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## Single oxygen vacancies of (TiO<sub>2</sub>)<sub>35</sub> as a prototype of reduced nanoparticle: Implication to photocatalytic activity

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Titanium dioxide (TiO<sub>2</sub>), as a semiconductor metal oxide, has been one of the most popular materials studied in the field of photocatalysis. In the present study, the properties of single oxygen vacancies of (TiO<sub>2</sub>)<sub>35</sub>, a prototype of anatase nanoparticle, were investigated by DFT calculations. (TiO<sub>2</sub>)<sub>35</sub> is the minimum sized model (~ 2 nm) as bipyramidal nanoparticle with anatase phase and eight {101} facets. All the available oxygen vacancies at various sites according to position, coordination number, and distance from the center atom were examined. The geometric, energetic and electronic properties of the reduced TiO<sub>2</sub> clusters were analyzed by hybrid DFT functionals with different Hartree-Fock exchange ratio (0, 12.5 and 25 %). It was found that the structure of pristine (TiO<sub>2</sub>)<sub>35</sub> is somewhat different from bulk lattice with relatively high surface to volume ratio. Moreover, the particular high (three)-coordinated oxygen atom is energetically most favorable for oxygen vacancy formation from nanoparticle mainly due to substantially high relaxation energy. TiO<sub>2</sub> nanoparticle has low oxygen vacancy formation energy and narrow band gap by defect state, and can be utilized as an efficient photocatalyst material.

### Introduction

Titanium dioxide (TiO<sub>2</sub>) is an important metal oxide for a number of applications including photocatalysis<sup>1, 2</sup> and solar cells.<sup>3-5</sup> To use solar energy as a sustainable energy source, semiconductors for water splitting photocatalyst have to satisfy demands such as optimal band gap, low cost, nontoxicity, stability, and so on. In spite of excellent properties of TiO<sub>2</sub> as a photocatalytic material, its wide band gap (~ 3.2 eV) leads to low efficiency for visible light absorption. Hence many strategies have been developed to reduce the band gap by means of native defects,<sup>6</sup> chemical doping,<sup>7-10</sup> and point defects.<sup>11-14</sup>

Among three kinds of TiO<sub>2</sub> polymorph (anatase, rutile and brookite), rutile is the most stable bulk phase, while most nanomaterials prefer anatase structure due to the lower surface energy of anatase phase than others.<sup>15-17</sup> Nanoparticles (NPs) show remarkably high catalytic performance compared with bulk phase due to large surface area and quantum confinement effect. Though many results have been reported on the properties of TiO<sub>2</sub> systems, theoretical studies are commonly concerning about periodic bulk or surface models. Compared to TiO<sub>2</sub> bulk, NPs are composed of strained lattices, mixed phases or interfaces with

several defects.<sup>18</sup> On the other hand, the isolated TiO<sub>2</sub> clusters, Ti<sub>n</sub>O<sub>2n</sub> (n < 17),<sup>10, 19-21</sup> have been investigated to compare their structures and properties with those of the bulk phases. However, the structure of clusters composed of few atoms is substantially different from that of the TiO<sub>2</sub> bulk and the cluster size is too small to explain the experimental observation. Thus, a systematic investigation on geometric and electronic properties of TiO<sub>2</sub> NPs, with enough size to maintain lattice structure and facet, different from bulk or slab surface is challenging and attractive. Our recent study revealed that the calculated cluster (TiO<sub>2</sub>)<sub>35</sub> retained the facets found in nanoparticles studied in experiment,<sup>22</sup> thus clusters smaller in size than (TiO<sub>2</sub>)<sub>35</sub> may not give electronic and optical properties of nanoparticles.

Point defects such as oxygen vacancy (O<sub>v</sub>) and titanium interstitial play an important role in photocatalytic reaction. O<sub>v</sub>, one neutral oxygen vacancy, provides two excess electrons to TiO<sub>2</sub> system and these electrons are responsible for the reduction of Ti<sup>4+</sup> to Ti<sup>3+</sup>. The formation of Ti<sup>3+</sup> species upon reduced TiO<sub>2</sub> were confirmed by several kinds of experimental observations, such as photoelectron spectroscopy,<sup>23</sup> electron paramagnetic resonance (EPR),<sup>11</sup> and shift in the core level binding energies.<sup>24</sup> The defect states originating from trapped electrons appear around 1.0 eV below the conduction band minimum (CBM), which induces band gap narrowing as optimal value for photocatalyst.<sup>23, 25-27</sup> Many theoretical studies were also conducted about the properties of O<sub>v</sub> in TiO<sub>2</sub> system such as O<sub>v</sub> in bulk,<sup>9, 28-34</sup> surface and subsurface,<sup>35, 36</sup> and polaronic nature induced by O<sub>v</sub><sup>37-39</sup> using various calculation methods. However, to the best of our knowledge, the property of O<sub>v</sub> in isolated system considering the effect of

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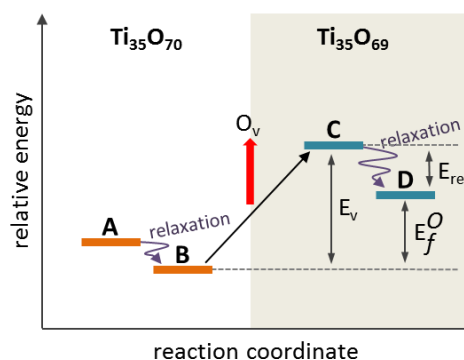
various oxygen sites, even in small cluster model, is not reported yet. Therefore, understanding  $O_v$  in  $TiO_2$  NPs would be interesting for applications as an efficient photocatalytic material.

The analysis of excess electron or  $Ti^{3+}$  centers is important to understand  $O_v$  in  $TiO_2$  NP. From theoretical aspect, the computational methods based on density functional theory (DFT) have been chosen to describe diverse properties of many materials, but there are several serious problems that could be addressed depending on methodology. Actually, it is well known that DFT method using Perdew, Burke and Ernzerhof (PBE) functional,<sup>40</sup> one of the most commonly used DFT functional classified as Generalized Gradient Approximation (GGA) functionals, describes dispersive-unpaired electrons in order to reduce the Coulomb repulsion even in fully localized systems.<sup>41-44</sup> Owing to such kind of dispersive effect on unpaired electrons, abnormally strong delocalized solutions were obtained for reduced  $TiO_2$  systems. Moreover, PBE functional gives underestimated band gap for  $TiO_2$  systems. To solve these problems, usage of hybrid DFT functionals containing certain amount of Hartree-Fock exchange was suggested. Among many hybrid DFT functionals, B3LYP (20 %Fock)<sup>45</sup> and PBE0 (25 %Fock)<sup>46</sup> have been most widely used in theoretical studies. Even though hybrid functional properly described the presence of localized defect state on reduced  $TiO_2$ ,<sup>47</sup> these popular hybrid functionals containing high amount of HF generally give the overestimated band gap of oxide semiconductors.<sup>48</sup>

