

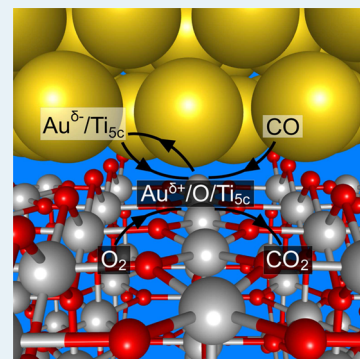
CO Oxidation at the Au/TiO<sub>2</sub> Boundary: The Role of the Au/Ti<sub>5c</sub> Site

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**ABSTRACT:** Density functional theory is used to determine the reaction mechanisms of CO oxidation and the active oxygen species on a Au/TiO<sub>2</sub> model catalyst. The model consists of a Au rod supported along the TiO<sub>2</sub> [110] direction of the TiO<sub>2</sub>(110) surface. An interfacial Au/Ti<sub>5c</sub> site at the interface boundary is identified to be particularly active toward O<sub>2</sub> adsorption and dissociation. At this site, O<sub>2</sub> dissociation has an energy barrier of 0.5 eV, which is facile at room temperature. The resulting adsorbed Au/O/Ti<sub>5c</sub> oxygen species are shown to be stable and active for CO oxidation under relevant reaction conditions with an activation energy of 0.24 eV. Furthermore, the adsorbed Au/O/Ti<sub>5c</sub> oxygen species functions as an electron reservoir, and it lowers the oxygen vacancy formation energy of a surface lattice oxygen (O<sub>brl</sub>), as well as the Ti interstitial formation energy, due to electron transfer from high-energy defect states to low-energy *p*-states of the adsorbed Au/O/Ti<sub>5c</sub> oxygen species. Hence, the O<sub>brl</sub> species is activated at the oxidized Au/TiO<sub>2</sub> interface boundary and the energy barrier of CO oxidation with O<sub>brl</sub> is calculated to be 0.55 eV. Thus, the CO oxidation reaction can proceed at room temperature either via a Langmuir–Hinshelwood mechanism with an adsorbed Au/O/Ti<sub>5c</sub> oxygen species or via a Au-assisted Mars–van Krevelen mechanism with O<sub>brl</sub>.

**KEYWORDS:** CO oxidation, Au/TiO<sub>2</sub>, gold catalysis, heterogeneous catalysis, density functional theory



## 1. INTRODUCTION

Oxide-supported Au nanoparticle catalysts have attracted enormous interest because they exhibit high activity for a number of different reactions.<sup>1–4</sup> CO oxidation on TiO<sub>2</sub> supported Au nanoparticles catalysts (Au/TiO<sub>2</sub>) has received the most intense investigation to elucidate the origin of the high catalytic activity at low temperature. However, due to the complex nature of the metal–oxide interface, there is a lack of consensus regarding several essential aspects of this reaction. The most important debate is the nature of the active site, and especially the site responsible for O<sub>2</sub> activation, which is the most energy intensive elementary step. In recent reviews,<sup>5,6</sup> various proposed active sites are summarized. The list includes metallic Au,<sup>7,8</sup> cationic Au,<sup>9,10</sup> under-coordinated Au,<sup>11–13</sup> and perimeter sites at the interface between the Au nanoparticle and the TiO<sub>2</sub> support.<sup>14–16</sup>

Recent studies have provided new insights understanding toward the nature of the active site. Green et al. found that CO oxidation occurs at the exposed metal–support interface at low temperature (*T* = 120 K) using IR spectroscopy.<sup>17</sup> The accompanying density function theory (DFT) calculations further assign the active site of O<sub>2</sub> activation to be the dual (Au–Ti) site at the interface boundary. The reaction mechanism is resolved to be that of adsorbed molecular O<sub>2</sub> reacting with adsorbed CO on the TiO<sub>2</sub> surface via a coadsorption CO–O<sub>2</sub> complex. In a number of theoretical studies,<sup>18–21</sup> molecularly adsorbed O<sub>2</sub> is also identified as an active oxygen species. However, desorption of the molecular O<sub>2</sub> is observed at 170 K in the work by Stiehl et al.,<sup>22,23</sup> indicating a different CO oxidation reaction mechanism at the higher reaction temperatures of relevance.

