SnO}$ -derived states being introduced above the original VB edge of  $\text{TiO}_2$ , which reduces the energy gap over unmodified  $\text{TiO}_2$ , while for  $\text{SnO}_2$  the lack of the lone pair means there is little if any band gap change [29, 33].

In light of this interesting effect due to the stereochemical lone pair, we present in this paper a first principles analysis of  $\text{TiO}_2$  rutile (110) and anatase (101) and (001) surfaces modified with  $\text{Bi}_2\text{O}_3$  nanoclusters, which contain  $\text{Bi}^{3+}$  species that have a stereochemically active lone pair [36], which is weaker than in  $\text{SnO}$ . The presence of  $\text{Bi}^{3+}$  in materials such as  $\text{BiVO}_4$  and  $\text{Bi}_2\text{WO}_6$  is considered to be important for their photocatalytic activity in that it is important in determining the nature of the valence band of the material [36, 37].

We show from our first principles simulations that the effect of  $\text{Bi}_2\text{O}_3$  modifications to rutile and anatase depends on the crystal form of  $\text{TiO}_2$ : modifying rutile (110) with  $\text{Bi}_2\text{O}_3$  nanoclusters results in a reduction of the energy gap compared with unmodified rutile, giving enhanced visible light absorption and charge separation. However, modifying anatase  $\text{TiO}_2$  gives little change to the band gap of  $\text{TiO}_2$  and will not enhance charge separation. Thus both the modifier and the crystal form of  $\text{TiO}_2$  can be used to tune the activity of modified  $\text{TiO}_2$  by inducing enhanced visible or UV light absorption.

## 2. Computational Methods

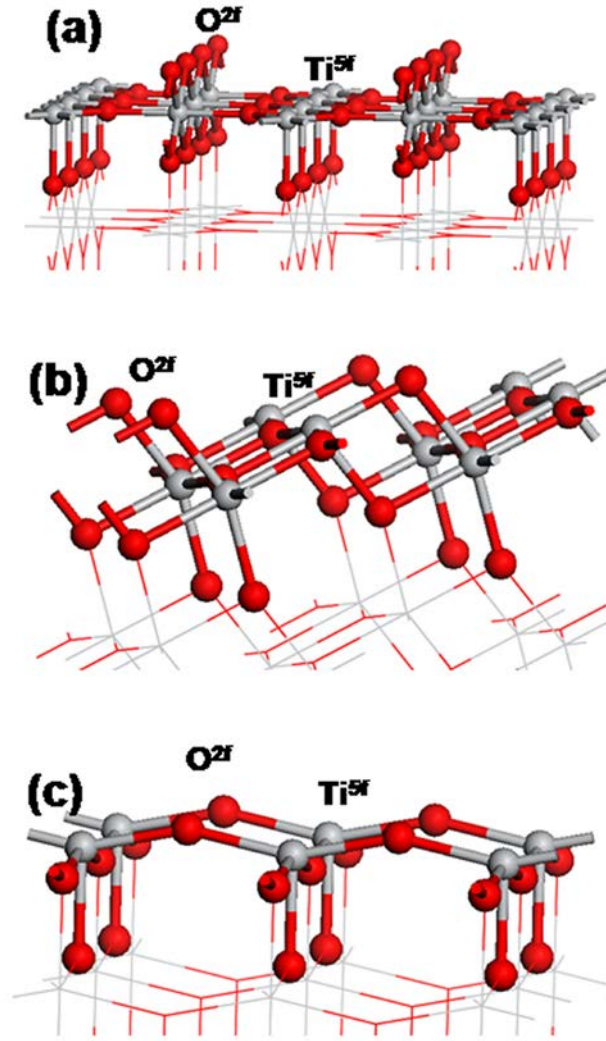
To model  $\text{TiO}_2$  rutile (110) surface, we use a three dimensional periodic slab model within the VASP code [38]. The valence electrons were described by a plane wave basis set and the cut-off for the kinetic energy is 396 eV. The number of valence electrons is 4 for Ti, 5 for Bi and 6 for O. A recent study highlighted that the Ti semi-core 3s and 3p states can have an effect on the computed properties of bulk  $\text{TiO}_2$  [39], we have also repeated selected calculations with a larger 12 valence electron PAW potential on the Ti atoms in each surface; the results of this comparison are discussed in section 3 and given in detail in the Supporting Information.

The exchange-correlation functional is the Perdew-Wang 91 [40] approximation. We use

a Monkhorst-Pack ( $2\times 1\times 1$ ) k-point sampling grid in all calculations. In describing Ti  $3d$  states and in particular for structures that can contain reduced  $\text{Ti}^{3+}$  species as a result of transferring electrons to previously (formally) empty Ti  $3d$  states, the well known DFT+U approach [41,42] is applied and we use a value of  $U = 4.5$  eV on the Ti  $3d$  states that has been used in our previous work on this topic [30, 32, 33]. For Bi, the electronic states for both oxidation states are consistently described by DFT so no +U correction is applied here. To examine any effects due to applying DFT+U on the relative positions of the  $\text{TiO}_2$  and  $\text{Bi}_2\text{O}_3$  energy states and consequent modifications to the energy gap of  $\text{TiO}_2$ , we have also repeated some calculations using DFT without the +U correction and the details are presented in the supporting information. While hybrid DFT could be used instead of DFT+U, the size of our systems precludes the use of hybrid DFT within a plane wave basis set.