Herein, we systemically investigate the properties of stoichiometric  $(TiO_2)_{35}$  anatase NP and neutral single oxygen removed one. The bipyramidal  $(TiO_2)_{35}$  NP, maintaining anatase structure after geometrical relaxation, seems to be a proper model to study the physical and electronic properties of oxygen vacancy in  $TiO_2$  NP by comparing those of bulk and slab surface. Furthermore, the size ( $\sim 2$  nm) is also appropriate to rationalize the experimental result about  $TiO_2$  NPs. Various oxygen vacant sites, representing the whole one, are examined according to position, coordination number (CN) and bond length with adjoined Ti. A modified PBE0 hybrid,<sup>34</sup> which is considered to be suitable to describe  $O_v$  properties of  $TiO_2$  bulk, is used to compare with more popular functionals (PBE and PBE0). Unlike in the bulk material, the well-ordered  $TiO_2$  anatase structure is partially changed for relatively high surface to volume ratio and also because of the appearance of some under-coordinated atoms ( $Ti_{4c}$ ,  $Ti_{5c}$  and  $O_{1c}$ ) in the nanoparticle. Moreover, oxygen vacancy formation energy ( $E_f^O$ ) of the particular three-coordinated facet site is surprisingly small than those on other  $TiO_2$  systems.

## Computational detail

All calculations were carried out using the first-principles electronic structure theory based on DFT using all electron numerical atom-centered orbitals that is supplied by Fritz Haber Institute *ab initio* molecular simulations (FHI-aims) program package.<sup>49</sup> DFT calculations have been conducted by different hybrid functionals (the exact HF exchange is partly



**Fig. 1** The energy diagram according to  $O_v$  calculation sequence. **A** is initial bipyramidal  $TiO_2$  NP ( $Ti_{35}O_{70}$ ) modeled from  $TiO_2$  anatase bulk structure and **B** is the optimized geometry of **A**. **C** ( $Ti_{35}O_{69}$ ) has the same geometry as **B** with one oxygen removal. **D** is the optimized structure of **C**.

mixed-in with the DFT exchange) with tight grid and tier-1 basis set. We have used PBE (0 %Fock), modified PBE0 (12.5 %Fock, hereafter referred to as PBEx)<sup>34</sup> and PBE0 (25 %Fock) functionals in this study. PBEx functional was a newly devised one that contains the optimal %Fock confirmed by the calculated electronic structures and physical properties for  $O_v$  in  $TiO_2$  bulk polymorphs.<sup>34</sup> PBE results would be less reliable in this  $O_v$  study, but the results of three functionals are presented in this paper to compare the functional effect in the description of  $TiO_2$  NP properties. For the case of  $O_v$ , with two excess electrons, closed-shell singlet and open-shell triplet states were calculated and we analysed the result from the more stable one. The scalar-relativistic effects treated at the scaled zero-order regular with collinear spin (ZORA) level were taken into account. To optimize pristine and reduced NPs, the convergence criteria for geometry relaxations were set to  $10^{-2}$  eV/Å.

The oxygen vacancy formation energy ( $E_f^O$ ) at various oxygen sites is calculated as:

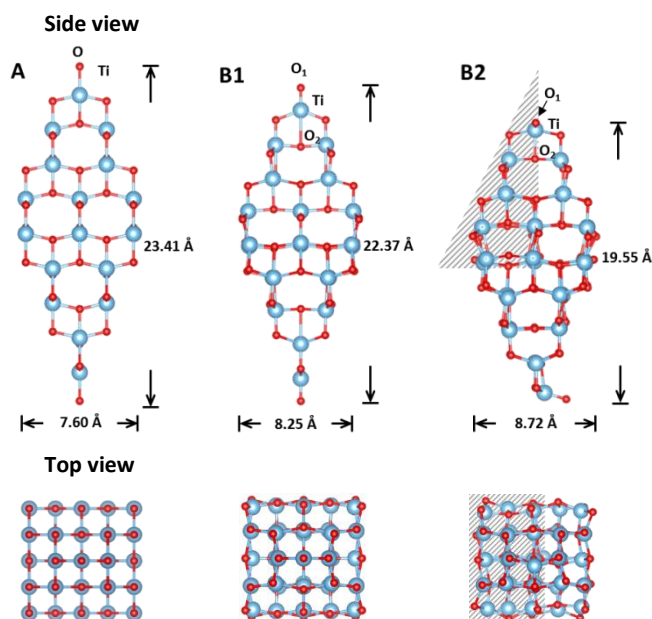
$$E_f^O = E(Ti_{35}O_{69}) + \frac{1}{2}E(O_2) - E(Ti_{35}O_{70}) \quad (1)$$

where  $E(Ti_{35}O_{70})$  and  $E(Ti_{35}O_{69})$  are the total energies of the pristine and reduced  $TiO_2$  NP that are fully relaxed structures using each functional, respectively.  $E(O_2)$  is the energy of  $O_2$  molecule in its triplet ground state. Herein, positive value of  $E_f^O$  stands for the extra energy required to form  $O_v$ . Fig. 1 shows the schematic energy diagram of  $O_v$  formation according to our calculation process. **A** is initial pristine, bulk cut,  $TiO_2$  NP (**A** in Fig. 2) that is modeled from  $TiO_2$  anatase bulk structure and **B** is the relaxed one. **C** is the single point geometry of  $Ti_{35}O_{69}$  NP with one oxygen atom is removed from **B**. **D** is the optimized structure of **C**. Here, we define the following energetics.

$$E_f^O = E(D) + \frac{1}{2}E(O_2) - E(B) \quad (2)$$

$$E_v = E(C) - E(B) + \frac{1}{2}E(O_2) \quad (3)$$

$$E_{rel} = E_v - E_f^O = E(C) - E(D) \quad (4)$$



**Fig. 2** Pristine  $\text{TiO}_2$  NP structures are presented. Blue and red spheres denote titanium and oxygen atoms, respectively. Oxygen atoms marked in gray color represent the single oxygen vacancy site domain.

where  $E(\mathbf{B})$ ,  $E(\mathbf{C})$  and  $E(\mathbf{D})$  are the energy of **B**, **C** and **D** structures, respectively. Vertical energy ( $E_v$ ) and relaxation energy ( $E_{\text{rel}}$ ) are introduced to analyze  $E_f^0$ .