Based on multipulse measurements performed in a temporal analysis of products (TAP) reactor at temperature between 353 and 673 K, Behm and co-workers have identified the active oxygen species to be atomic surface lattice oxygen at the perimeter of Au nanoparticles.<sup>24–26</sup> Accordingly, the reaction mechanism is determined to be a Au-assisted Mars–van Krevelen (MvK) mechanism, in which surface lattice oxygen at, or close to, perimeter sites is consumed by coupling with CO and replenished by O<sub>2</sub> dissociative adsorption. A recent theoretical study by the Hammer group supports the Au-assisted MvK mechanism and further points out that only the surface lattice oxygen along the [110] direction of the support is catalytically active, and not along the [001] direction.<sup>27</sup> It remains unclear, however, how the Au nanoparticle activates the surface lattice oxygen: are active metal–support interactions at the interface playing a role, or does Au provide anchoring sites for CO so that it can react with nearby surface lattice oxygen? Furthermore, the experimental assignment of the active oxygen species in these studies is based on macroscopic observations and not directly from characterization methods with atomic resolution, so it is possible that the active role of other oxygen species has been overlooked.

This study addresses the electronic structure of the Au/TiO<sub>2</sub> interface and the adsorption and dissociation of O<sub>2</sub> at the interface. We have found that O<sub>2</sub> dissociation is facile at an electron-rich Au/Ti<sub>5c</sub> site at the interface boundary. The resulting adsorbed atomic oxygen at the Au/Ti<sub>5c</sub> site is stable

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under typical reaction conditions and active toward CO oxidation. This atomic oxygen species is also found to play a role in activating surface lattice oxygen at the interface perimeter.

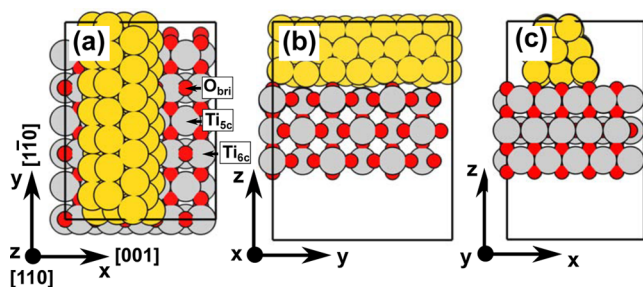
## 2. COMPUTATIONAL METHODS

Plane-wave based spin-polarized DFT calculations were performed using the Vienna Ab initio Simulation Package.<sup>28–30</sup>

The generalized gradient approximation with the Perdew–Wang (PW91) functional<sup>31</sup> was used to describe the exchange and correlation energy. Electron–ion interactions were treated by the projector augmented wave method.<sup>32</sup> In all calculations, the energy cutoff of the plane wave basis set was 400 eV. The DFT+*U* method was applied to 3d orbitals of Ti to correct the on-site Coulomb interactions.<sup>33</sup> The value of  $U_{\text{eff}}$  was chosen to be 4.0 eV to reproduce the electronic structure that has been observed experimentally.<sup>34,35</sup> Due to the large model employed, a  $\Gamma$  point sampling of the Brillouin zone was used to calculate the total energy of the system. Optimized structures were obtained by minimizing the forces on each ion until they fell below 0.05 eV/Å. Transition states were determined with the climbing image nudged elastic band method.<sup>36,37</sup> A Bader analysis was employed to determine the local charge of atoms in the system.<sup>38–40</sup>