The rutile (110) surface (figure 1(a)) is terminated by two-fold coordinated bridging O atoms and the Ti atoms in the surface are 5-fold and 6-fold coordinated. A ( $2\times 4$ ) surface supercell expansion is employed. For anatase, the (101) and unreconstructed (001) surface are shown in figures 1(b) and (c); we have successfully used the unreconstructed (001) surface in our other studies [32]. Both anatase surfaces are characterised by two-fold coordinated oxygen atoms terminating the surface layer and the outermost Ti atoms are 5-fold coordinated. A ( $4\times 2$ ) surface supercell expansion of anatase (101) and (001) is employed. These surface supercells allow adsorption of isolated nanoclusters and the vacuum gap in all cases is 12 Å. The surface models are stoichiometric with no defects and no adsorbed hydroxyl species, both of which are well known defects in  $\text{TiO}_2$  surfaces, but this model suffices for understanding the basic properties of modified  $\text{TiO}_2$ . The convergence criteria for the electronic and ionic relaxations are 0.0001 eV and 0.02 eV/Å. For the consistency in the calculation we also applied the same supercell and

technical parameters for the bare  $\text{TiO}_2$  surface and free clusters.



**Figure 1:** Atomic structures of the bare (a) rutile (110), (b) anatase (101) and (c) unreconstructed anatase (001) surfaces used in this work. Two-fold coordinated oxygen and five-fold coordinated Ti are indicated as  $\text{O}^{2f}$  and  $\text{Ti}^{5f}$ .

The clusters are positioned on the  $\text{TiO}_2$  surfaces and the adsorption energy is computed from:

$$E_{\text{ads}} = E((\text{Bi}_2\text{O}_3)\text{-TiO}_2) - \{ E(\text{Bi}_2\text{O}_3) + E(\text{TiO}_2) \} \quad (1)$$

Where  $E((\text{Bi}_2\text{O}_3)\text{-TiO}_2)$  is the total energy of the  $\text{Bi}_2\text{O}_3$  nanocluster supported on the anatase surface and  $E(\text{Bi}_2\text{O}_3)$  and  $E(\text{TiO}_2)$  are the total energies of the free  $\text{Bi}_2\text{O}_3$  cluster and the unmodified anatase surface. A negative adsorption energy indicates that cluster adsorption is stable.

To examine how surface modification of  $\text{TiO}_2$  affects electron and hole localisation over unmodified  $\text{TiO}_2$  and to examine the energetics of this process, we study a model of photoexcited  $\text{Bi}_2\text{O}_3$ -modified rutile (110) and anatase (101). The photoexcited system is modelled as the lowest energy DFT+U solution for an imposed triplet electronic state. This model generates an excited electron and a hole by construction in which the excited electron is found in the conduction band and the hole is found in the valence band. We and others have previously discussed in detail this approach in refs. [31, 33, 43 - 45]. The following energies are calculated:

The ground state energy of the system, denoted  $E^{\text{singlet}}$

A single point energy of a triplet state, at the ground state geometry, denoted  $E^{\text{unrelaxed}}$

An ionic relaxation of the triplet electronic state,  $E^{\text{relaxed}}$ .

From these energies, we extract

(1) The singlet-triplet vertical unrelaxed excitation energy:  $E^{\text{vertical}} = E^{\text{singlet}} - E^{\text{unrelaxed}}$

(2) The singlet-triplet excitation energy:  $E^{\text{S-T}} = E^{\text{singlet}} - E^{\text{relaxed}}$ . This energy should not be compared to the optical gap, nor is it the excitation energy that would be obtained from a time dependent DFT simulation of the lowest energy excited state, but it can be compared between modifications of  $\text{TiO}_2$  to assess the effect of the modifier on the band gap shift [31, 33].

(3) The electron and hole trapping energy:  $E^{\text{relax}} = E^{\text{relaxed}} - E^{\text{unrelaxed}}$ .  $E^{\text{relax}}$  is the energy gained when the electron and hole are trapped at their Ti and O sites (forming polarons) accompanied by structural relaxation around the polarons.

The resulting energies will be underestimated due to well known deficiencies in DFT, but are useful in making comparisons between similar systems, e.g. refs. [31, 32, 44].

### 3. Results

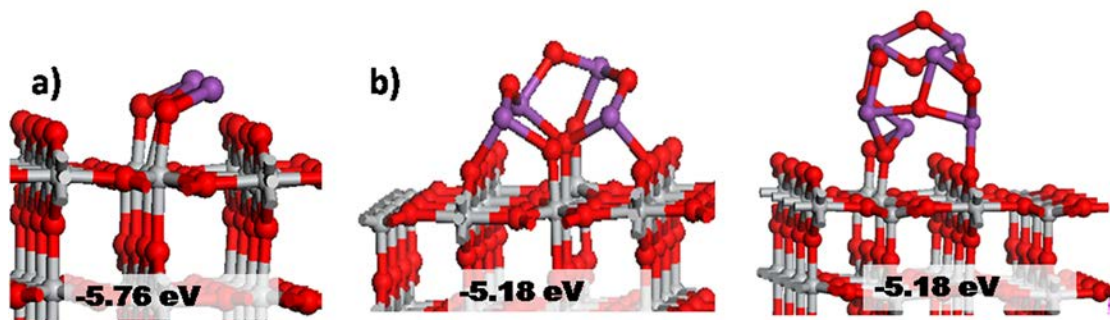
#### 3.1 Adsorption Energies and Structures of $\text{TiO}_2$ Rutile and Anatase Modified with $\text{Bi}_2\text{O}_3$ Nanoclusters

Figure 2 presents the relaxed atomic structures together with adsorption energies for representative structures of the model rutile (110) surface modified with  $\text{Bi}_2\text{O}_3$ ,  $\text{Bi}_4\text{O}_6$  and  $\text{Bi}_6\text{O}_9$  nanoclusters. All nanoclusters adsorb strongly at the rutile (110) surface, showing large negative adsorption energies of -5.76 eV for  $\text{Bi}_2\text{O}_3$  and -5.18 eV for the other nanoclusters and create new interfacial metal-oxygen bonds. The magnitude of these energies indicates that the nanoclusters will be anchored at the surface and will not aggregate into large particles or films [46].