## Results and discussion

Fig. 2 shows the structures of pristine  $(\text{TiO}_2)_{35}$ . The  $\text{TiO}_2$  NP was basically designed as the bipyramidal anatase structure (A) that was suggested by Barnard et al.<sup>50</sup> The initial structure was constructed by cutting  $\{101\}$  surface planes known to have the lowest surface energy for anatase  $\text{TiO}_2$  polymorph. Thus, the strategy of designing NP follows the Wulff-construction method.<sup>51</sup> There are two different optimized geometries (denoted as B1 and B2) for **B** of  $(\text{TiO}_2)_{35}$  NP. B1 coincides with the optimized geometry of  $\text{TiO}_2$  NP in previous studies,<sup>50, 52</sup> where titanium atoms are relaxed inwards, oxygen atoms moves outward directions, and the  $\text{O}_1\text{-Ti-O}_2$  is almost linear (with angle of  $179.9^\circ$ ). However, Ti-O at both tips of B2 are bent to opposite sides (with angle  $\text{O}_1\text{-Ti-O}_2$  of  $113.2^\circ$ ) and titanium and oxygen atoms are more relaxed to each direction. As a result, the height of  $\text{TiO}_2$  NP is more shortened and the width becomes wider than B1. To the best of our knowledge, B2 was not reported yet, but it is more stable than B1 by around 1.06 eV for all the DFT functionals used. Unlike  $\text{TiO}_2$  bulk structure, the geometry of NP would easily change to decrease the higher surface to bulk ratio. In this study, the more stable B2 is adopted as  $\text{TiO}_2$  NP structure (**B** in Fig. 1). In  $\text{TiO}_2$  anatase bulk structure, axial Ti-O bond ( $\text{Ti-O}_{ax}$ , 2.01 Å) is longer than equatorial ones ( $\text{Ti-O}_{eq}$ , 1.94 Å) from DFT calculation (Fig. S1),<sup>7, 28</sup> which is slightly longer than experimental values (1.976 Å and 1.946 Å at 15 K).<sup>53</sup> Despite the lengths of  $\text{Ti-O}_{ax}$  and  $\text{Ti-O}_{eq}$  were set as 2.003 Å and 1.946 Å, respectively, in the initial geometry (A), brought from our

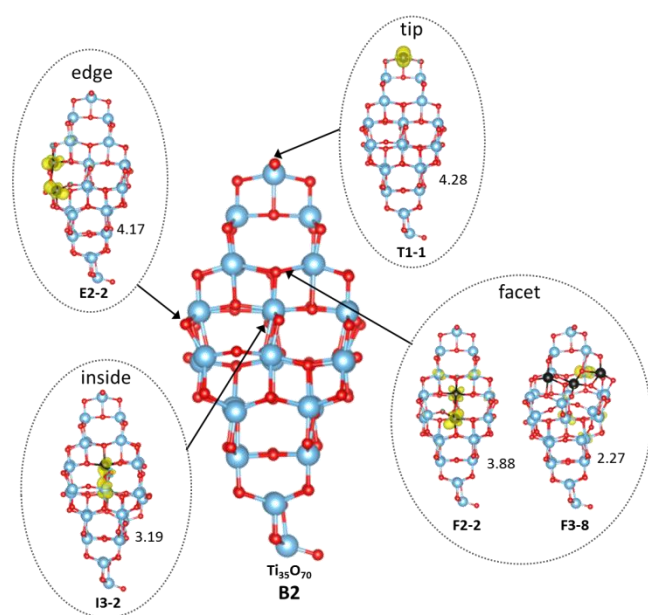
**Table 1** Geometrical parameters (height and width, in Å) and the energy values (in eV) of HOMO, LUMO, and HOMO-LUMO gap ( $\Delta E_{\text{H-L}}$ ) of B1 and B2.

		height	width	HOMO	LUMO	$\Delta E_{\text{H-L}}$
PBE	straight tip (B1)	22.54	8.31	-7.41	-4.98	2.43
	bent tip (B2)	19.64	8.78	-7.45	-4.85	2.60
PBEx	straight tip (B1)	22.37	8.25	-8.19	-4.60	3.59
	bent tip (B2)	19.55	8.72	-8.27	-4.46	3.81
PBE0	straight tip (B1)	22.22	8.20	-9.00	-4.19	4.81
	bent tip (B2)	19.43	8.66	-9.08	-4.04	5.05

previous study of  $\text{TiO}_2$  anatase bulk structure,<sup>34</sup> the distance of terminal  $\text{Ti-O}_1$  changed to  $1.592 \sim 1.619$  Å (depending on DFT functionals) and  $\text{Ti-O}_{ax}$  becomes shorter than  $\text{Ti-O}_{eq}$  around some 3-coordinated oxygen atoms ( $\text{O}_{3c}$ ) in B2 structure. The symmetry of well-ordered  $\text{TiO}_2$  anatase structure, consisting of  $\text{Ti}_{6c}$  and  $\text{O}_{2c}$ , is broken due to some under-coordinated titanium ( $\text{Ti}_{4c}$ ,  $\text{Ti}_{5c}$ ) and oxygen atoms ( $\text{O}_{1c}$ ) and bent  $\text{Ti-O}_1$  at tips.

Table 1 lists the calculated geometrical parameters and energy values of  $(\text{TiO}_2)_{35}$  NP depending on the structure types (B1 and B2) and DFT functional. The structural differences between B1 and B2 are similar in all DFT functionals used, as described above. In spite of the structural similarity, the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) ( $\Delta E_{\text{H-L}}$ ) depends highly on the functionals, as expected. For comparison, the calculated energy values of bulk anatase  $\text{TiO}_2$  are given in Table S1.<sup>28, 34, 39, 66</sup> Actually,  $\Delta E_{\text{H-L}}$  is only an approximation to the band gap and the quality of approximation is determined by the calculation methods.<sup>54</sup> In the case of DFT, it depends on the exchange-correlation potential and the ratio of HF in functional.<sup>55-57</sup> Among the values of  $\Delta E_{\text{H-L}}$ , the PBEx results are analogous with the experimental band gap of bulk anatase (3.20 eV<sup>58-60</sup>) and the  $\text{TiO}_2$  NP (mixture of rutile and anatase phase; ca. 3.10 eV<sup>61-63</sup>). Moreover, previous studies reported that optical band gap of  $\text{TiO}_2$  nanocrystal becomes large as crystal size decrease.<sup>27, 64, 65</sup> Therefore PBEx functional seems to be appropriate for the DFT calculation of  $\text{TiO}_2$  NP on the basis of the calculated  $\Delta E_{\text{H-L}}$  value. Hence, the structures and data calculated using PBEx are mainly presented for the sake of simplicity. Nevertheless, the results of PBE and PBE0 are included in the electronic supplementary information.

The properties of  $\text{O}_v$  in  $(\text{TiO}_2)_{35}$  NP were investigated by one neutral oxygen atom removal from B2. Among total 70 oxygen atoms in the  $(\text{TiO}_2)_{35}$  NP, there are 25 non-superimposable oxygen atoms by symmetry operation. Thus, 25 oxygen sites (marked in gray color in Fig. 2) were selected and removed one by one to examine the properties of single oxygen vacancy, which covers entire single oxygen vacancies. These vacancies were classified as tip (T), edge (E), facet (F),



**Fig. 3** Calculated structure of B2 and five representative structures for single oxygen vacant  $\text{Ti}_{35}\text{O}_{69}$  NP (D) at various  $\text{O}_v$  sites. Yellow color shows the spin density in isosurface of  $0.05 \text{ e}\cdot\text{au}^{-3}$ . Blue, red, and black spheres denote titanium, oxygen and first neighbored titanium atoms to the  $\text{O}_v$  site, respectively.  $E_f^O$  values in eV are also included.

and inside (I) type depending on the position of oxygen removed.

