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# Tailoring surface morphology on anatase TiO<sub>2</sub> supported Au nanoclusters: implications for O<sub>2</sub> activation†

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Strong interaction between the support surface and metal clusters activates the adsorbed molecules at the metal cluster–support interface. Using plane-wave DFT calculations, we precisely model the interface between anatase TiO<sub>2</sub> and small Au nanoclusters. Our study focusses on the adsorption and activation of oxygen molecules on anatase TiO<sub>2</sub>, considering the influence of oxygen vacancies and steps on the surface. We find that the plane (101) and the stepped (103) surfaces do not support O<sub>2</sub> activation, but the presence of oxygen vacancies results in strong adsorption and O–O bond length elongation. Modifying the TiO<sub>2</sub> surface with supported small Au<sub>*n*</sub> nanoclusters (*n* = 3–5) also significantly enhances O<sub>2</sub> adsorption and stretches the O–O bond. We observe that manipulating the cluster orientation through discrete rotations results in improved O<sub>2</sub> adsorption and promotes charge transfer from the surface to the molecule. We propose that the orientation of the supported cluster may be manipulated by making the cluster adsorb at the step-edge of (103) TiO<sub>2</sub>. This results in activated O<sub>2</sub> at the cluster–support interface, with a peroxide-range bond length and a low barrier for dissociation. Our modeling demonstrates a straightforward means of exploiting the interface morphology for O<sub>2</sub> activation under low precious metal loading, which has important implications for electrocatalytic oxidation reactions and the rational design of supported catalysts.

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## 1. Introduction

Activation of molecular oxygen adsorbed over a catalyst surface is a critical step in several important processes such as catalytic oxidation reactions, photocatalysis, CO oxidation, propylene epoxidation, corrosion control, chemical sensing, *etc.*<sup>1–4</sup> For example, the electrocatalytic oxygen reduction reaction (ORR) which occurs in hydrogen fuel cells is initiated by the adsorption and activation of an O<sub>2</sub> molecule on a catalyst surface.<sup>5</sup> The catalyst here may be a metal, non-metal or metal oxide. The progress of the ORR greatly depends on the bonding and activation of O<sub>2</sub> on the active site on the catalyst surface. Understanding and controlling O<sub>2</sub> activation provides a handle over phenomena like corrosion and oxide layer formation, which have immense practical implications.<sup>6</sup> In general, the reactivity of a surface to O<sub>2</sub> is indicated by the strength of the binding, measured in terms of the adsorption energy, the O–O bond length *etc.*<sup>7,8</sup> Therefore, a study of how surface properties and their modification affect oxygen binding and activation can provide fruitful insights for desirable ends like controlling

corrosion or designing efficient catalysts for oxidation reactions.

The study of O<sub>2</sub> binding and activation on metal and alloy surfaces has received a fair bit of attention over the years, both experimentally and theoretically. A comprehensive review of the area may be found in the work of Montemore *et al.*<sup>9</sup> With reference to the ORR in particular and electrocatalysis in general, the search for efficient and earth abundant catalysts to replace expensive and kinetically sluggish Pt or Pt-based materials is an ongoing research endeavour. Development of such alternative catalysts can lead to the large scale deployment of fuel cells in place of fossil fuels, which would lead to the realization of some of our green energy aspirations. One class of alternate materials being pursued here are metal oxides, particularly transition metal oxides. Transition metal oxides (TMOs) have gained significant interest over time as applicable active materials in the fields of catalysis, energy storage and sensing, due to their low cost, variable oxidation state, ease of synthesis, stability, corrosion resistance and environmental friendliness.<sup>10–13</sup>

Titanium dioxide (TiO<sub>2</sub>) is a very well-known material amongst TMOs, due to its relatively large abundance, non-toxicity and several applications as a wide band gap electronic material and a photocatalyst.<sup>14</sup> TiO<sub>2</sub> occurs in nature in the form of rutile and anatase, of which rutile is thermodynamically more stable, but anatase is catalytically and technologically an

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important TMO.<sup>15</sup> Over the past decade or so, the study of interaction between TiO<sub>2</sub> and O<sub>2</sub> molecules has attracted considerable interest. It happens that the anatase TiO<sub>2</sub> surface is relatively inactive to the O<sub>2</sub> molecule, and therefore not a suitable catalyst for the ORR. The surface becomes active when an excess of electrons is present.<sup>16</sup> The adsorption of O<sub>2</sub> on TiO<sub>2</sub> is generally associated with the withdrawal of negative charge from the surface.<sup>17–19</sup> Adsorbed O<sub>2</sub> exists in either a peroxide (O<sub>2</sub><sup>2-</sup>), or superoxide (O<sub>2</sub><sup>-</sup>) state, or may get dissociated into two O<sup>2-</sup> ions.<sup>9</sup>

Varied attempts have been made to enhance the activity of the TiO<sub>2</sub> surface towards O<sub>2</sub>. Adsorbed metal single atoms or nanoscale clusters, surface defects, steps and dopant atoms can play a significant role in activating the surface.<sup>20</sup> The interface formed between the metal oxide surface and the metal clusters dispersed over it plays an important role in the catalytic oxidation processes.<sup>21,22</sup> The geometric structure and electronic properties of the metal clusters can get significantly modified by the supporting metal oxides, and thereby have a significant impact on their catalytic properties.<sup>23</sup> Gold nanoparticles exhibit high catalytic activity for many reactions when dispersed on metal oxides. Interestingly, both Au and metal oxides individually were considered to be inactive for numerous catalytic reactions.<sup>24</sup> However, they combine to form a very active interface. The pioneering work of Haruta<sup>25</sup> has led to extensive experimental studies on Au/oxide systems, yielding significant results, and it is established that the catalytic activity of Au-based systems greatly depends on the choice of the underlying oxides.

Among all the catalytic reactions involving Au, the activation of O<sub>2</sub> holds particular significance in the research field of Au/oxide systems. Strategies are currently being developed for the activation of O<sub>2</sub> molecules using the Au-metal oxide interface. It is found that the catalytic activity of Au depends considerably on the nature of the support, the synthesis method and the size of Au nanoparticles. The most commonly used oxide supports for Au nanoparticles are TiO<sub>2</sub>, ZnO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>.<sup>26,27</sup> The structural aspects of Au clusters supported on TiO<sub>2</sub> were investigated by Hemmingson *et al.* using high-resolution electron microscopy (HREM).<sup>21</sup> It was discovered that the catalytic activity can be tuned by controlling the size of the Au nanoparticles, and the oxygen molecule is activated at the interface of Au/TiO<sub>2</sub>.<sup>28–30</sup> Green *et al.*<sup>31</sup> experimentally and theoretically provided insights into the activation of Au clusters supported on rutile TiO<sub>2</sub>. The transmission IR spectroscopic data indicated the direct involvement of the Au–Ti<sup>4+</sup> at the interface in the activation of O<sub>2</sub>. While most researchers agree that the activation of O<sub>2</sub> is favoured at the perimeter site, the elementary process leading to O<sub>2</sub> activation, whether solely on the Au clusters or at the cluster–support interface, is debatable.<sup>24,27,32,33</sup> Moreover, a decrease in the size of the clusters resulted in a decrease in the activity of Au clusters.<sup>34</sup> The interactions between Au and TiO<sub>2</sub> support have been extensively studied using density functional theory (DFT).<sup>35,36</sup> The results suggest that the adsorption strength of Au/TiO<sub>2</sub> is sensitive to both the cluster size and facet. Additionally, the interface's geometric

and electronic structure plays crucial roles in the catalytic activity.