A comparison between the 4 valence and 12 valence electron potentials for Ti, as well as between the DFT+U correction on Ti 3d states and no DFT+U correction indicates that the effect of the potential or the DFT+U correction is not significant, in that the strong adsorption of  $\text{Bi}_2\text{O}_3$  nanoclusters at rutile (110) is not affected.

The  $\text{Bi}_2\text{O}_3$  nanocluster bonds to the rutile (110) surface with three new bonds between oxygen from the nanocluster and Ti from the surface, with O-Ti distances of 1.91, 1.93 and 2.10 Å. Bi atoms in the nanocluster bind to two bridging oxygen from the surface, with O-Bi distances of 2.24 and 2.26 Å, which are consistent with Bi-O distances in  $\text{Bi}_2\text{O}_3$ . Within the

$\text{Bi}_2\text{O}_3$  nanocluster, the Bi-O distances are 2.02 and 2.21 Å for one Bi atom and 2.05 and 2.23 Å for the second Bi atom.

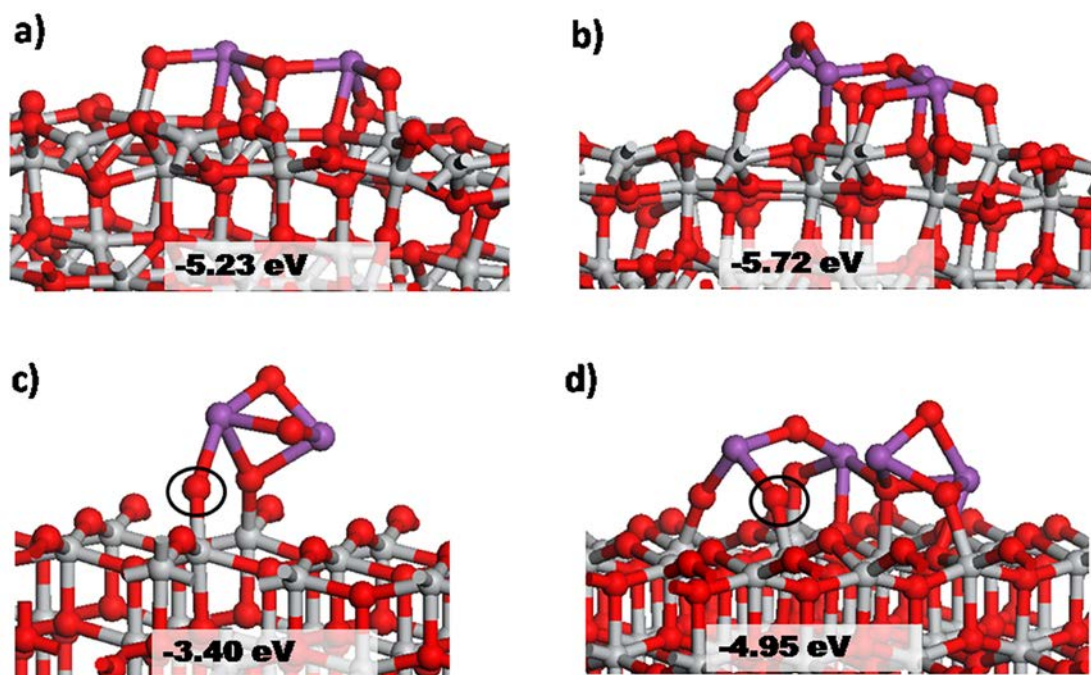


**Figure 1.** Relaxed adsorption structures with adsorption energies given in eV for (a)  $\text{Bi}_2\text{O}_3$ , (b)  $\text{Bi}_4\text{O}_6$  and (c)  $\text{Bi}_6\text{O}_9$  nanoclusters supported on rutile (110)  $\text{TiO}_2$ . Ti atoms are grey spheres, oxygen is red and Bi atoms are purple and this colour scheme is used throughout the paper.

The adsorption of the  $\text{Bi}_4\text{O}_6$  nanocluster results in five new bonds between the nanocluster and the surface. There are two bonds from Bi atoms to bridging surface oxygen, which have Bi-O distances of 2.17 Å. There are three new bonds between oxygen in the nanocluster and the 5-fold coordinated Ti surface atoms, with Ti-O distances in the range of 1.83 Å to 2.05 Å. In the largest  $\text{Bi}_2\text{O}_3$  nanocluster, there is a new Bi-O bond to bridging oxygen in the surface, with a distance of 2.37 Å, while oxygen from the nanocluster bind to Ti atoms in the surface, with Ti-O distances of 1.94 and 1.86 Å. Bi-O distances in the nanocluster range from 2.09 to 2.28 Å, with low coordinated oxygen in the nanocluster displaying the longest Bi-O distances.

Comparing with Bi-O bond distances in bulk  $\text{Bi}_2\text{O}_3$ , which lie in the range of 2.19 Å to 2.59 Å [47], the Bi-O distances in the nanoclusters are generally shorter, arising from the lower coordination of Bi in the nanoclusters compared to bulk. The surface Ti atoms that bind to the

nanocluster are pulled out of the surface layer by the interaction with oxygen and this displacement is around 0.45 Å, lengthening the subsurface Ti-O distances involving these Ti atoms to around 2.20 Å.



**Figure 3.** Relaxed adsorption structures with adsorption energies given in eV for (a)  $\text{Bi}_2\text{O}_3$  modified anatase (101) (b)  $\text{Bi}_4\text{O}_6$  modified anatase (101), (c)  $\text{Bi}_2\text{O}_3$  modified anatase (001) and (d)  $\text{Bi}_4\text{O}_6$  modified anatase (001). The colour scheme is the same as figure 2 and the rings around oxygen atoms in (c) and (d) indicate oxygen from the anatase (001) surface that are pulled out of the surface layer upon interaction with the  $\text{Bi}_2\text{O}_3$  nanoclusters.