Fig. 3 displays the calculated structure of B2 and five representative structures for single oxygen vacant  $\text{Ti}_{35}\text{O}_{69}$  NP that were fully optimized after single oxygen atom removal from B2. These structures have the lowest  $E_f^O$  in each domain type (T, E, F, and I) of vacant oxygen atom sites depending on position and CN (Table 2). We name each single oxygen vacant state as  $X_m\text{-}n$  where  $X/m$  designates domain type/CN, and  $n$  is sequentially numbered according to the distance of the removed oxygen from the center of mass. For example, **F2-2** represents the oxygen vacant state where the oxygen second nearest from the center of mass and coordinated with two Ti atoms (CN=2) in facet domain was removed. The structures and energy values calculated using PBE and PBE0 functionals were presented in supporting information (Fig. S2 and S3). The spin densities are mainly distributed on d-orbital (mostly  $d_{z^2}$ , and partially  $d_{x^2-y^2}$ ) and the degree of localization on the neighboring Ti atoms which are reduced to  $\text{Ti}^{3+}$  and the corresponding distribution of spin density varies with the functional, which is similar to previous studies.<sup>28, 38</sup> One should warn that when fully localized solutions are involved, possible low lying electronic isomers may exist which differ in the position of the  $\text{Ti}^{3+}$  cation in the NP. However, these have not been further considered here. As %Fock increases in the DFT functional (PBE < PBE0 < PBE0),  $\text{O}_v$  from NP results in a solution that the spin density of two excess electrons are localized in some particular parts of NP. The excess electrons would initially move to the first-neighboring titanium atoms. In most cases, the spin density distribution is shown at these adjacent titanium atoms. Excess electrons stay at the only one nearest titanium atom in **T1-1**. For most of the reduced NPs with  $\text{O}_v$  at

edge and facet domains, excess electrons remain at least one nearest Ti atom and one disperse to other Ti atoms or transferred to another first-neighboring Ti. The excess electrons are mainly localized at the closer Ti atoms from the vacant site among two or three adjoined Ti atoms. In all  $\text{O}_v$  states generated in Inside domain and several  $\text{O}_v$  states in Facet domain that result in the reduced NPs having relatively more deformed structure, electrons transfer to Ti sites at longer distance from the oxygen vacant site. The geometrical distortion concomitant with localized spin stabilization contributes to relatively high  $E_{\text{rel}}$  and thus decrease  $E_f^O$ . **I3-2** has the lowest  $E_f^O$  value from the PBE result, while **F3-8** from the PBE0 and PBE0 results. This implies that the effect of %Fock on the properties of  $\text{O}_v$  may be site dependent and highlights the importance of using a DFT method properly describing as many properties of these materials as possible.

Reorganization of the structure around the vacant space (distance to neighboring titanium atoms) and the presence of two excess electrons induced by  $\text{O}_v$  would be major factors in the relaxation of the reduced  $\text{TiO}_2$  NP. The optimized structures and the lowest  $E_f^O$  sites are different depending on

**Table 2** Calculated (PBE0) values (in eV) of vertical energy ( $E_v$ ), relaxation energy ( $E_{\text{rel}}$ ), oxygen vacancy formation energy ( $E_f^O$ ), and energy level of oxygen vacancy defect state below LUMO ( $S_v\text{-}1$  and  $S_v\text{-}2$ ). All values are lined up in order of vacant oxygen atom distance from center of mass within each classification. In each classification, the lowest  $E_f^O$  value words in bold type.

position	CN <sup>a</sup>	site <sup>b</sup>	$E_v$	$E_{\text{rel}}$	$E_f^O$	$S_v\text{-}1$	$S_v\text{-}2$		
tip	1	<b>T1-1</b>	4.54	0.26	<b>4.28</b>	0.47	0.64		
		E2-1	5.87	1.38	4.49	0.81	1.64		
		E2-2	5.97	1.79	<b>4.17</b>	1.02	1.75		
edge	2	E2-3	5.97	1.61	4.37	0.84	1.85		
		E2-4	5.77	1.19	4.58	0.75	0.95		
		E2-5	6.14	1.27	4.87	0.72	1.55		
		E2-6	5.86	1.44	4.42	1.00	1.39		
		E2-7	5.98	0.83	5.15	0.84	1.74		
		facet	2	F2-1	5.47	1.53	3.94	0.68	1.28
				F2-2	5.29	1.40	<b>3.88</b>	0.68	1.28
F2-3	6.01			1.57	4.44	0.74	1.69		
3	F3-1		5.91	1.54	4.37	0.84	1.85		
	F3-2		6.03	1.76	4.27	0.55	1.78		
	F3-3		6.02	1.51	4.51	0.73	1.75		
	F3-4		6.23	2.03	4.21	1.09	1.43		
	F3-5		6.92	2.02	4.89	1.02	1.10		
	F3-6		6.36	1.71	4.65	0.86	1.71		
	F3-7		6.63	1.50	5.13	1.20	1.32		
inside	3	F3-8	6.48	4.21	<b>2.27</b>	0.71	1.17		
		F3-9	5.12	0.73	4.39		1.84		
		F3-10	5.63	0.84	4.79		1.65		
inside	3	I3-1	6.14	1.86	4.28	1.22	1.87		
		I3-2	5.76	2.57	<b>3.19</b>	0.96	1.15		
		I3-3	6.09	2.87	3.23	0.94	1.10		
		I3-4	6.06	1.91	4.15	0.93	2.06		

<sup>a</sup> CN is number of first neighboring titanium atoms to removed oxygen atom.

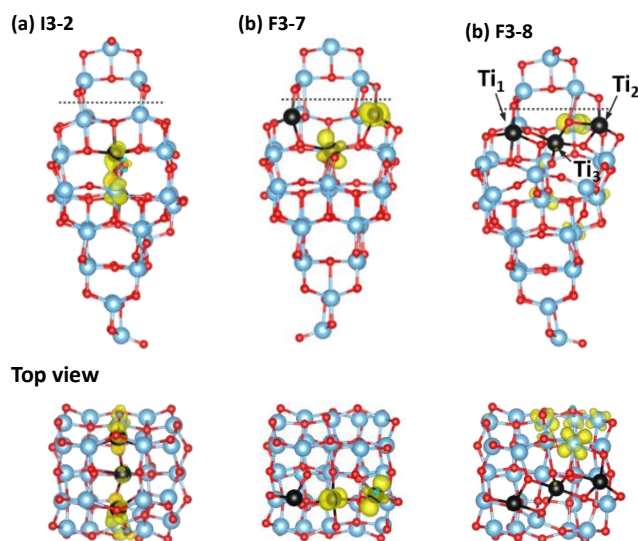
<sup>b</sup> site is designated as combination of position, CN, and the order of vacant oxygen atom distant from center of mass.

the exchange functionals because the distribution of two excess electrons is strongly affected by the amount of non-local HF exchange. Table 2 lists the values of  $E_v$  [eq. (3)],  $E_{rel}$  [eq. (4)],  $E_f^O$  [eq. (2)], and energy level of oxygen vacancy defect state below LUMO ( $S_{v-1}$  and  $S_{v-2}$ ) as calculated using PBE functional. The data from PBE and PBE0 functionals is listed in Table S2.  $E_v$  generally increases with CN regardless of functional; the sites having the highest and lowest  $E_v$  are tip (**T1-1**) and 3-coordinated facet (PBE: **F3-8**, PBEx and PBE0: **F3-5**), respectively. However, the tendency of  $E_{rel}$  is quite different according to the functional due to the two factors, geometrical relaxation and distribution of excess electrons, which influence relaxation of reduced NP.