Stepped edges are common defects found on the surface of crystalline materials. Despite being ubiquitous, they have been studied less extensively compared to other defects such as vacancies and interstitials. High-index surfaces exhibit unique properties compared to low-index surfaces because of their low coordination.<sup>37</sup> Surface facets characterized by Miller indices  $\{h, k, l\}$  with at least one index greater than one, can be termed stepped surfaces. The step edges serve as active sites for the adsorption of molecules and also act as nucleation centres when metals are deposited on the oxide surface.<sup>38–40</sup> The stepped surface of anatase TiO<sub>2</sub> is of great interest and has been amply investigated by Gong *et al.*<sup>41,42</sup> They observed that, depending on the terrace/step configuration, the steps can exhibit lower reactivity compared to the flat terraces. Rieboldt<sup>43</sup> and co-workers experimentally studied vicinal rutile TiO<sub>2</sub> surfaces and found that they have a strong influence on O<sub>2</sub> due to the presence of step edges. Additionally, these surfaces are characterized by smaller gap states compared to flat surfaces. High-resolution TEM images show that the (103) surface of anatase nanoparticle can be exposed depending on the processing conditions.<sup>44</sup> The work function of the TiO<sub>2</sub> (441) surface was smaller by 0.7 eV compared to (110)<sup>45</sup> due to Fermi-level pinning and downward band bending toward the surface. Du *et al.* recently reported that the larger Au nanoparticles exhibit a higher encapsulation tendency in the Au/TiO<sub>2</sub> system due to size-dependent strong metal–support interaction.<sup>46</sup>

In the present work, we have looked at O<sub>2</sub> adsorption on plane, stepped, reduced and Au cluster decorated surfaces of anatase TiO<sub>2</sub>. We have used plane-wave DFT calculations to model O<sub>2</sub> adsorption, probing adsorption energy and the O–O bond length as descriptors of O<sub>2</sub> activation over these surfaces. We attempt to demonstrate that alteration of surface morphology of anatase TiO<sub>2</sub> through the presence of vacancies and steps, as well as supported Au clusters, at minimal Au loading, can lead to enhanced O<sub>2</sub> activation. We find that the orientation of the Au nanoclusters plays an important role in enhancing O<sub>2</sub> binding to the surface. We point out a simple way to realize such optimal orientation, *viz.*, cluster adsorption at the step-edge in the stepped TiO<sub>2</sub> surface. In the next section, we describe the computational methodology and in the subsequent section our results. Finally, we summarize and conclude our work.

## 2. Computational methods

All calculations in this work were performed using a spin-polarized density functional theory (DFT) approach with the Vienna *Ab initio* Simulation Package (VASP).<sup>47,48</sup> The core electrons were treated using the projector augmented wave (PAW)<sup>49,50</sup> method. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE)<sup>51</sup> functional was employed to describe the exchange–correlation energy. The DFT-D2 method proposed by Grimme<sup>52,53</sup> was used to model the dispersive interactions. The wave functions were expanded in a plane wave basis with an energy cut-off of 520 eV, and



Gaussian smearing of 0.05 eV was applied. The Brillouin zone was sampled using  $5 \times 5 \times 1$  Monkhorst–Pack grid<sup>54</sup> for the surface slab. A 15 Å vacuum was included to avoid the spurious periodic interaction along the  $z$ -axis. The structural relaxation was carried out until the force on each atom was less than  $0.01 \text{ eV \AA}^{-1}$ . It is well known that the standard DFT fails to model Ti atoms, primarily due to the self-interaction error inherent in the functionals used in the GGA. The GGA+ $U$  method was employed to calculate the electronic structure to overcome this limitation. The value of Hubbard parameter  $U$  was set to 4.2 eV, which is similar to the previous work<sup>55,56</sup>

The optimized lattice parameters for the bulk anatase  $\text{TiO}_2$  ( $a = 3.88 \text{ \AA}$  and  $c = 9.58 \text{ \AA}$ ), and calculated bond lengths (Ti–O) in apical (2.01 Å) and basal (1.98 Å) directions agree with previous experimental values.<sup>57</sup> In this work, we have considered the (101) plane and (103) stepped surfaces of anatase  $\text{TiO}_2$ . The (101) and (103) surfaces were modelled using a  $3 \times 1$  supercell consisting of 108 and 144 atoms, respectively. Au clusters were modelled in a unit cell of  $15 \times 15 \times 15 \text{ \AA}$ , considering only the  $\Gamma$ -point. To identify the minimum energy path (MEP) for  $\text{O}_2$  dissociation on the  $\text{TiO}_2$  surface, the climbing image-nudged elastic band (CI-NEB)<sup>58</sup> method was utilized to determine the transition state. The activation energy is defined as  $E_a = E_{\text{TS}} - E_{\text{IS}}$ , where  $E_{\text{TS}}$  and  $E_{\text{IS}}$  are the energies of the transition state and initial state, respectively. Bader charge<sup>59</sup> analysis was employed to determine the local charge of the atom.

The surface energy ( $\gamma$ ) is calculated using the expression:

$$\gamma = \frac{1}{2A} [E_{\text{slab}} - nE_{\text{unit}}] \quad (1)$$

where  $A$  and  $E_{\text{slab}}$  represent the surface area and the total energy of the slabs, respectively,  $E_{\text{unit}}$  is the energy of  $\text{TiO}_2$  unit in bulk, and  $n$  stands for the number of the basic  $\text{TiO}_2$  units in the slab.

The adsorption energy of the molecular  $\text{O}_2$  is determined as:

$$E_{\text{O}_2 \text{ ad}} = E_{\text{O}_2+\text{surf}} - E_{\text{surf}} - E_{\text{O}_2} \quad (2)$$

where  $E_{\text{O}_2+\text{surf}}$ ,  $E_{\text{surf}}$ , and  $E_{\text{O}_2}$  denote the total energy of  $\text{O}_2$  adsorbed on the slab surface, the bare slab, and an isolated  $\text{O}_2$  molecule respectively. A more negative value indicates stronger adsorption. The usual gas phase  $\text{O}_2$  bond length is 1.23 Å. The strength of  $\text{O}_2$  adsorption can also be evaluated by the stretching of the O–O bond length, which is used as one of the descriptors for  $\text{O}_2$  adsorption.

The O vacancy is created in both (101) and (103) surfaces, with the formation energy given by the following equation:

$$E_{\text{f}} = E_{\text{def}} - E_{\text{pri}} - (1/2)E_{\text{O}_2} \quad (3)$$

where  $E_{\text{def}}$  is the energy of the defective surface,  $E_{\text{pri}}$  is the energy of the pristine slab and  $E_{\text{O}_2}$  is the energy of the  $\text{O}_2$  gas molecule in its ground state.

The binding energy per Au for the  $\text{Au}_n$  cluster on the  $\text{TiO}_2$  substrate is calculated using the formula

$$E_{\text{BE}} = (1/n)[E_{\text{tot}} - E_{\text{slab}} - n \times E_{\text{Au}}] \quad (4)$$

where  $E_{\text{tot}}$  is the total energy of  $\text{Au/TiO}_2$ ,  $E_{\text{slab}}$  is the energy of the relaxed (101)/(103) slab,  $E_{\text{Au}}$  is the energy of an isolated single Au atom and  $n$  is the number of Au atoms on the slab. The negative value of  $E_{\text{BE}}$  indicates energetically favourable interaction between Au clusters and  $\text{TiO}_2$  surfaces. We have also performed *ab initio* MD (AIMD) simulations to study the stability of the Au clusters supported on  $\text{TiO}_2$  at room temperature.

## 3. Results and discussion

### 3.1 $\text{O}_2$ adsorption on (101) and (103) anatase $\text{TiO}_2$

Bulk anatase  $\text{TiO}_2$  is cleaved into two different facets, the usual (101) and the stepped (103). The surface energy is calculated using the formula (1). The (101) facet has a surface energy of  $0.46 \text{ J m}^{-2}$  which is comparable to the previously calculated values.<sup>60</sup> The optimized configuration of (101) is shown in Fig. 1(a) and (b). The (101) surface consists of fully saturated six-coordinated Ti and three-coordinated O atoms, as well as unsaturated five-coordinated Ti and two-coordinated O atoms on the surface. The (103) facet has two possible terminations that are commonly discussed: the “faceted” (103)<sub>f</sub> and “smooth” denoted as (103)<sub>s</sub>.<sup>60</sup> The surface energy of (103)<sub>f</sub> is  $1.12 \text{ J m}^{-2}$ , which is greater than  $1.08 \text{ J m}^{-2}$  of (103)<sub>s</sub>. This trend is similar to that observed in previous calculations,<sup>61</sup> and this surface energy is lower than that of (001).<sup>62</sup> Hence, the (103)<sub>s</sub> is stable, and we consider the (103)<sub>s</sub> facet throughout our calculation, denoted by (103). The optimized configuration is shown in Fig. 1(c) and (d). The hydration surface energy is also calculated for the (103) surface (for details, see S1†) at different coverage, and it is interesting to note that the surface energy of (103) is reduced for this coverage, when compared to those of (101). This indicates that hydration stabilizes the (103) surface over the (101).