Figure 3 shows the atomic structure of  $\text{Bi}_2\text{O}_3$  and  $\text{Bi}_4\text{O}_6$  nanoclusters adsorbed on the anatase (101) and (001) surfaces. Both  $\text{Bi}_2\text{O}_3$  nanoclusters adsorb strongly at the two anatase surface, making a number of new nanocluster-surface interfacial bonds. The adsorption energies at both anatase surfaces are negative, again indicating a strong interfacial interaction between the nanocluster and the surface. The adsorption energies at anatase (101) are similar



to those are rutile (110) and both are notably larger than at anatase (001). The origin of this difference will be discussed in the following paragraphs. We further find that the strong adsorption of  $\text{Bi}_2\text{O}_3$  nanoclusters at anatase (001) is not affected by using the 12 valence electron potential on Ti or a lack of +U correction on the Ti 3d states (see supporting information).

For  $\text{Bi}_2\text{O}_3$  adsorbed at the anatase (101) surface, there is one new bond between each oxygen in the nanocluster and a 5-fold coordinated surface Ti atom, with O-Ti distances of 1.88, 1.90 and 2.04 Å. Each Bi in the nanocluster binds to two surface terminating oxygen atoms, with Bi-O distances of 2.22 and 2.27 Å, typical of Bi-O distances. Within the nanocluster, the Bi-O distances are 2.13 – 2.27 Å, similar to  $\text{Bi}_2\text{O}_3$  adsorbed at rutile (110).

At anatase (001), the  $\text{Bi}_2\text{O}_3$  nanocluster adsorbs in an interesting fashion. There is a new O-Ti bond involving oxygen from the nanocluster, with an O-Ti distance of 1.92 Å. When the nanocluster adsorbs at anatase (001), a surface oxygen atom is pulled out of the terminating layer of oxygen atoms to make a new bond to a Bi atom in the nanocluster, with a Bi-O distance of 2.19 Å; the removal of an oxygen from the anatase (001) surface upon adsorption of metal oxide nanoclusters has been seen in our previous work on  $\text{SnO}_2$  [29] and  $\text{SnO}$  [33] modified anatase (001). There is an energy cost associated with displacing this oxygen off its lattice site and since the overall adsorption energy is a balance between energy gained when making new interfacial bonds and the energy cost to distort the surface, this energy cost contributes to the smaller nanocluster adsorption energy found at anatase (001) compared to rutile (110) or anatase (101). Within the  $\text{Bi}_2\text{O}_3$  nanocluster, the Bi-O distances are 2.06 – 2.33 Å.

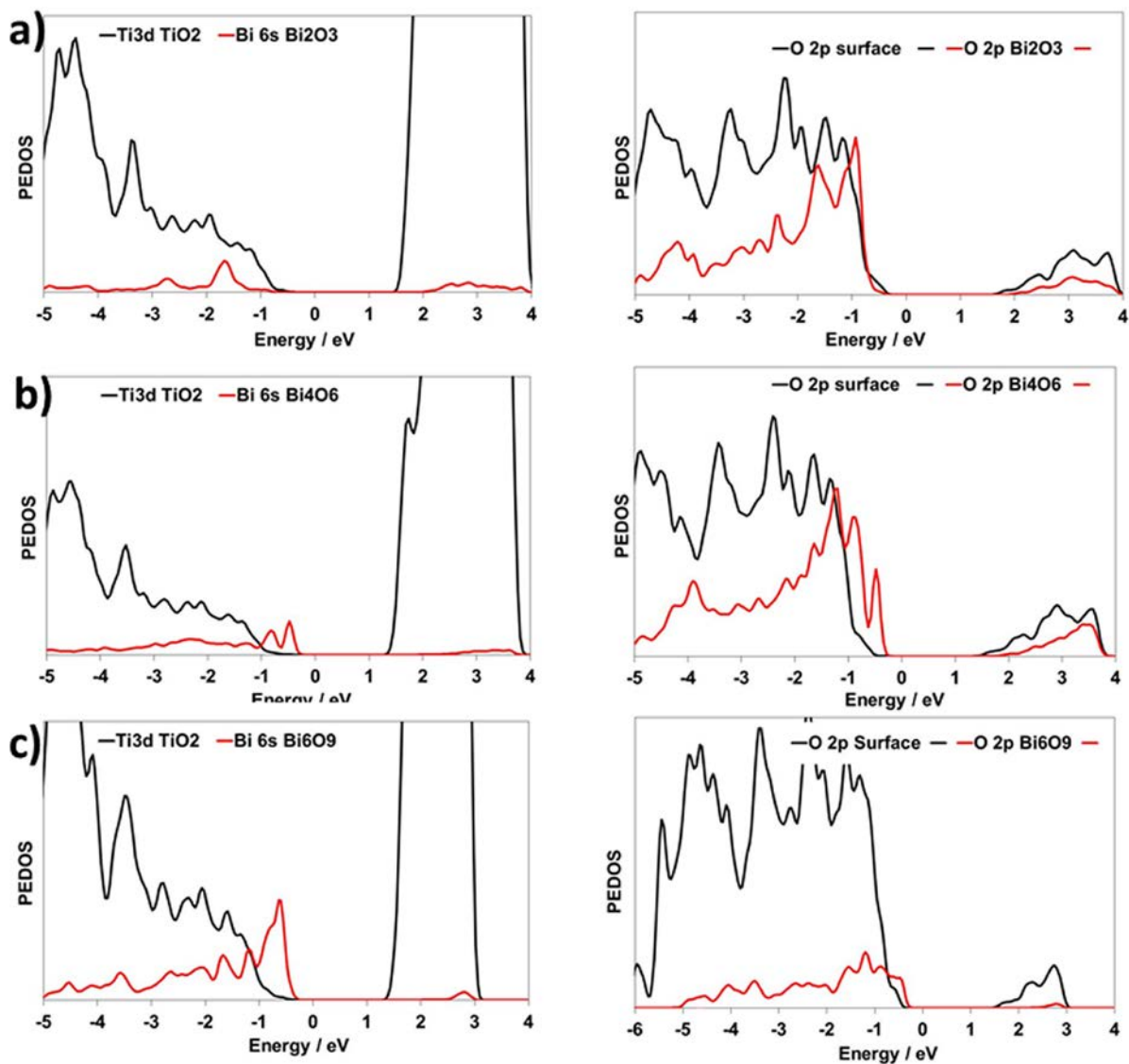
For  $\text{Bi}_4\text{O}_6$  adsorption at both surfaces, we observe again that at anatase (001) an oxygen from the surface layer of anatase (001) is pulled out of the surface to make a new Bi-O bond, with a Bi-O distance of 2.06 Å. This Bi is only 3-fold coordinated, with short Bi-O distances of