The range of  $E_f^O$  is 2.81 ~ 5.61 eV in PBE, 2.27 ~ 5.46 eV in PBEx and 2.05 ~ 5.12 eV in PBE0; all functionals provide a similar qualitative picture but with some remarkable differences as well. The average value (PBE: 4.19, PBEx: 4.28, PBE0: 4.16 eV) is quite close to  $E_f^O$  in TiO<sub>2</sub> Bulk (Table S1),<sup>28, 34, 39, 66</sup> but it is much lower when the O atom is removed from some specific sites. This is because of the relaxation of the reduced TiO<sub>2</sub> system upon vacancy formation which varies depending on the features of O<sub>v</sub> site that is determined by the influence of vacant space and excess electron on surrounding titanium atoms. In the reduced anatase TiO<sub>2</sub> bulk, there is only single type (3-coordinated one) of O<sub>v</sub> site and the relaxation effects were smaller than in the TiO<sub>2</sub> NP;<sup>32, 34</sup> atoms surrounding vacant site maintained pristine TiO<sub>2</sub> structure, and excess electrons were distributed over the three Ti atoms directly adjacent to the O<sub>v</sub> site. For comparison, dissociation energy of O<sub>2</sub> molecule was calculated using three functionals. The value (PBE: 6.77 eV, PBEx: 7.69 eV, PBE0: 8.62 eV) increases as %Fock increases. Fig. S4 presents the changes of  $E_f^O$  against vacant oxygen atom distance from center of mass. The range of  $E_f^O$ , except for particularly low  $E_f^O$  (**F3-8**) in PBEx and PBE0 results, is narrowed as %Fock increases. As % Fock decreases, the localized and delocalized characters of the excess electrons are mixed, and the range of  $E_f^O$  becomes broader. Even the same (3)-coordinated oxygen atoms have led to different features when the O<sub>v</sub> is formed in the TiO<sub>2</sub> NP. The oxygen sites having the lowest  $E_f^O$  are **I3-2** in PBE, and **F3-8** in PBEx and PBE0. It is worth pointing out that the situation here is different from the O<sub>v</sub> tendency in ceria (CeO<sub>2</sub>) NPs<sup>67, 68</sup> where removal of a low (2)-coordinated oxygen requires the lowest energy. Interestingly, however, high (3)-coordinated oxygen sites have the lowest  $E_f^O$  in TiO<sub>2</sub> NP because relaxation effect is quite large. According to the definition of  $E_f^O$  in eq. (2), the value of  $E_f^O$  decreases as the  $E_v$  decreases and  $E_{rel}$  increases. Although **T1-1** is the outermost site,  $E_f^O$  is quite high as 4.28 eV because of the lowest  $E_{rel}$  (0.26 eV). The **F3-8** as the most stable O<sub>v</sub> site is coincident with previous result that the subsurface O<sub>v</sub> (CN=3) is more stable than the surface O<sub>v</sub> (CN=2) in TiO<sub>2</sub> anatase slabs from the calculation of  $E_f^O$  for different surface and subsurface sites in various TiO<sub>2</sub> slab models using the hybrid DFT functionals;<sup>36</sup> a feature which is also in agreement with experiment.<sup>17</sup>

In order to understand the reason of **F3-8** site having the lowest  $E_f^O$  in PBEx and PBE0 calculations, we carefully analyzed

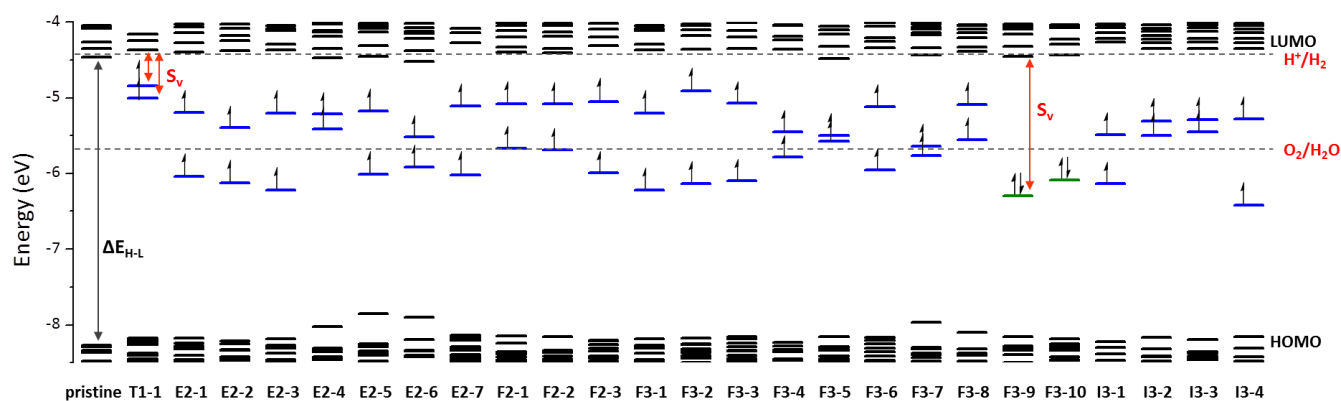
#### Side view



**Fig. 4** PBEx calculated structures of Ti<sub>35</sub>O<sub>69</sub> NP with oxygen removed at three O<sub>3c</sub> sites that where Ti-O<sub>ax</sub> is shorter than the two Ti-O<sub>eq</sub> distances. The isovalue of spin density is 0.05 e-au<sup>-3</sup>. For clarity, atoms above the dotted line were removed in top view structures.

the geometrical differences between each of oxygen sites in optimized pristine TiO<sub>2</sub> NP. Normally, the O<sub>3c</sub> has two short Ti-O<sub>eq</sub> (ca. 1.94 Å) and one long Ti-O<sub>ax</sub> (ca. 2.01 Å) in bulk anatase lattice,<sup>7, 28</sup> as shown in Fig. S1. However, among 14 O<sub>3c</sub> sites, we found that, in the pristine NP, only three O<sub>3c</sub> sites showed that Ti-O<sub>ax</sub> is shorter than two Ti-O<sub>eq</sub>. The reduced NPs with oxygen removed at these O<sub>3c</sub> sites were shown in Fig. 4 (PBE and PBE0 results are in Fig. S5). The lengths of Ti-O<sub>ax</sub> and Ti-O<sub>eq</sub> at three sites (**I3-2**, **F3-7** and **F3-8**) are listed in Table S3. At **I3-2**, Ti-O<sub>ax</sub> is shorter than two analogous-lengths Ti-O<sub>eq</sub>. In other words, though Ti-O<sub>ax</sub> shortens, O<sub>3c</sub> is still symmetrically located from both side titanium atoms. In reduced TiO<sub>2</sub> NP, the vacant space remains after relaxation and excess electrons tend to spread to surface along nearest-neighboring titanium atoms. It was found that the spin density is localized at low-coordinated surface titanium atoms as the %Fock increases.