The optimized configuration of the (103) surface consists of four-coordinated Ti ( $\text{Ti}_{4c}$ ) and three types of two-coordinated O ( $\text{O}_{2c}$ ), in addition to the usual coordination present in (101) anatase  $\text{TiO}_2$ , and one three-coordinated ( $\text{O}_{3c1}$ ) (see Fig. 1(c) and (d)). The three types of  $\text{O}_{2c}$  are: (a) linear along the  $b$ -axis making an angle of  $152^\circ$  ( $\text{O}_{2c1}$ ), (b) inclined at an angle of  $161^\circ$  ( $\text{O}_{2c2}$ ) and (c) bend at an angle of  $101^\circ$  ( $\text{O}_{2c3}$ ). Relaxation of the (103) stepped surface leads to satisfaction of unsaturated surface bonds and a 3% stabilization of the system. In the relaxed geometry, the angle between  $\text{Ti}_{4c}\text{--O--Ti}_{4c}$  along the  $b$ -axis is contracted by  $4^\circ$ , while the angle made in the  $b$ - $c$  plane is increased by  $5^\circ$ .

To compare the electronic structure of two facets, the PDOS of (101) and (103) are calculated and plotted as Fig. 1(e) and (f), respectively. No significant change in the band gap is observable. In both cases, the top of the valence band (VB) is composed of O 2p states, and the bottom of the conduction band (CB) is composed of Ti 3d states, consistent with the previous literature.<sup>63</sup> In (101), the valence band maximum (VBM) is dominated by  $p_x$  and  $p_z$ , and the conduction band minimum (CBM) is composed of the dominant  $t_{2g}$  states of Ti ( $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$ ). In case (103), all the states of O 2p are present in the VBM, and the CBM consists of Ti 3d. This may be due to



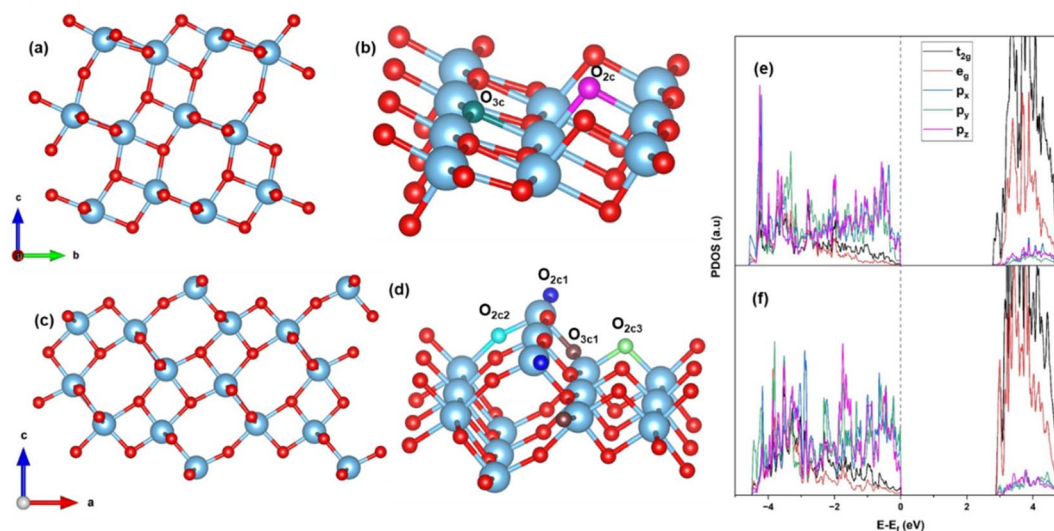


Fig. 1 (101) TiO<sub>2</sub> (a) side view (b) close view; (103) TiO<sub>2</sub> (c) side view (d) close view; PDOS of (e) (101) and (f) (103) TiO<sub>2</sub>.

the lowering of the symmetry following the formation of a surface. The Ti–O–Ti bond angles of (103) are larger compared to (101), resulting in better availability of oxygen for bonding with other species. All these contribute to making the (103) stepped surface a more active site for binding of adsorbates.

However, we find that the binding of the O<sub>2</sub> molecule to the (103) facet improves only marginally, despite all considerations of the previous paragraph. The adsorption energy of the O<sub>2</sub> molecule is calculated on (101) and (103) using formula (2). The

O<sub>2</sub> molecule gets physisorbed in both cases. There is a slight increase in the adsorption energy of O<sub>2</sub> in the case of the stepped surface (−0.17 eV) compared to the plane (−0.13 eV) surface of TiO<sub>2</sub>. The gas phase O–O bond length of 1.23 Å remains unaltered after adsorption. Thus, O<sub>2</sub> molecules desorb easily from (101) and (103) TiO<sub>2</sub> surfaces.

### 3.2 O<sub>2</sub> adsorption on reduced (101) and (103) TiO<sub>2</sub> surfaces

We now discuss the case of oxygen defects on the TiO<sub>2</sub> (101) and (103) surfaces. The formation energy of oxygen vacancies for both (101) and (103) surfaces is calculated using eqn (3) and is tabulated in Table 1. A large positive value indicates that more energy is needed to form the defect. The surface site defects V<sub>2c</sub> and V<sub>3c</sub> correspond to the vacancies created upon the removal of an O<sub>2c</sub> and O<sub>3c</sub> atom from the (101) surface (see Fig. 2(a)). Thus, it takes more energy to remove the O<sub>3c</sub> than the O<sub>2c</sub> atom. In the case of the (103) surface, V<sub>2c1</sub>, V<sub>2c2</sub>, V<sub>2c3</sub>, and V<sub>3c1</sub> indicate the removal of O<sub>2c1</sub>, O<sub>2c2</sub>, O<sub>2c3</sub> and O<sub>3c1</sub> atoms, respectively, from the surface (see Fig. 2(b)). The formation energy is lowest for the removal of the O<sub>2c3</sub> atom compared to all other sites.

Table 1 Computed formation energy values for defects on TiO<sub>2</sub> (101) and (103) surfaces

Surface	Site	Formation energy (eV)
(101)	V <sub>2c</sub>	4.23
	V <sub>3c</sub>	5.02
(103)	V <sub>2c1</sub>	5.43
	V <sub>2c2</sub>	4.71
	V <sub>2c3</sub>	3.22
	V <sub>3c1</sub>	4.93

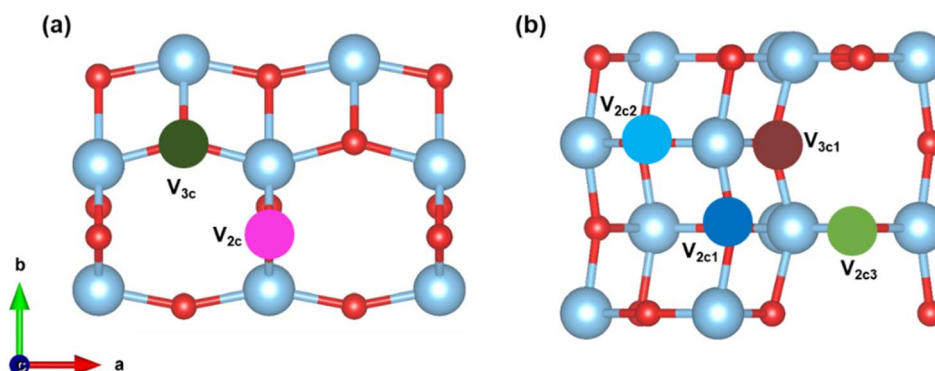


Fig. 2 The top view of the vacant surface of (a) (101) and (b) (103).