2.07 and 2.11 Å to oxygen in the nanocluster. Two further nanocluster Bi atoms make new bonds to anatase (001), with Bi-O distances of 2.16 and 2.35 Å. There are three new O-Ti bonds between nanocluster oxygen and Ti in the surface, with distances of 1.86, 2.08 and 2.10 Å. At the (101) surface, four new Bi-O bonds to the surface are formed, with Bi-O distances of 2.14, 2.24, 2.14 and 2.17 Å, which are typical of the Bi-O distances found in the interface between the nanocluster and the surface. There are also four new bonds between nanocluster oxygen and surface Ti, with distances of 1.87, 1.89, 2.0, 2.01 and 2.06 Å; the shortest O-Ti distances are for the 2-coordinated oxygen atoms in the nanocluster.

### **3.2 Electronic Structure and Band Gap Changes in TiO<sub>2</sub> Rutile and Anatase Surfaces Modified with Bi<sub>2</sub>O<sub>3</sub> Nanoclusters.**

Figures 4 to 6 present the electronic density of states (PEDOS) projected onto Bi 6s and O 2p states of the Bi<sub>2</sub>O<sub>3</sub> nanoclusters and Ti 3d and O 2p states of TiO<sub>2</sub> modified with Bi<sub>2</sub>O<sub>3</sub> nanoclusters. The PEDOS are shown for rutile (110) in figure 4, anatase (101) in figure 5, and anatase (001) in figure 6. The PEDOS plots allow us to investigate any band gap changes due to modifying TiO<sub>2</sub> with Bi<sub>2</sub>O<sub>3</sub> nanoclusters.

The PEDOS plots show that the effect of the Bi<sub>2</sub>O<sub>3</sub> modification of rutile (110) depends on the nanocluster size; this corresponds to a change in nanocluster loading in experimental work on surface modification of TiO<sub>2</sub> [29]. The modification of rutile (110) with the Bi<sub>2</sub>O<sub>3</sub> nanocluster makes no change in the energy gap of TiO<sub>2</sub>. The Bi 6s and Bi<sub>2</sub>O<sub>3</sub>-derived O 2p states lie below the VB edge of TiO<sub>2</sub> and will therefore not modify the energy gap. Similarly, empty Bi<sub>2</sub>O<sub>3</sub> nanocluster states lie above the rutile (110) CB edge. Thus, the VB-CB gap in unmodified and Bi<sub>2</sub>O<sub>3</sub>-modified TiO<sub>2</sub> is 2.1 eV in both cases.



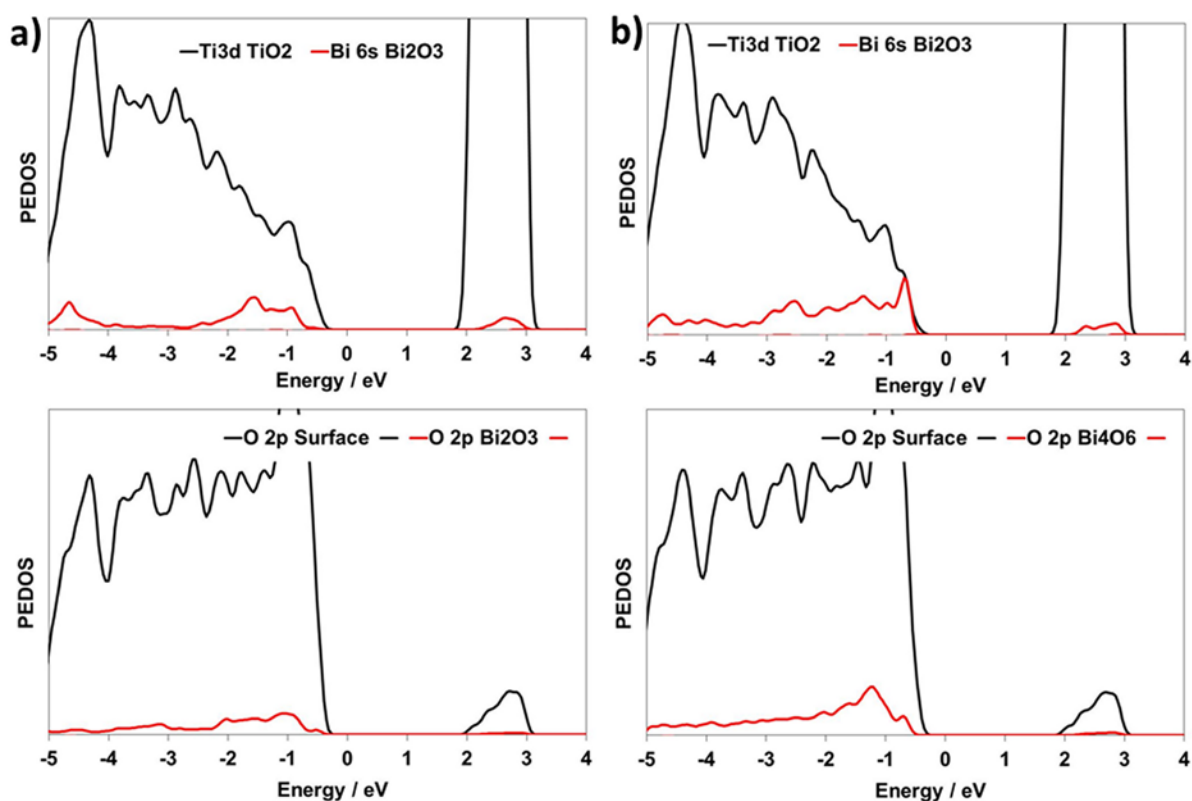
**Figure 4:** Electronic density of states projected (PEDOS) onto Bi 6s and Ti 3d (left panels) and O2p (from the nanocluster and the  $\text{TiO}_2$  surface, right panels) states for (a)  $\text{Bi}_2\text{O}_3$ , (b)  $\text{Bi}_4\text{O}_6$  and (c)  $\text{Bi}_6\text{O}_9$  nanoclusters supported on  $\text{TiO}_2$  rutile (110) surface. The zero of energy is the Fermi level.