However, more complicated structural features appear for the reduced NP with O<sub>v</sub> at **F3-7** (b) and **F3-8** (c). Even though these two facet sites are opposite in approximately symmetrical TiO<sub>2</sub> NP structure, the properties of O<sub>v</sub> are quite different. At **F3-7**, vacant space is maintained and excess electrons are localized at two closer titanium atoms among three nearby titanium atoms, which is similar to the results at other O<sub>3c</sub> sites. On the other hand, at **F3-8**, the location of atoms surrounding O<sub>v</sub> site changes obviously and two of three adjacent titanium atoms (black spheres) form additional coordination with nearby oxygen atom. In other words, after O<sub>v</sub> formation, Ti<sub>1</sub> and Ti<sub>2</sub> are additionally coordinated with nearby oxygen atom and only Ti<sub>3</sub> loses 1 CN through large geometrical change. Thus, CNs of Ti<sub>1</sub>, Ti<sub>2</sub>, and Ti<sub>3</sub> are 5, 5, and 6 in pristine NP and 5, 5, and 5 in reduced NP, respectively. At the PBEx level of theory, one excess electron is localized at next-neighboring titanium atom and the other is delocalized at



**Fig. 5** Kohn-Sham orbitals energy level diagram of  $\text{Ti}_{35}\text{O}_{69}$  NPs and  $\text{Ti}_{35}\text{O}_{70}$ . The triplet state energy levels are for spin-up eigenvalues. The dotted lines indicate the standard redox potentials for water splitting at pH = 0. The singly occupied and doubly occupied defect states are denoted in blue and green for triplet and singlet states, respectively. Other occupied and unoccupied molecular orbitals are shown in black.

opposite side surface titanium atoms that is next to the spin delocalized one. In PBE0 results, one electron stays at  $\text{Ti}_3$  and the other is localized at next neighboring surface titanium atom. However, unlike PBE and PBE0, PBE functional could not appropriately predict the distinct features of  $\text{O}_v$  at **F3-8**. The empty space still remains (each adjacent titanium atom loses 1 CN and keeps 5 CN), the geometrical change is less noticeable and the excess electrons migrate to surface titanium atoms. It means that the reduced NP structure is strongly altered by the description of excess electrons. Though spin density distribution was different in PBE and PBE0, it is important to highlight that the large relaxation effect at **F3-8** site was predicted with both functionals.

One distinct difference between **F3-7** and **F3-8** sites is the dangling oxygen atom bending toward **F3-8**; for this reason,  $\text{O}_{3c}$  geometry seems to be much deformed at **F3-8**. Thus, we argue that the relaxation of oxygen vacant structure would be affected by the geometrical singularity of pristine  $\text{TiO}_2$  anatase NP, in which the normal  $\text{O}_{3c}$  structure is broken and Ti-O of both tips are asymmetrically bent to opposite sides. At **F3-8** site,  $E_{\text{rel}}$  is predominantly large, and  $E_f^{\text{O}}$  is the lowest. In other words, **F3-8** would be the most preferred  $\text{O}_v$  site from thermodynamic point of view. The geometrical change and localization of spin density are consistent with polaronic effect accompanying excess electron in reduced  $\text{TiO}_2$  surface; excess electrons by  $\text{O}_v$  are localized near the surface vacant site and lattice distortion is induced in polaronic (delocalized) solution.<sup>17, 69</sup>

The presence of  $\text{Ti}^{3+}$  ions in reduced  $\text{TiO}_2$  system was confirmed by band gap narrowing that results from the electronic structure change induced by the  $\text{O}_v$ .<sup>23, 25-27</sup> The defect state appeared at around 1 eV below the conduction band minimum (CBM) from the experimental results in  $\text{TiO}_2$  systems.<sup>27</sup> Fig.5 presents molecular orbitals energy level diagram of  $\text{Ti}_{35}\text{O}_{69}$  NP at 25  $\text{O}_v$  sites (PBE and PBE0 results are in Fig. S6). The defect states are presented as singly (triplet state) or doubly (singlet state) occupied molecular orbital. Because molecular orbital energy levels of up- and down-spin in triplet states were very similar except for defect states, only up-spin eigenvalues are presented. The spin-unrestricted triplet state was dominantly more stable than the closed-shell

singlet one in most of the reduced  $\text{TiO}_2$  NPs. It clearly showed that the defect states exist between HOMO and LUMO level and the values of  $\Delta E_{\text{H-L}}$  and  $S_v$  vary with  $\text{O}_v$  site and functional. Not only  $\Delta E_{\text{H-L}}$  but also  $S_v$  increased with the increasing amount of %Fock in reduced  $\text{TiO}_2$  NPs. The range  $S_v$  is 0.01 ~ 0.83 eV in PBE, 0.47 ~ 2.06 eV in PBE and 1.42 ~ 3.32 eV in PBE0 and the results of PBE are best matched to the experimental values. The position of the HOMO and LUMO energy levels was also changed upon  $\text{O}_v$  formation. These changes allow for new electronic transitions from both HOMO and defect states to LUMO, and from HOMO to defect states. For this reason, oxygen vacancy leads to bandgap narrowing of  $\text{TiO}_2$  NPs, which would be responsible for visible light absorption. Furthermore, in comparison with the standard redox potentials for water splitting (at pH = 0),<sup>2, 70-72</sup> the HOMO level must be located below the oxygen evolution (OER) potential ( $\text{O}_2/\text{H}_2\text{O}$ ), whereas LUMO level must exceed the hydrogen evolution reduction (HER) potential ( $\text{H}^+/\text{H}_2$ ). LUMO positioned close to HER potential and defect state appeared near to OER potential could make reduced  $\text{TiO}_2$  NPs as promising candidates for photocatalytic water splitting. In the aspect of redox potential, 17-like sites would be suitable for photocatalyst, but the defect states of  $\text{O}_v$  sites having low  $E_f^{\text{O}}$  (**F3-8** and **I3-2**) are higher than OER potential. However, the correlation between  $\text{O}_v$  sites and photocatalytic activity was not shown. Actually, these results are not enough to be convinced that oxygen removed  $\text{TiO}_2$  NPs can be applied to visible light adsorbing photocatalyst for water splitting. Future work should therefore include a more systematic study of reduced  $\text{TiO}_2$  NPs in solution, the dynamics of photoexcited state of reduced  $\text{TiO}_2$  NPs,  $\text{O}_v$  site migration behavior, and multi-oxygen vacancy effect.