We create oxygen vacancies both on the plane (101) and stepped (103) TiO<sub>2</sub> (shown in Fig. 2) and compare both cases. After relaxation, in the case of V<sub>2c</sub> (removing the O<sub>2c</sub> atom from the (101) surface), the Ti atom moves downwards by a distance of 0.16 Å, while the bottom oxygen atom is shifted upward by a distance of 0.18 Å. For the V<sub>3c</sub> (removing the O<sub>3c</sub> atom from the (101) surface) vacancy, there was no change in the position of the Ti atom in the *c*-direction, but it is shifted by 0.18 Å in the lateral direction. On the vacant surface with V<sub>2c1</sub>, the uncoordinated Ti atom was shifted away from the vacant site by 0.42 Å. Consequently, the adjacent Ti–O bond distance was reduced by 0.20 Å. On the V<sub>2c2</sub> vacant surface, the Ti has been displaced to the vacant site by a distance of 0.40 Å. At the V<sub>2c3</sub> vacant site, the bottom oxygen atom shifted upwards by 1.08 Å, while the six-coordinated Ti atom moved along the surface by 0.50 Å. On the V<sub>3c1</sub> vacant surface, the oxygen atom originally coordinated to O<sub>2c1</sub> becomes three-coordinated, leading to a reduction in the Ti–O bond distance from 2.46 Å to 2.11 Å. These geometries are displayed in Fig. S2.†

The adsorption energy of an O<sub>2</sub> molecule is calculated on the reduced surfaces of (101) and (103). The adsorbed O<sub>2</sub> configuration is shown in Fig. S3.† In the case of V<sub>2c</sub> and V<sub>3c</sub> of (101), the O<sub>2</sub> molecule adsorbs at the Ti site, with O–O stretching of 1.46 Å and 1.48 Å, respectively, bringing these to the peroxide regime. The adsorption energy, O–O bond length and charge transfer to the molecule are tabulated in Table 2. The capability to absorb more than one oxygen molecule and activate these is important to enhance the efficiency of processes like the ORR. The study of O<sub>2</sub> coverage can provide insights into the correlation between excess electron charge and the reactivity of the TiO<sub>2</sub> surface.<sup>16</sup> For more than one O<sub>2</sub> adsorbed, we report the average value of adsorption energy, bond length and charge transfer. As the adsorbed O<sub>2</sub> acts as an electron scavenger, it inhibits further adsorption of O<sub>2</sub> molecules. We observe that the average adsorption energy is lowered, in the case of two molecules, with reduced stretching of the O–O bond. The average charge transfer is also lower in the case of two O<sub>2</sub>. What happens is thus: the first O<sub>2</sub> molecule becomes trapped at the lattice site upon adsorption, thereby withdrawing all available electron density and thus, the second molecule is only physisorbed on the nearest Ti site available. These optimized configurations for V<sub>2c</sub> and V<sub>3c</sub> are shown in Fig. S4.†

The average adsorption energy, bond length and charge transferred for adsorption of up to three O<sub>2</sub> on the reduced (103) surface are tabulated in Table 3. The first O<sub>2</sub> is adsorbed

Table 2 Oxygen adsorption on the reduced (101) TiO<sub>2</sub> surface

	No. of O <sub>2</sub> molecules	Sites	
		V <sub>2c</sub>	V <sub>3c</sub>
E <sub>ads</sub> (eV)	1	−3.70	−4.35
	2	−1.94	−2.24
d <sub>O–O</sub> (Å)	1	1.46	1.48
	2	1.34	1.36
Q  e	1	0.92	1.08
	2	0.46	0.54

Table 3 Oxygen adsorption on the reduced (103) TiO<sub>2</sub> surface

	No. of O <sub>2</sub> molecules	Sites			
		V <sub>2c1</sub>	V <sub>2c2</sub>	V <sub>2c3</sub>	V <sub>3c1</sub>
E <sub>ads</sub> (eV)	1	−5.09	−3.76	−3.02	−2.73
	2	−2.68	−2.47	−1.97	−2.35
	3	—	−1.56	−1.52	−1.66
d <sub>O–O</sub> (Å)	1	1.46	1.47	1.46	1.45
	2	1.34	1.33	1.33	1.34
	3	—	1.30	1.29	1.30
Q  e	1	1.10	0.82	0.86	0.88
	2	0.56	0.50	0.48	0.52
	3	—	0.34	0.32	0.35

strongly, with a bond length in the peroxide regime. This is comparable with the case of the reduced (101) surface. In the case of V<sub>2c1</sub>, the adsorption of the second O<sub>2</sub> molecule is much reduced, while there is practically no binding for the third. On the other hand, for V<sub>2c2</sub>, V<sub>2c3</sub> and V<sub>3c1</sub> sites, the first adsorbed O<sub>2</sub> does not fill the vacant lattice site. The configuration of this adsorbed O<sub>2</sub> is displayed in ESI Fig. S4.† Therefore, the second O<sub>2</sub> has significant average adsorption energy, on the nearest Ti site available. This adsorbed O<sub>2</sub> has a bond length in the superoxide regime. The third O<sub>2</sub> is weakly bound, by physisorption since there is hardly any charge available on the surface, following the second binding. Thus, we see a graded lowering of the average adsorption energy and bond length with the number of O<sub>2</sub> adsorbed in Table 3.

In order to understand further the capture of O<sub>2</sub> by a vacant surface site, we performed CI-NEB calculations on reduced (101) and (103) TiO<sub>2</sub> and the details of CI-NEB can be found in S2.† We found that an energy barrier exists for the adsorbed O<sub>2</sub> to move to the vacant lattice site, in the case of V<sub>2c2</sub>, V<sub>2c3</sub>, and V<sub>3c1</sub> on the reduced (103) surface. This barrier is estimated to be 1.15 eV, 1.98 eV, and 0.78 eV respectively (see Fig. S5†). This is not the case for V<sub>2c1</sub> on reduced (103), or V<sub>2c</sub> and V<sub>3c</sub> on reduced (101), where the transfer is barrierless. It may hence be concluded that the advantage of vacancies on reduced (103) TiO<sub>2</sub> is that these provide multiple sites for O<sub>2</sub> activation, hosting more than one activated O<sub>2</sub> (as seen from Fig. S4†), resulting in improved efficiency for catalytic reactions.

### 3.3 O<sub>2</sub> adsorption over Au clusters supported on (101) and (103) TiO<sub>2</sub>

Next, we investigate a strategy to enhance O<sub>2</sub> activation over low loading of small Au clusters supported on (101) and (103) TiO<sub>2</sub> surfaces. Small Au clusters have been rigorously studied over several years, owing to a wide range of applications in catalysis, nanophotonics *etc.*<sup>64</sup> The formation of energetically stable Au<sub>*n*</sub> on the (101) surface is discussed by Wan *et al.*<sup>35</sup> and Vittadini *et al.*<sup>65</sup> To find a stable structure for Au<sub>*n*</sub>, (*n* = 3–5), on stoichiometric (101) and (103), we grow the cluster over the surface step-by-step, adding one Au atom at a time and re-optimizing the geometry of the entire system. In this case, the binding energy per Au is calculated using eqn (4).