However when we examine the PEDOS for the larger  $\text{Bi}_4\text{O}_6$  and  $\text{Bi}_6\text{O}_9$  nanoclusters, we find in both cases, the modification of rutile (110) introduces new electronic states derived from  $\text{Bi}_2\text{O}_3$  into the band gap of rutile  $\text{TiO}_2$ . These states are derived from the Bi6s-O2p

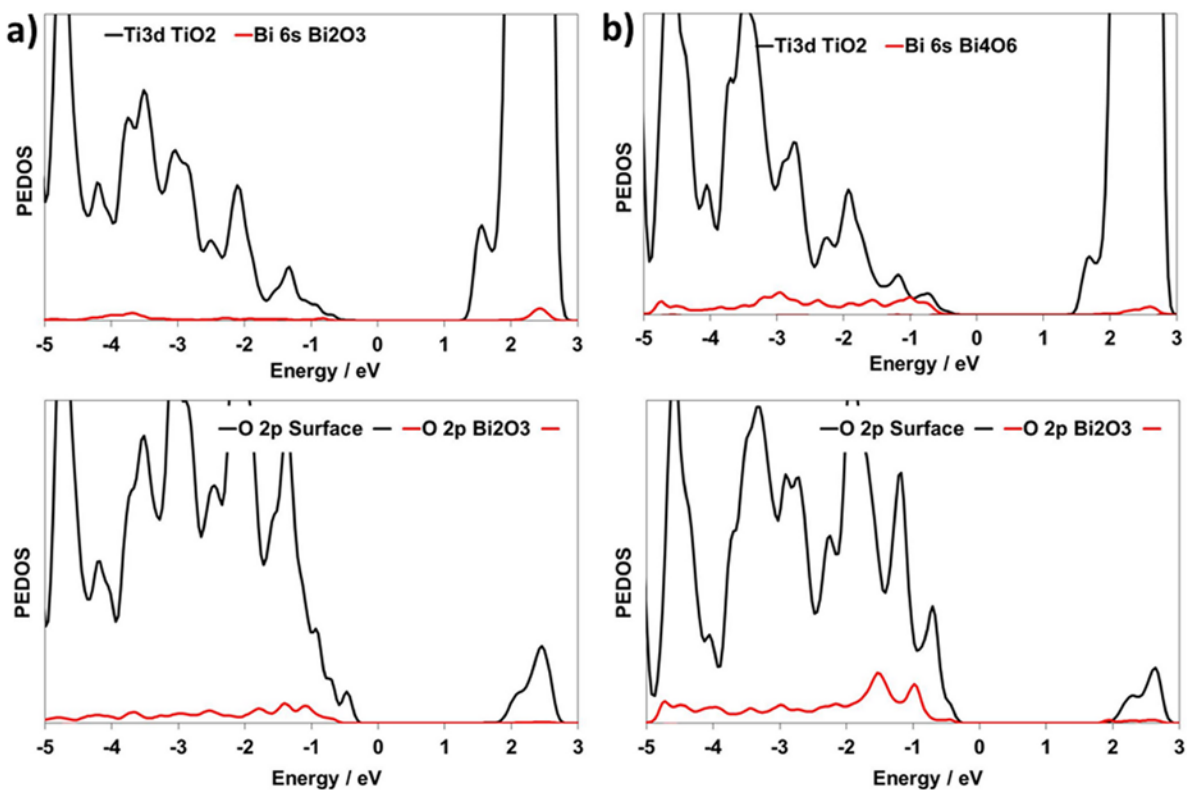
interaction, that is the lone pair, in the  $\text{Bi}_2\text{O}_3$  nanoclusters. These nanocluster derived states lie above the valence band edge of the rutile (110) surface, and as a consequence the original band gap of  $\text{TiO}_2$  will be reduced by the upwards shift in the energy of the valence band edge. The CB edge is unmodified by the surface modification. This size of the shift in the energy gap is 0.3 eV for the  $\text{Bi}_4\text{O}_6$  nanocluster and 0.1 eV for the  $\text{Bi}_6\text{O}_9$  nanocluster and for the former nanocluster, may be large enough to induce some visible light absorption upon photoexcitation. We will return to this point in a subsequent section.

When we compare the effect of the Ti potential and the +U correction on the PEDOS of  $\text{Bi}_2\text{O}_3$ -rutile (110), see supporting information, we find that there is no change to the general picture discussed above. Irrespective of the choice of Ti potential or DFT+U correction, there is no change to the VB or CB edges of rutile (110). This provides confidence in our chosen computational set-up for this problem.