## Conclusions

We investigated the properties of neutral single oxygen vacancy in  $(\text{TiO}_2)_{35}$  anatase nanoparticle focusing on the effect of the different possible vacant sites by DFT calculations using various DFT methods including hybrid functionals. Oxygen sites in  $(\text{TiO}_2)_{35}$  are classified by position with respect to the center

of mass, coordination number and bond length with first-neighboring Ti. We examined 25 oxygen sites that could represent whole oxygen sites under symmetry operations. Atomic and electronic structures of pristine and reduced TiO<sub>2</sub> nanoparticles were obtained using PBE based hybrid functionals; PBE (0 %Fock), PBE0 (25 %Fock), and newly defined PBEx (12.5 %Fock).<sup>34</sup> Slightly differently from bulk structure, upon oxygen vacancy formation, the symmetry is broken and the two dangling oxygen atoms at both tips are bent to opposite sides due to high surface to bulk ratio and some under-coordinated atoms (Ti<sub>4c</sub>, Ti<sub>5c</sub> and O<sub>1c</sub>) in nanoparticle. The properties of oxygen vacancy in the (TiO<sub>2</sub>)<sub>35</sub> nanoparticle depend on vacant site and %Fock of the functional used.

Oxygen vacancy formation energy and the band edge energy levels of the defect state are quite dependent on vacant sites. Energetically most favourable oxygen atom for vacancy formation from nanoparticle is high (three)-coordinated one in facet domain which is in contrast with results reported for ceria nanoparticles.<sup>67, 68</sup> This is because the relaxation energy is largest at the particular facet site of which 3-coordinated structure with surrounding titanium atoms is broken from normal one in TiO<sub>2</sub> anatase system. The result predicted by the PBEx functional corresponds to HOMO-LUMO gap of pristine nanoparticle of 3.81 eV and defect state of reduced nanoparticle in the 0.47 ~ 2.06 eV range below LUMO energy level.

Finally, our study shows that introducing one O vacancy in the (TiO<sub>2</sub>)<sub>35</sub> anatase nanoparticle gives rise to significant differences in the pristine and reduced structure in comparison with bulk system. Moreover, oxygen vacancy formation energy (2.27 eV) is surprisingly small compared with that of bulk or slab surface, and the energies of defect states induced by O vacancy are close to oxygen evolution potential. These could provide an evidence of the importance of the oxygen vacancy of TiO<sub>2</sub> nanoparticles for efficient photocatalyst.

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## References

- 1 I. Justicia, P. Ordejón, G. Canto, J. L. Mozos, J. Fraxedas, G. A. Battiston, R. Gerbasi and A. Figueras, *Adv. Mater.*, 2002, **14**, 1399-1402.
- 2 M. Ni, M. K. H. Leung, D. Y. C. Leung and K. Sumathy, *Renew. Sustainable Energy Rev.*, 2007, **11**, 401-425.
- 3 U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer and M. Gratzel, *Nature*, 1998, **395**, 583-585.
- 4 N. G. Park, J. van de Lagemaat and A. J. Frank, *J. Phys. Chem. B*, 2000, **104**, 8989-8994.
- 5 M. Gratzel, *Nature*, 2001, **414**, 338-344.
- 6 S. Na-Phattalung, M. F. Smith, K. Kim, M.-H. Du, S.-H. Wei, S. B. Zhang and S. Limpijumng, *Phys. Rev. B*, 2006, **73**, 125205.
- 7 C. Di Valentin, G. Pacchioni and A. Selloni, *Chem. Mater.*, 2005, **17**, 6656-6665.
- 8 N. Serpone, *J. Phys. Chem. B*, 2006, **110**, 24287-24293.
- 9 C. Di Valentin, G. Pacchioni and A. Selloni, *J. Phys. Chem. C*, 2009, **113**, 20543-20552.
- 10 S. A. Shevlin and S. M. Woodley, *J. Phys. Chem. C*, 2010, **114**, 17333-17343.
- 11 T. Sekiya, T. Yagisawa, N. Kamiya, D. Das Mulmi, S. Kurita, Y. Murakami and T. Kodaira, *J. Phys. Soc. Jpn.*, 2004, **73**, 703-710.
- 12 S. Wendt, P. T. Sprunger, E. Lira, G. K. H. Madsen, Z. Li, J. Ø. Hansen, J. Matthiesen, A. Blekinge-Rasmussen, E. Lægsgaard, B. Hammer and F. Besenbacher, *Science*, 2008, **320**, 1755-1759.
- 13 A. Naldoni, M. Allieta, S. Santangelo, M. Marelli, F. Fabbri, S. Cappelli, C. L. Bianchi, R. Psaro and V. Dal Santo, *J. Am. Chem. Soc.*, 2012, **134**, 7600-7603.
- 14 X. Pan, M.-Q. Yang, X. Fu, N. Zhang and Y.-J. Xu, *Nanoscale*, 2013, **5**, 3601-3614.
- 15 H. Zhang and J. F. Banfield, *J. Mater. Chem.*, 1998, **8**, 2073-2076.
- 16 M. R. Ranade, A. Navrotsky, H. Z. Zhang, J. F. Banfield, S. H. Elder, A. Zaban, P. H. Borse, S. K. Kulkarni, G. S. Doran and H. J. Whitfield, *Proc. Natl. Acad. Sci. U. S. A.*, 2002, **99**, 6476-6481.
- 17 M. Setvin, C. Franchini, X. Hao, M. Schmid, A. Janotti, M. Kalkak, C. G. Van de Walle, G. Kresse and U. Diebold, *Phys. Rev. Lett.*, 2014, **113**, 086402.
- 18 L. Sang, Y. Zhao and C. Burda, *Chem. Rev.*, 2014, **114**, 9283-9318.
- 19 Z.-w. Qu and G.-J. Kroes, *J. Phys. Chem. B*, 2006, **110**, 8998-9007.
- 20 Z.-w. Qu and G.-J. Kroes, *J. Phys. Chem. C*, 2007, **111**, 16808-16817.
- 21 S. Li and D. A. Dixon, *J. Phys. Chem. A*, 2008, **112**, 6646-6666.
- 22 D. Cho, K. C. Ko, O. Lamiel-Garcia, S. T. Bromley, J. Y. Lee and F. Illas, *J. Chem. Theory Comput.*, 2016, DOI: 10.1021/acs.jctc.6b00519.
- 23 M. Nolan, S. D. Elliott, J. S. Mulley, R. A. Bennett, M. Basham and P. Mulheran, *Phys. Rev. B*, 2008, **77**, 235424.
- 24 J. Nerlov, S. V. Christensen, S. Weichel, E. H. Pedersen and P. J. Møller, *Surf. Sci.*, 1997, **371**, 321-336.
- 25 M. A. Henderson, W. S. Epling, C. H. F. Peden and C. L. Perkins, *J. Phys. Chem. B*, 2003, **107**, 534-545.
- 26 N. D. Abazović, M. I. Čomor, M. D. Dramićanin, D. J. Jovanović, S. P. Ahrenkiel and J. M. Nedeljković, *J. Phys. Chem. B*, 2006, **110**, 25366-25370.
- 27 F. Fabbri, F. Detto, N. Armani, N. Satoh, T. Besagni, M. Pavesi and G. Salviati, *J. Phys. Chem. C*, 2013, **117**, 3729-3738.
- 28 E. Finazzi, C. Di Valentin, G. Pacchioni and A. Selloni, *J. Chem. Phys.*, 2008, **129**, 154113.
- 29 G. Mattioli, F. Filippone, P. Alippi and A. Amore Bonapasta, *Phys. Rev. B*, 2008, **78**, 241201.