## 3. RESULTS AND DISCUSSION

**3.1. Model of the Au/TiO<sub>2</sub> Interface.** The interface a TiO<sub>2</sub> supported Au nanoparticle is modeled by a periodic one-dimensional Au rod deposited along the TiO<sub>2</sub> [110] direction of a rutile TiO<sub>2</sub>(110) slab. In a previous study,<sup>18</sup> a Au rod was placed along the [001] direction on the TiO<sub>2</sub> substrate in order to minimize the lattice mismatch between Au and the substrate, and to minimize the system size required. However, recent environmental transmission electron microscopy measurements have shown that the dominant surface direction of the interface perimeter is along the <110> direction.<sup>41</sup> Accordingly, we orient the Au rod along the [110] direction in order to be consistent with the experimental observation, even though the lattice mismatch between Au and the TiO<sub>2</sub> substrate is greater in this direction. The model employed throughout this study is shown in Figure 1. The Au rod contains three layers; the interfacial layer has the structure of the Au(111) surface. In order to minimize the strain, a long Au rod consisting of seven Au atoms along the [110] direction is used. The lattice constants calculated in this work are  $a = 4.17$  Å for fcc Au and  $a = 4.69$  Å,  $c = 3.03$  Å for rutile TiO<sub>2</sub>. Based on these lattice constants, the Au rod is compressed by 3.7% in the axial



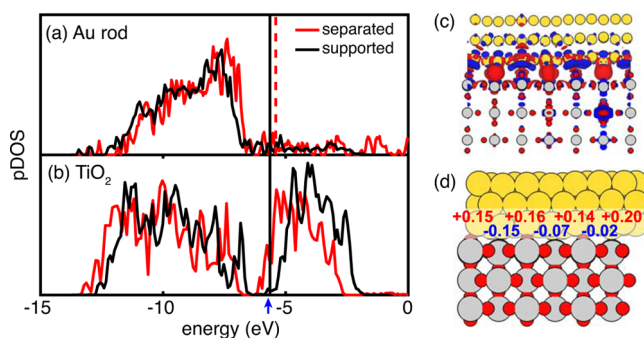
**Figure 1.** Au rod supported on the rutile TiO<sub>2</sub>(110) surface: (a) top, (b) front, and (c) side views. The bridging oxygen, the coordinatively unsaturated Ti site, and the coordinatively saturated Ti site on the TiO<sub>2</sub>(110) surface are denoted as O<sub>brid</sub>, Ti<sub>sc</sub>, and Ti<sub>sc</sub>.

direction to be commensurate with the  $p(5 \times 3)$  TiO<sub>2</sub>(110) substrate in the [110] direction. The TiO<sub>2</sub> substrate contains three stoichiometric TiO<sub>2</sub> layers. The top TiO<sub>2</sub> layer is allowed to relax while the bottom two layers are fixed in bulk lattice positions.

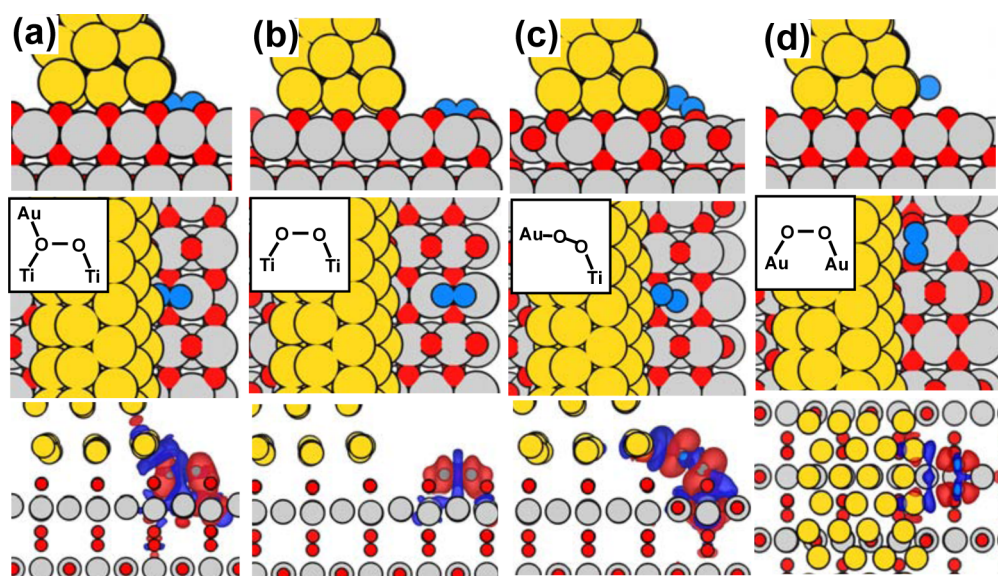
## 3.2. Electronic Structure of the Au/TiO<sub>2</sub> Interface.