In figures 5 and 6 we display the PEDOS for anatase (101) and (001) surfaces modified with  $\text{Bi}_2\text{O}_3$  and  $\text{Bi}_4\text{O}_6$  nanoclusters. From the PEDOS a striking difference with modified rutile (110) is immediately apparent. The PEDOS for  $\text{Bi}_4\text{O}_6$ -modified anatase (101) and (001) does not show a change in the nature of the valence band edge – the  $\text{Bi}_2\text{O}_3$  derived electronic states lie below the CB edge of both anatase surfaces, with the VB to CB energy gap unchanged over unmodified anatase (101) and (001), at 2.3 eV.



**Figure 5:** Electronic density of states projected (PEDOS) onto Bi 6s and Ti 3d (top panels) and O2p (from the nanocluster and the TiO<sub>2</sub> surface, bottom panel) states. (a) Bi<sub>2</sub>O<sub>3</sub> and (b) Bi<sub>4</sub>O<sub>6</sub> nanocluster modified anatase (101) surface. The zero of energy is the Fermi level.



**Figure 6:** Electronic density of states projected (PEDOS) onto Bi 6s and Ti 3d (top panels) and O2p (from the nanocluster and the TiO<sub>2</sub> surface, bottom panel) states. (a) Bi<sub>2</sub>O<sub>3</sub> and (b) Bi<sub>4</sub>O<sub>6</sub> nanocluster modified anatase (001) surface. The zero of energy is the Fermi level.

The final point from the PEDOS analysis is the composition of the VB and CB in modified TiO<sub>2</sub> which will give an indication of the expected sites for electron and hole localisation which is important for charge separation and photocatalytic activity. Taking, Bi<sub>4</sub>O<sub>6</sub> modified rutile and anatase surfaces as an example, in Bi<sub>4</sub>O<sub>6</sub>-rutile, the valence band edge is derived primarily from Bi 6s and O 2p states in the nanocluster and the conduction band edge is derived from Ti 3d states of the surface. This composition of the VB and CB edges will result in hole localisation on the Bi<sub>4</sub>O<sub>6</sub> nanocluster and electron localisation on the rutile (110) surface which will enhance electron/hole separation after photoexcitation.

On the other hand, for  $\text{Bi}_4\text{O}_6$ -modified anatase surfaces a different fate is predicted for the photoexcited electrons and holes: both electrons and hole will be localised onto the rutile (110) surface, which will lead to no improvement in charge carrier separation upon excitation with light of energy around the band gap energy. However, comparing to other oxide-modified anatase structures where no visible light activity is induced, e.g.  $\text{SnO}_2$ -modified anatase [23, 29], the presence of unoccupied  $\text{Bi}_4\text{O}_6$  states above the  $\text{TiO}_2$  CB means that with sufficiently energetic UV radiation, an electron can be promoted to empty  $\text{Bi}_4\text{O}_6$  nanocluster states that would facilitate charge separation in this case. The excited electron could reduce  $\text{O}_2$  to superoxide, which would be reactive in decomposition of organic molecules.

We have previously shown that  $\text{FeO}_x$  [27],  $\text{Ga}_2\text{O}_3$  [31] and  $\text{NiO}$  [32] nanocluster modification of rutile  $\text{TiO}_2$  can also produce a similar band gap narrowing to  $\text{Bi}_4\text{O}_6/\text{Bi}_6\text{O}_9$ -modified rutile, due to a widening of the valence band arising from an upwards shift in the VB edge as a result of the introduction of electronic states from the oxide nanocluster above the  $\text{TiO}_2$  VB edge. All these oxides form strong interfacial bonds to rutile, which is a key factor in determining the effect of the oxide nanocluster modification on the electronic structure. There have been fewer such studies on modified anatase, but we have found that the larger energy gap for anatase compared to rutile can result in no change in the energy gap for modified anatase, e.g. for  $\text{SnO}_2$  [29], which is also found in the present work.

#### **4. Electron and Hole Localisation in a Model of the Photoexcited State**

To study charge separation and localisation in  $\text{Bi}_2\text{O}_3$  modified  $\text{TiO}_2$ , we use a model of the photoexcited state, as discussed in section 2. For unmodified  $\text{TiO}_2$  refs. 31, 43 and 44 have examined electron and hole localisation in bulk anatase and the (101) surface [43], in rutile

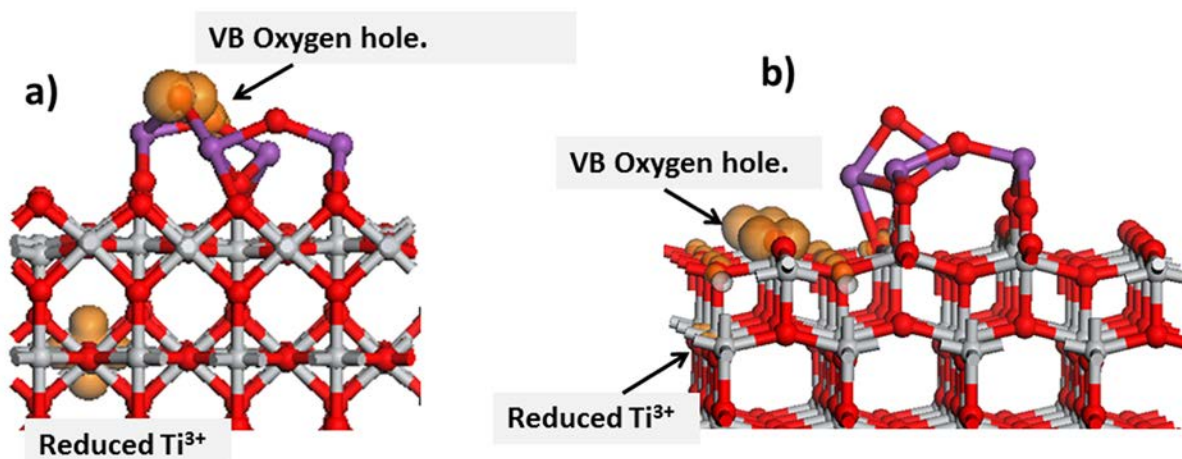
(110) [31, 44] and in modified rutile (110) [31]. Hybrid DFT or DFT+U are required in order to describe the localised charge carriers and their polaronic nature.