- 30 A. Janotti, J. B. Varley, P. Rinke, N. Umezawa, G. Kresse and C. G. Van de Walle, *Phys. Rev. B*, 2010, **81**, 085212.
- 31 B. J. Morgan and G. W. Watson, *J. Phys. Chem. C*, 2010, **114**, 2321-2328.
- 32 P. Deák, B. Aradi and T. Frauenheim, *Phys. Rev. B*, 2012, **86**, 195206.
- 33 H.-Y. Lee, S. J. Clark and J. Robertson, *Phys. Rev. B*, 2012, **86**, 075209.
- 34 K. C. Ko, O. Lamiel-Garcia, J. Y. Lee and F. Illas, *Phys. Chem. Chem. Phys.*, 2016, **18**, 12357-12367.
- 35 M. wang, M. Feng and Y. Lu, *Mod. Phys. Lett. B*, 2014, **28**, 1450076.
- 36 H. Li, Y. Guo and J. Robertson, *J. Phys. Chem. C*, 2015, **119**, 18160-18166.
- 37 B. J. Morgan and G. W. Watson, *Phys. Rev. B*, 2009, **80**, 233102.
- 38 S. Taizo, Y. Kenji, M. Susanne and S. Biplab, *J. Phys.: Condens. Matter*, 2012, **24**, 435504.
- 39 P. Deák, J. Kullgren and T. Frauenheim, *Phys. Status Solidi RRL*, 2014, **8**, 583-586.
- 40 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
- 41 M. Sodupe, J. Bertran, L. Rodríguez-Santiago and E. J. Baerends, *J. Phys. Chem. A*, 1999, **103**, 166-170.
- 42 J. Lægsgaard and K. Stokbro, *Phys. Rev. B*, 2000, **61**, 12590-12593.
- 43 M. Magagnini, P. Giannozzi and A. Dal Corso, *Phys. Rev. B*, 2000, **61**, 2621-2625.
- 44 I. de P. R. Moreira, F. Illas and R. L. Martin, *Phys. Rev. B*, 2002, **65**, 155102.
- 45 J. P. Perdew, M. Ernzerhof and K. Burke, *J. Chem. Phys.*, 1996, **105**, 9982-9985.
- 46 C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158-6170.
- 47 C. Di Valentin, G. Pacchioni and A. Selloni, *Phys. Rev. Lett.*, 2006, **97**, 166803.
- 48 M. Gerosa, C. E. Bottani, L. Caramella, G. Onida, C. Di Valentin and G. Pacchioni, *Phys. Rev. B*, 2015, **91**, 155201.
- 49 V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler, *Comput. Phys. Commun.*, 2009, **180**, 2175-2196.
- 50 A. S. Barnard, S. Erdin, Y. Lin, P. Zapol and J. W. Halley, *Phys. Rev. B*, 2006, **73**, 205405.
- 51 G. Wulff, *Z. Kristallogr. Material.*, 1901, **34**, 449-530.
- 52 L. Yinkai, L. Huijun and X. Wei, *Modelling Simul. Mater. Sci. Eng.*, 2010, **18**, 025004.
- 53 J. K. Burdett, T. Hughbanks, G. J. Miller, J. W. Richardson and J. V. Smith, *J. Am. Chem. Soc.*, 1987, **109**, 3639-3646.
- 54 J.-L. Bredas, *Mater. Horiz.*, 2014, **1**, 17-19.
- 55 F. Labat, P. Baranek, C. Domain, C. Minot and C. Adamo, *J. Chem. Phys.*, 2007, **126**, 154703.
- 56 C. J. Cramer and D. G. Truhlar, *Phys. Chem. Chem. Phys.*, 2009, **11**, 10757-10816.
- 57 G. Fazio, L. Ferrighi and C. Di Valentin, *J. Phys. Chem. C*, 2015, **119**, 20735-20746.
- 58 H. Minoura, M. Nasu and Y. Takahashi, *Ber. Bunsenges. Phys. Chem.*, 1985, **89**, 1064-1069.
- 59 L. Kavan, M. Grätzel, S. E. Gilbert, C. Klemenz and H. J. Scheel, *J. Am. Chem. Soc.*, 1996, **118**, 6716-6723.
- 60 D. Reyes-Coronado, G. Rodríguez-Gattorno, M. E. Espinosa-Pesqueira, C. Cab, R. d. Coss and G. Oskam, *Nanotechnology*, 2008, **19**, 145605.
- 61 S. Kalathil, M. M. Khan, S. A. Ansari, J. Lee and M. H. Cho, *Nanoscale*, 2013, **5**, 6323-6326.
- 62 Q. Kang, J. Cao, Y. Zhang, L. Liu, H. Xu and J. Ye, *J. Mater. Chem. A*, 2013, **1**, 5766-5774.
- 63 M. M. Khan, S. A. Ansari, D. Pradhan, M. O. Ansari, D. H. Han, J. Lee and M. H. Cho, *J. Mater. Chem. A*, 2014, **2**, 637-644.
- 64 S. Monticone, R. Tufeu, A. V. Kanaev, E. Scolan and C. Sanchez, *Appl. Surf. Sci.*, 2000, **162-163**, 565-570.
- 65 L. Ming, C. Kui, W. Wenjian, S. Chenlu, D. Piyi, S. Ge, X. Gang and H. Gaorong, *J. Phys. D: Appl. Phys.*, 2009, **42**, 105414.
- 66 T. Yamamoto and T. Ohno, *Phys. Chem. Chem. Phys.*, 2012, **14**, 589-598.
- 67 A. Migani, G. N. Vayssilov, S. T. Bromley, F. Illas and K. M. Neyman, *J. Mater. Chem.*, 2010, **20**, 10535-10546.
- 68 A. Migani, G. N. Vayssilov, S. T. Bromley, F. Illas and K. M. Neyman, *Chem. Commun.*, 2010, **46**, 5936-5938.
- 69 N. A. Deskins and M. Dupuis, *Phys. Rev. B*, 2007, **75**, 195212.
- 70 W.-J. Chun, A. Ishikawa, H. Fujisawa, T. Takata, J. N. Kondo, M. Hara, M. Kawai, Y. Matsumoto and K. Domen, *J. Phys. Chem. B*, 2003, **107**, 1798-1803.
- 71 T. Hisatomi, J. Kubota and K. Domen, *Chem. Soc. Rev.*, 2014, **43**, 7520-7535.
- 72 A. K. Singh, K. Mathew, H. L. Zhuang and R. G. Hennig, *J. Phys. Chem. Lett.*, 2015, **6**, 1087-1098.