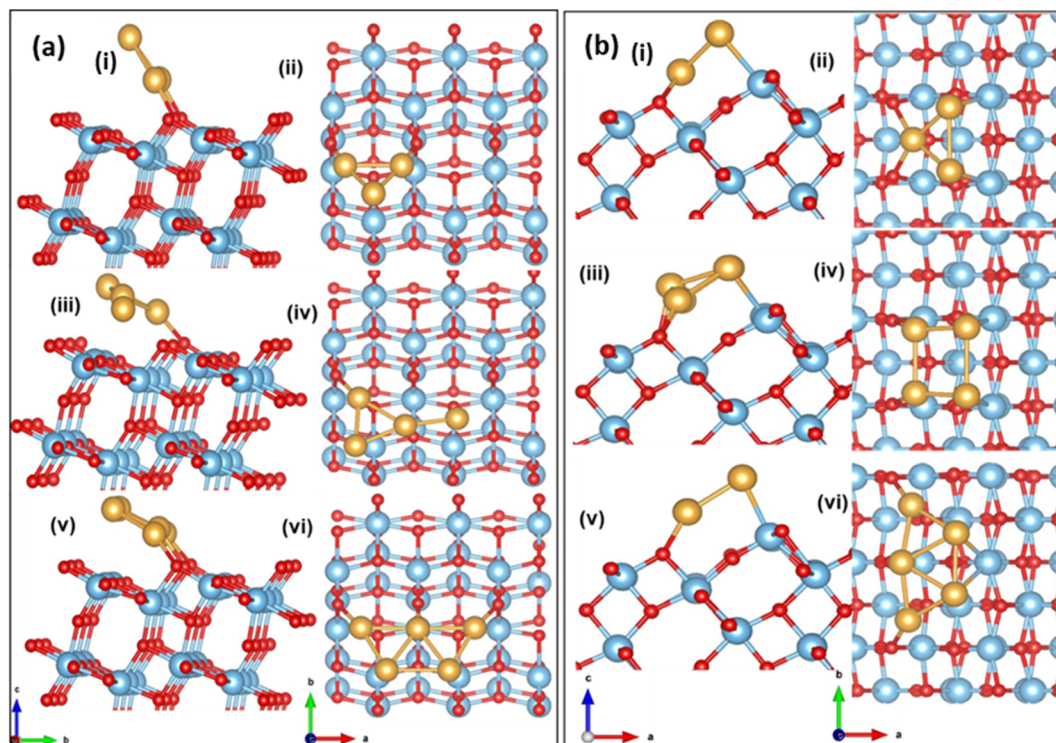


Fig. 3 Side view and top view of the optimized configuration of  $Au_n/TiO_2$  (a) (101); (b) (103) (i and ii)  $n = 3$ , (iii and iv)  $n = 4$ , (v and vi)  $n = 5$ .

The optimized configuration of an isolated  $Au_3$  cluster exhibits a planar, triangular geometry, which is more stable than the linear trimer. After adsorption and relaxation, the two Au atoms of the  $Au_3$  cluster bind to the  $O_{2c}$  of the (101)  $TiO_2$  surface with a binding energy of  $-2.28$  eV and an  $Au-O_{2c}$  bond length of  $2.04$  Å. The  $Au_3$  cluster is inclined at an angle of  $120^\circ$ , to the  $a$ -axis. The optimized configuration is shown in Fig. 3(a) (i and ii). In  $Au_4/TiO_2$ , the fourth Au atom is attached to the optimized  $Au_3/TiO_2$  structure and has a binding energy of  $-2.37$  eV. Of the two Au atoms attached to the  $O_{2c}$  in the case of  $Au_3/TiO_2$ , one Au gets detached in the case of  $Au_4/TiO_2$  and is tilted at an angle of  $148^\circ$ . The optimized configuration is shown in Fig. 3(a) (iii and iv). The most stable  $Au_5$  on (101)  $TiO_2$  is in the form of a planar trapezoidal structure. The three Au atoms are bonded with  $O_{2c}$  with an  $Au-O_{2c}$  bond length of  $2.13$  Å with a binding energy of  $-2.50$  eV. The  $Au_5$  cluster gets tilted at an angle of  $154^\circ$ . The stable structure is shown in Fig. 3(a) (v and vi).

$Au_n$  ( $n = 3-5$ ) has different possible binding sites on the (103) surface. Among these, three types of two-coordinated oxygen

sites ( $O_{2c1}$ ,  $O_{2c2}$ , and  $O_{2c3}$ ) are present. The planar  $Au_3$  cluster is grown atom by atom, and the binding energy is calculated using eqn (4). The favourable configuration of  $Au_3$  has a binding energy of  $-2.39$  eV at the  $O_{2c2}$  site with an  $Au-O_{2c2}$  bond length of  $2.24$  Å. The optimized configuration is shown in Fig. 3(b) (i and ii). The  $Au_3$  cluster on (103) is tilted at an angle of  $48^\circ$  to the  $b$ -axis. The  $Au_4$  cluster binds to the (103) with a binding energy of  $-2.62$  eV and adopts a square geometry after adsorption. The bond lengths  $Au-O_{2c2}$  and  $Au-Ti$  are  $2.08$  Å and  $2.72$  Å, respectively. The cluster is tilted at an angle of  $38^\circ$  (see Fig. 3(b) (iii and iv)). The  $Au_5$  cluster binds on the (103) surface in a trapezoidal geometry with a binding energy of  $-2.70$  eV and has an  $Au-O_{2c2}$  bond length of  $2.20$  Å, with a tilting angle of  $40^\circ$  (see Fig. 3(b) (v and vi)). The binding energy of the cluster in case of stepped surfaces is higher due to the availability of more states at the step edge.

The adsorption of  $O_2$  molecules on the optimized configuration of Au supported (101) and (103) surfaces has been investigated, and the results are tabulated in Table 4. Here, we have considered  $O_2$  adsorption on Ti atoms at the interface and

Table 4 The adsorption energy (in eV) and the O–O bond length (in Å) for the  $O_2$  molecule on  $Au_n$  ( $n = 3, 4$  and  $5$ ) supported on (101) and (103) surfaces, considering the active sites on  $Ti_{5c}$  (101)/ $Ti_{4c}$  (103) and Au

$Au_n$ ( $n$ )	(101)				(103)			
	$E_{ads}$ (eV) ( $Ti_{5c}$ )	$d_{O-O}$ (Å)	$E_{ads}$ (eV) (on Au)	$d_{O-O}$ (Å)	$E_{ads}$ (eV) ( $Ti_{4c}$ )	$d_{O-O}$ (Å)	$E_{ads}$ (eV) (on Au)	$d_{O-O}$ (Å)
3	−0.73	1.32	−0.39	1.27	−1.66	1.43	−0.78	1.30
4	−0.44	1.32	−0.38	1.24	−1.88	1.44	−0.90	1.36
5	−0.99	1.34	−0.85	1.32	−1.84	1.44	−1.10	1.35



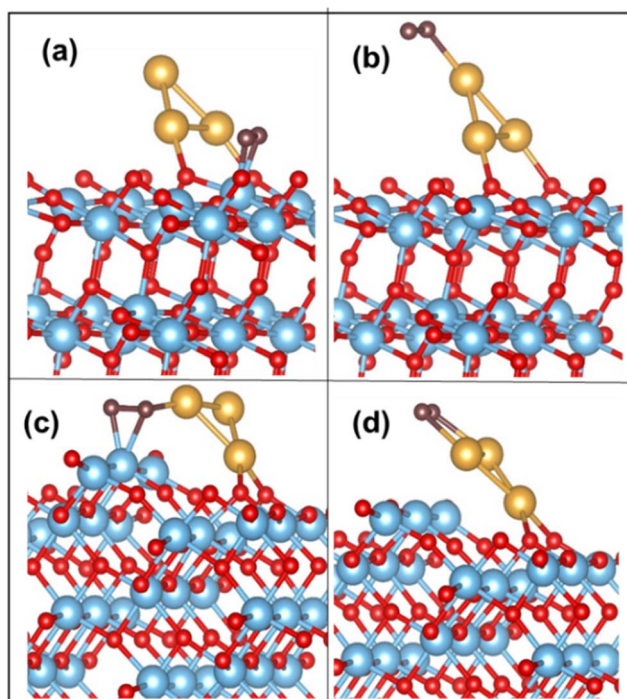


Fig. 4 O<sub>2</sub> adsorption on (a) Ti<sub>5c</sub> and (b) Au on the Au<sub>3</sub>/TiO<sub>2</sub> (101) surface; (c) Ti<sub>4c</sub> and (d) Au on the Au<sub>3</sub>/TiO<sub>2</sub> (103) surface.

low-coordinated Au sites on the cluster. At the interface, the preferred adsorption sites are Ti<sub>5c</sub> and Ti<sub>4c</sub>, for (101) and (103) respectively. As Table 4 shows (see col. 4 and 8), there is weaker adsorption for O<sub>2</sub> on the Au cluster itself, which is significant only in the case of the (103) surface.