Figure 7 shows the computed excess spin density for two examples: (1) the  $\text{Bi}_4\text{O}_6$  nanocluster supported on rutile (110) and (2) the  $\text{Bi}_4\text{O}_6$  nanocluster supported on anatase (001). The spin density is used to determine the positions of the electron and hole and their localisation in the photoexcited state.

In the photoexcited state of  $\text{Bi}_4\text{O}_6$ -modified rutile, the electron is localised on a surface Ti site which reduced to  $\text{Ti}^{3+}$  species and this is further confirmed by a calculated Bader charge [48] of 1.67 electrons and a computed spin magnetisation of 0.9 electrons. This localisation is accompanied by a strong elongation in the Ti-O distances of 0.1 Å, typical of the elongation of Ti-O distances around a  $\text{Ti}^{3+}$  polaron. The electronic hole is localised on a 2-fold coordinated oxygen atom in the  $\text{Bi}_4\text{O}_6$  nanocluster, with a computed Bader charge of 6.7 electrons and a spin magnetisation of 0.73 electrons. The Bi-O distances around this oxygen are elongated to 2.29 and 2.37 Å, consistent with a localised oxygen hole polaron. There is a slight spreading of the hole onto a second O atom from the cluster, which has a small change in the Bader charge from 7.30 electrons for  $\text{O}^{2-}$  to 7.09 and a small spin magnetisation 0.14 electrons. Nonetheless, it is clear that the valence band hole localises onto a low coordinated oxygen site in the  $\text{Bi}_4\text{O}_6$  nanocluster.

We see that there is no  $\text{Bi}^{3+}$  contribution to the electronic hole despite the presence of Bi 6s electronic states around the valence band edge. This would be consistent with the weaker lone pair effect in  $\text{Bi}_2\text{O}_3$ , when compared to  $\text{SnO}$ , which shows a stronger lone pair effect [35].





**Figure 7.** Computed excess spin density isosurfaces for the photoexcited state of the  $\text{Bi}_4\text{O}_6$  cluster supported on (a) the rutile (110) surface and (b) the anatase (001) surface. The spin density isosurfaces enclose spin densities up to  $0.02 \text{ electrons} / \text{\AA}^3$ .

Figure 7(b) shows the spin density for  $\text{Bi}_4\text{O}_6$ -modified anatase (001). Here we see a difference compared to  $\text{Bi}_4\text{O}_6$  modified rutile. There is no localisation of the excited electron or hole onto the nanocluster, which is consistent with the simple analysis of the DOS presented above, which indicates that the photoexcited hole would be found on oxygen from anatase and the photoexcited electron would be found on Ti from anatase. The spin density shows that the hole is spread over two surface oxygen atoms (similar to hole localisation on bare anatase (001) [33]), while the electron is spread over subsurface Ti atoms, each of which is partially reduced.

The singlet-triplet excitation energy for  $\text{Bi}_4\text{O}_6$ -modified rutile (110) is 1.20 eV, which is smaller than the same energy for unmodified rutile (110), which is 1.69 eV [31]. This is consistent with the finding from the DOS analysis and indicate that this modification of rutile will be beneficial in inducing absorption of longer wavelength light. The relaxation energy is

0.83 eV, which is consistent with localisation of the hole on the nanocluster and subsequent relaxation of the structure in response to the formation of the localised oxygen hole [31, 33]. For  $\text{Bi}_4\text{O}_6$ -modified anatase, the computed singlet-triplet excitation energy is 1.89 eV, which is a small reduction over the vertical singlet-triplet energy of 2.01 eV, consistent with the electron and hole being found on the surface, where large relaxations are not possible. These findings support the analysis of the density of states that modifying rutile with  $\text{Bi}_2\text{O}_3$  nanoclusters can reduce the energy gap, but that modifying anatase will not reduce the energy gap.

## 5. Conclusions

We have presented the results of a first principles DFT analysis of modification of  $\text{TiO}_2$  rutile (110) and anatase (101) and (001) with nanoclusters of bismuth oxide. We investigated the changes in the band gap of the modified material over pure  $\text{TiO}_2$  rutile (110) together with the potential of enhanced electron/hole separation upon photoexcitation.

Our DFT results reveal that modification of rutile (110) with  $\text{Bi}_2\text{O}_3$  nanoclusters can induce a reduction of the original band gap of unmodified rutile (110), by an upwards shift in the valence band edge and this is dominated by Bi 6s and O 2p states from the  $\text{Bi}_2\text{O}_3$  nanocluster. The exact effect depends on the size, or loading, of the nanocluster on the surface. This will reduce the band gap but the reduction may not be sufficiently large to induce activity in the visible region upon photoexcitation. Enhanced activity in the UV region will be likely. In contrast, modifying anatase surfaces with  $\text{Bi}_2\text{O}_3$  nanoclusters will lead to no change in the band gap, with no modifications to the valence or conduction band.

A model of the photoexcited states shows that the  $\text{Bi}_2\text{O}_3$ -rutile structure will enhance the separation of hole and electrons upon photoexcitation by localising the hole and electron on the nanocluster and the surface, respectively. A comparison with SnO modified  $\text{TiO}_2$  rutile (110) [33] shows that the lone pair effect is weaker in  $\text{Bi}_2\text{O}_3$  than in SnO nanoclusters which is similar to the findings of bulk SnO and  $\text{Bi}_2\text{O}_3$  [35]. For  $\text{Bi}_2\text{O}_3$  modified anatase, the electron and hole are localised onto the anatase surface.

These results show that the change in the key properties for photocatalytic activity in  $\text{TiO}_2$  can be modified by choice of  $\text{TiO}_2$  crystal form and the size (or loading) of the modifying oxide nanocluster.

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