On the Au<sub>3</sub> supported (101) surface, the O<sub>2</sub> molecule undergoes adsorption in a side-on configuration, with an adsorption energy of  $-0.73$  eV. The O–O bond length is elongated to  $1.32$  Å from the gas-phase bond length of  $1.23$  Å, and the Ti–O bond length is  $2.05$  Å. The optimized configurations of O<sub>2</sub> on Au<sub>3</sub>/TiO<sub>2</sub> (101) and (103) are depicted in Fig. 4(a) and (b). This trend is similarly observed for Au<sub>4</sub> and Au<sub>5</sub>, where O<sub>2</sub> adsorbs on the Ti<sub>5c</sub> site with the elongation of the O–O bond

(see Table 4). The corresponding configurations are not displayed here, for the sake of brevity. In all cases, the O–O bond exhibits an average length of  $1.32$  Å, which puts it in the superoxide regime. The adsorbed O<sub>2</sub> has a magnetic moment of  $1 \mu_B$ , which indeed confirms the superoxide state.<sup>9</sup>

To explore further the interaction of the adsorbed O<sub>2</sub> with the Au<sub>3</sub> cluster, we first rotate the cluster from  $0^\circ$  to  $180^\circ$  along the *a*-axis, as illustrated in Fig. 5(a), on the (101) surface. As the cluster is rotated through discrete angles, the O–O bond length shrinks and goes through a minimum. Correspondingly, the Au–O distance undergoes a maximum. It is interesting to note that the maximal stretching of the O–O bond occurs at angles where the cluster Au atoms are closest to the adsorbed oxygen. From the plot in Fig. 5(a), these angles are  $20^\circ$  and  $160^\circ$  with the *a*-axis, and the O–O bond stretches by  $0.04$  Å, with an Au–O bond distance of  $2.20$  Å. For an angle of  $60^\circ$ , where the Au<sub>3</sub> cluster is farthest away from the O<sub>2</sub>, the O–O stretching is minimized.

We also rotate the Au<sub>3</sub> cluster with respect to the *c*-axis (see Fig. 5(b)). The variation of the O–O bond length as a function of Au–O is plotted in Fig. 5(b). The O–O bonding exhibits maximum elongation at an angle of  $60^\circ$ , with the O–O bond length at  $1.36$  Å. At this point, the Au–O distance is  $2.30$  Å. The minimal stretching occurs at angles of  $0^\circ$  and  $140^\circ$ . The O–O bond undergoes maximum stretching when Au is closest to the O atom, forming a Ti–(O–O)–Au configuration. Thus, we understand from the above exercise that in terms of the O–O stretching, O<sub>2</sub> activation may be achieved by re-orienting the Au<sub>3</sub> cluster with respect to the adsorbed molecule, such that in some configurations, the Au atoms are close to the O<sub>2</sub> molecule.

The above discussed rotation of the Au<sub>3</sub> cluster (or Au<sub>*n*</sub> cluster) may be achieved through the application of a static electric field, lattice strain or steric effects due to bulky ligands.<sup>66,67</sup> There is yet another simpler way to achieve this bending, using naturally occurring surface imperfections. A stepped surface may naturally tilt the adsorbed cluster in a manner mimicking the *a*-axis rotation of Fig. 5(a). Thus, we propose that surface morphology may be used to tune cluster orientation. If we look at Au<sub>*n*</sub> cluster adsorption on a (103) TiO<sub>2</sub>

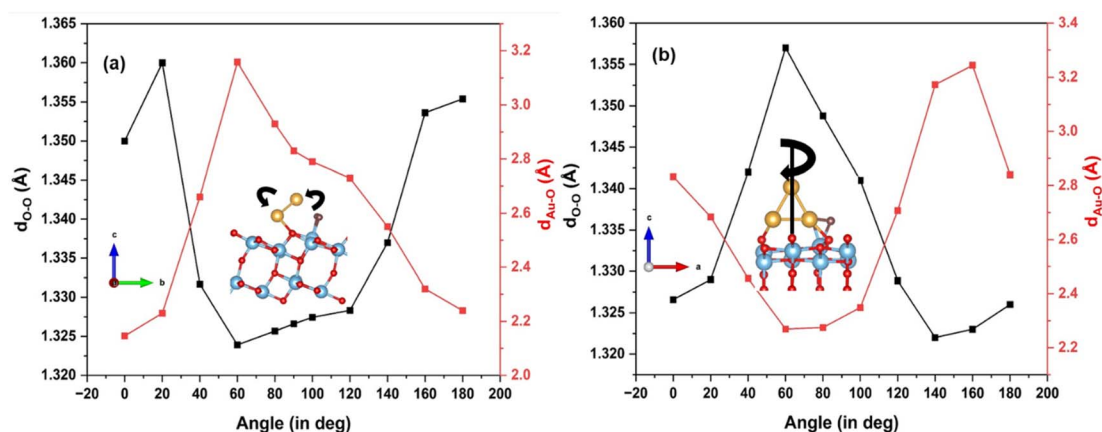


Fig. 5 Effect of Au<sub>3</sub> clusters supported on TiO<sub>2</sub> rotated along (a) *a*-axis; and (b) *c*-axis, on the O–O and Au–O bond lengths.



surface, the cluster inclines itself with the “kinks” on the (103) surface. The O<sub>2</sub> molecule adsorbs on the Ti<sub>4c</sub> site, with Au<sub>n</sub> at the perimeter, forming a Ti<sub>4c</sub>-(O-O)-Au bond. The calculated adsorption energy of O<sub>2</sub> for the Au<sub>3</sub> supported (103) surface is -1.66 eV, with the O-O distance stretched to 1.43 Å, corresponding to the peroxide bond length. The Au-O bond distance (*i.e.* O of O<sub>2</sub>) is measured at 2.07 Å. On the surface, we find that the Ti<sub>4c</sub> site is slightly lifted upward, by 0.20 Å, indicating a strong Ti-O interaction. The O-O activation also occurs on the Au cluster site exhibiting an adsorption energy of -0.78 eV. These optimized configurations of O<sub>2</sub> adsorbed on Au<sub>3</sub>/TiO<sub>2</sub> (103) are shown in Fig. 4(c) and (d). These findings hold true for Au<sub>n</sub> (*n* = 4, 5) clusters too. The corresponding binding energy values are tabulated in Table 4. The table reveals the O-O bond length in the peroxide regime. The calculated magnetic moment of the adsorbed O<sub>2</sub> species is close to 0 μ<sub>B</sub>. In the case of adsorption on the low coordinated Au on the cluster itself, Au<sub>n</sub> (*n* = 3-5) adsorb O<sub>2</sub> as superoxide species, as can be seen from calculated bond lengths (compared to weak binding on the Au/(101) TiO<sub>2</sub> surface) in Table 4. Thus, it appears that the interaction of the Au cluster with O<sub>2</sub> has been modified by the support (103) surface, into strong chemisorption, leading to activated O<sub>2</sub>.

To address the question of O<sub>2</sub> coverage, we calculate the adsorption energy for the second and third molecules, adsorbed on active sites on the surface. Table S1† displays the averages of adsorption energy per molecule, bond length and charge transfer (to O<sub>2</sub> molecule) for both (101) and (103) surfaces. For Au<sub>3</sub> supported (101), the adsorption energy of a single O<sub>2</sub> molecule is -0.85 eV accompanied by an electron transfer of 0.45*e*. The second and third molecules bind within the range of physisorption. In the case of (103), the addition of a second O<sub>2</sub> molecule results in an average adsorption energy of -1.10 eV, with a bond length of 1.31 Å falling within the superoxide range, and a charge transfer of 0.52*e*. The third O<sub>2</sub> molecule does not undergo chemisorption and exhibits an average adsorption energy of -0.83 eV. Consequently, the Au<sub>3</sub> supported (103)

surface shows an optimal O<sub>2</sub> binding compared to the (101) surface. The average adsorption energy per molecule for (103) is twice that of the (101) surface. Thus Au<sub>3</sub>/TiO<sub>2</sub> (103) can adsorb more than one O<sub>2</sub> molecule, in which two of them may be described as activated.

### 3.4 Stability and electronic structure considerations

To investigate the stability of the cluster configuration, molecular dynamics (MD) simulation for Au<sub>3</sub> on (101) and (103) is performed. The temperature is maintained at 300 K by using the Nose thermostat<sup>68</sup> for a duration of 6000 fs. Fig. S6(a)† depicts the time evolution for Au<sub>3</sub>/(101), along with the cluster configuration at 300 K. Monitoring the distance between Au and two-O<sub>2c</sub> (*d*<sub>1</sub> and *d*<sub>2</sub>) of TiO<sub>2</sub> reveals no observable fluctuations, with an average distance ranging from 2.02 to 2.39 Å, indicating dynamic stability. A similar situation (Fig. S6(b)†) is observed for (103), with an average distance of 2.05-2.57 Å. Thus, these structures are stable at room temperature.

The electronic structures of O<sub>2</sub> adsorbed Au<sub>3</sub> supported (101) and (103) TiO<sub>2</sub> are compared in Fig. 6(a) and (b). For the (101) surface we see localized states of Au 5d, below the Fermi energy, as well as O 2p from the adsorbed molecule. Additionally, we also notice Ti 3d states at the edge of the valence band. All these states are broadened out a little, indicating a weakly chemisorbed state for O<sub>2</sub> on the Au/TiO<sub>2</sub> (101) surface. In Fig. 6(b), over the (103) surface, we see a stronger hybridization between Au 5d, Ti 3d and O 2p states, whereby the cluster states now have a more delocalized character. Au 5d states have a larger contribution at the edge of the valence band, leading to the strengthening of O<sub>2</sub> adsorption. Looking at the difference charge density (or deformation density) plots in Fig. 6(c) and (d), it is clearly seen that there is no electron density accumulation in the O<sub>2</sub>-Au for Au/TiO<sub>2</sub> (101), while for Au/TiO<sub>2</sub> (103), excess charge density is present on the Au cluster, leading to enhanced O<sub>2</sub> adsorption. The charge accumulation on the O<sub>2</sub> is also enhanced, leading to the stretching of the O-O bond.

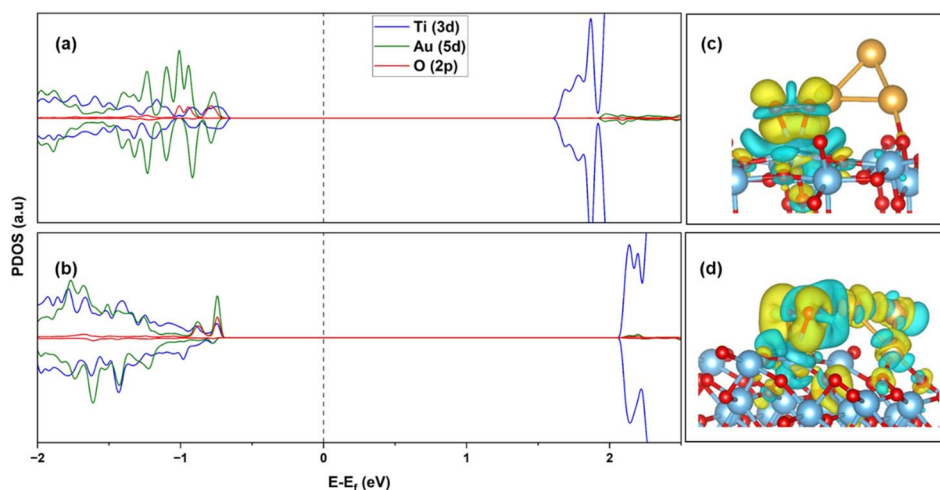


Fig. 6 PDOS of (a) Au<sub>3</sub>/TiO<sub>2</sub> (101), (b) Au<sub>3</sub>/TiO<sub>2</sub> (103), after O<sub>2</sub> adsorption; difference charge density plot of (c) O<sub>2</sub>/Au<sub>3</sub>/TiO<sub>2</sub> (101), (d) O<sub>2</sub>/Au<sub>3</sub>/TiO<sub>2</sub> (103). Yellow: charge accumulation; blue: charge depletion. Iso-surface level =  $2 \times 10^{-5} e \text{ \AA}^{-3}$ .



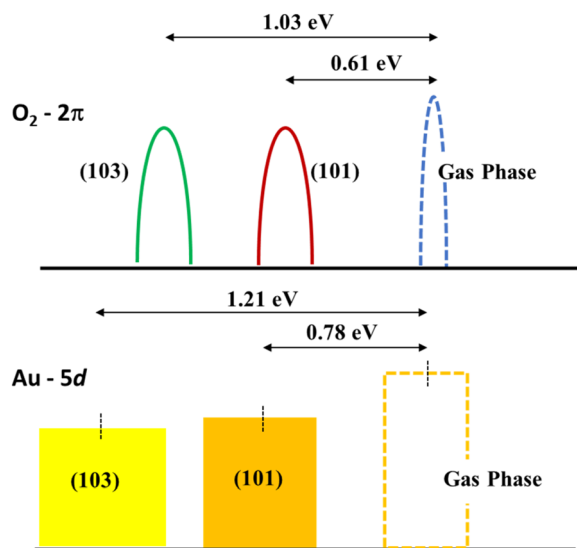


Fig. 7 Schematic illustration of the energy level shift for (101) and (103)  $\text{Au}_3/\text{TiO}_2$ .

Calculating Bader charges in the ground state, it is observed that a total charge of  $0.45e$  is transferred to the  $2\pi^*$  orbital of the  $\text{O}_2$  molecule in the  $\text{Au}_3/\text{TiO}_2$  (101) configuration. This transfer can be partially from Ti on the surface, and also from  $\text{Au}_3$ , through the surface (contributed during the relaxation of  $\text{Au}_3$  on

the surface). With the Au–O distance of  $3.70 \text{ \AA}$ , the probability of direct transfer between the Au cluster and  $\text{O}_2$  is very small. However, in the case of the  $\text{Au}_3/\text{TiO}_2$  (103), a transfer of  $0.78e$  is calculated to the  $\text{O}_2$  molecule. Now, the Au–O distance is  $2.07 \text{ \AA}$ , and the cluster interacts directly with the  $\text{O}_2$  molecule. Thus, charge transfer to  $\text{O}_2$  is now enabled through an additional channel: transfer from  $\text{Au}_3$  directly. The elongation of the O–O bond length can be attributed to the stronger interaction of the Au cluster with the  $\text{O}_2$  molecule, enabled by the (103) step. We may also say that  $\text{O}_2$  is stabilized at the Au– $\text{Ti}^{4+}$  interface through the formation of a di- $\sigma$  bond involving Au–(O–O)–Ti, which is consistent with interpretations from previous work.<sup>24,69</sup>

The role played by the (103) stepped surface can be understood in terms of the relative shift of the  $2\pi$  energy level of the  $\text{O}_2$  molecule and the d-band center<sup>70</sup> of  $\text{Au}_3$ . To obtain the energy of the  $2\pi$  state, we start with the ground state configuration of (101) with the  $\text{Au}_3$  cluster and  $\text{O}_2$  molecule, remove the  $\text{Au}_3$  completely, and then obtain the energy for the  $2\pi$  state of  $\text{O}_2$  through the energy calculations with the molecule placed  $2.10 \text{ \AA}$  and  $8.82 \text{ \AA}$  above (101). The difference in these energy values is a measure of the stabilization of the  $2\pi$  state due to bonding with the surface. This calculation is repeated for the (103) surface. We find that the energy of the  $2\pi$  level of the  $\text{O}_2$  molecule decreased by  $0.61 \text{ eV}$  for (101) and  $1.03 \text{ eV}$  for (103). In a similar manner, the d-band centre for  $\text{Au}_3$  over both (101) and

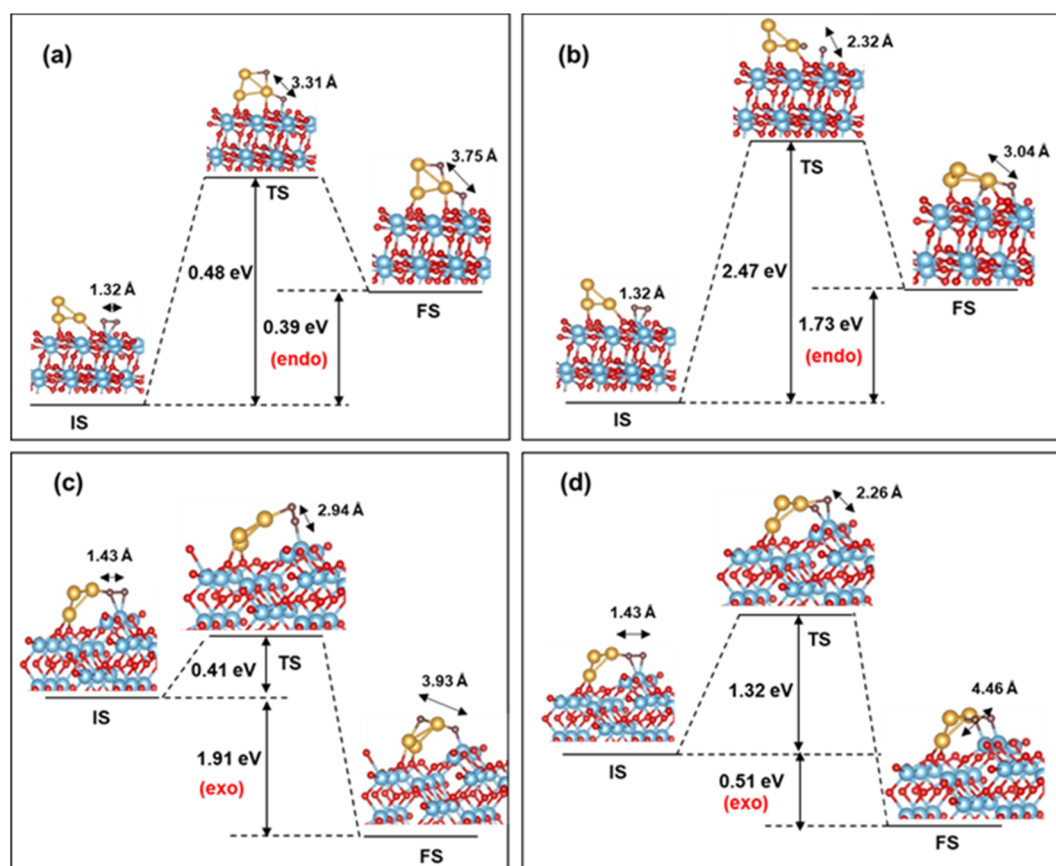


Fig. 8  $\text{O}_2$  dissociation barrier for (a) uplayered and (b) interfacial  $\text{Au}_3/\text{TiO}_2$  (101); (c) uplayered and (d) interfacial  $\text{Au}_3/\text{TiO}_2$  (103) (adsorbed  $\text{O}_2$  is in brown).



(103) was calculated without the O<sub>2</sub> molecule, with Au<sub>3</sub> positioned 2.06 Å and 10.70 Å above TiO<sub>2</sub>. The d-band centre is lowered to 0.78 eV for (101) and 1.21 eV for (103). The shifts of these two energy levels are indicated in Fig. 7. These two effects, namely the shifts of the O<sub>2</sub> 2π state and the d-band centre are indicators of O<sub>2</sub> activation which is enabled by (103) surface.

### 3.5 Activation barrier for O<sub>2</sub> dissociation for (101) and (103)

Next, we turn our attention to the dissociation process of O<sub>2</sub> on (101) and (103) Au<sub>3</sub>/TiO<sub>2</sub>. An estimate of the dissociation barrier is important information, in the context of CO oxidation as well as the ORR. For the CI-NEB pathway, we take the initial state (IS) as the ground state configuration of O<sub>2</sub> adsorbed on (101) and (103) Au<sub>3</sub>/TiO<sub>2</sub>. During the dissociation of O<sub>2</sub>, the dissociated O atom can migrate to two configurations: the “uplayered” and the “interfacial”. In the uplayered state, the oxygen atom after dissociation, attaches to the low coordinated site of Au<sub>3</sub>. In the interfacial state, the oxygen atom attaches itself to the neighbouring Ti. These configurations are illustrated in Fig. 8.

In the case of (101), the barrier for O<sub>2</sub> dissociation at the uplayered Au is 0.48 eV, which is favourable compared to the interfacial site with a barrier of 2.47 eV (refer to Fig. 8(a) and (b)). On the other hand, for (103) the barrier (0.41 eV) is notably lower for the uplayered site, making it kinetically favourable. The barrier for the interfacial site on the (103) surface is reduced by 1.15 eV in comparison to the (101) site, and the reaction is exothermic. Consequently, (103) Au<sub>3</sub>/TiO<sub>2</sub> exhibits superior O<sub>2</sub> dissociation compared to (101) Au<sub>3</sub>/TiO<sub>2</sub>. This conclusion is in line with the fact that the former activates adsorbed O<sub>2</sub> better than the latter. In contrast, the (101) or (103) TiO<sub>2</sub> without Au cluster has practically no stretching of the O–O bond, and hence very small probability for O<sub>2</sub> dissociation. As for non-supported Au clusters, the dissociation barrier is greater than 2 eV, according to the previous DFT studies.<sup>24</sup> Thus, we predict a lowering of the O<sub>2</sub> dissociation barrier in the case of Au supported stepped TiO<sub>2</sub> surfaces. This is comparable to Pt (111), where the dissociation barrier is 0.45 eV, as computed by DFT.<sup>71</sup> Our results are also comparable with studies on larger sized Au clusters on rutile TiO<sub>2</sub> (110), where barriers of the order of 0.4–0.6 eV are observed.<sup>72</sup> In particular, for the ORR, the nature of the activated state can provide information about the pathway, *i.e.* whether a four-electron or a two-electron pathway is likely to be followed, and thus the overall efficiency of the process. This is also true for any oxidation process on the surface, which involves the scission of the O–O bond in an activated state.

## 4. Conclusions

We have studied the adsorption and activation of oxygen molecules on plane (101), stepped (103) and reduced anatase TiO<sub>2</sub> surfaces in this paper using plane wave DFT-based modeling. While the (101) and (103) surfaces do not activate the adsorbed O<sub>2</sub> molecule, the reduced surfaces of the same adsorb O<sub>2</sub> strongly. If we consider multiple O<sub>2</sub> adsorption, it is seen that the reduced (103) TiO<sub>2</sub> surface binds more than one O<sub>2</sub> strongly. Hence, adsorption over vacancies is advantageous

in terms of greater coverage of activated O<sub>2</sub> when compared to (101) or (103) surfaces. Small sized Au clusters supported on the TiO<sub>2</sub> surface lead to strong adsorption and activation of O<sub>2</sub>. In particular, the orientation of these Au clusters can tune the activation of O<sub>2</sub>, which depends on the proximity of Au atoms to the molecule. One can manipulate the orientation of Au clusters on TiO<sub>2</sub> by adsorbing these on a step-edge of the surface. In such a configuration, we find a large stretching of the molecular O–O bond, into the peroxide regime, and strong binding. The electronic structure of the cluster–TiO<sub>2</sub> interface shows good hybridization between the Au d and O p states and considerable charge transfer to the O<sub>2</sub> molecule. In such an activated state, we find that the barrier for O<sub>2</sub> dissociation is lower compared to the case of free Au clusters or Au clusters supported on (101) TiO<sub>2</sub>. Thus, we have demonstrated a simple way to utilize the morphology of the surface to suitably orient the Au cluster for enhanced O<sub>2</sub> activation. Additionally, activated O<sub>2</sub> may also be contributed by the active sites on the gold cluster itself. Thus, there is an overall enhancement of O<sub>2</sub> activation through the Au cluster loading of the TiO<sub>2</sub> surface. Experimental verification of our proposal would open a new way to realize an active catalyst surface, supported by an inexpensive and earth-abundant material and realized at low Au loading. This has important implications for various catalytic oxidation reactions.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Author contributions

M. F. P.: conceptualization, formal analysis, investigation, visualization, writing – original draft. J. E. S.: conceptualization, formal analysis, investigation. R. C.: conceptualization, formal analysis, writing – review and editing, supervision, project administration.

## Conflicts of interest

There are no conflicts for the authors to declare.

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