Understanding the electronic structure of the Au/TiO<sub>2</sub> interface is important for elucidating the exceptional catalytic activity of the Au/TiO<sub>2</sub> catalyst, given that its constituents are catalytically inert, individually. When an interface is formed between a metal and a nonreactive (strongly ionic) oxide, interfacial electronic states appear primarily due to three types of interactions. The first effect is the conventional metal-induced gap states (MIGS), which are produced by the exponential decay of delocalized metal states within the insulator.<sup>42,43</sup> The characteristic of the conventional MIGS is a structureless continuum of states in the band gap of the oxide substrate. The second cause of interfacial states is the metal–oxygen bonding at the interface.<sup>44,45</sup> The metal–oxygen interaction results in donor- and acceptor-like states at well-defined energies located close the valence band maximum (VBM) and the conduction band minimum (CBM) of the oxide.<sup>46</sup> The third effect is the polarization of metal electrons by the electronic field of the substrate.<sup>47,48</sup> The polarization is analogous to the macroscopic image charge effect. As a result, metal electrons will populate/deplete the space between the deposited metal and the surface cation/anion. The interfacial states from the conventional MIGS and the metal–oxygen hybridization induce charge transfer across the interface creating an interface dipole moment. Polarization of the metal electrons also contributes to the interface dipole moment, although it does not involve any charge transfer across the interface. The work function of the metal and the oxide is shifted according to the direction of the interface dipole moment.

The projected density of states (pDOS) of the Au rod and the TiO<sub>2</sub> slab before and after interface formation are shown in Figure 2a,b. When separated, the Fermi energy ( $E_f$ ) of the Au rod is higher than the CBM of the TiO<sub>2</sub> slab, so that electrons flow from the Au rod to the TiO<sub>2</sub> substrate, making the oxide negatively charged. The negatively charged oxide is also manifest by the occupation of acceptor-like states near the CBM due to the metal–oxygen hybridization at the interface, as



**Figure 2.** Projected density of states (pDOS) of the (a) Au rod and (b) TiO<sub>2</sub> substrate before and after the Au is supported on the TiO<sub>2</sub> substrate. The electronic energy reference is the vacuum level in both cases. The charge redistribution due to the interface formation is plotted in (c), where red indicates electron accumulation and blue indicates electron depletion. The net Bader charges of the Au atoms along the interface boundary are shown in (d).



**Figure 3.** Structures of adsorbed O<sub>2</sub> (top and middle panels) and the charge redistribution upon O<sub>2</sub> adsorption (bottom) at different adsorption sites at the perimeter of the Au/TiO<sub>2</sub> interface boundary: (a) Au/Ti<sub>5c</sub>-Ti<sub>5c</sub>, (b) Ti<sub>5c</sub>-Ti<sub>5c</sub>, (c) Au-Ti<sub>5c</sub>, (d) Au-Au. The side and top views of the adsorption structures are shown in the top and middle panels, respectively. In this figure and in later figures, Au, Ti, and O atoms are represented by yellow, gray, red circles, respectively; adsorbed O<sub>2</sub> is cyan.

**Table 1. Properties of Adsorbed O<sub>2</sub> at Different Sites at the Perimeter of the Au/TiO<sub>2</sub> Interface Boundary and the Bare TiO<sub>2</sub> Surface, Including Bond Length, Net Charge, Magnetization, Binding and Dissociation Energies, and Activation Energy for Dissociation**

site	bond (Å)	charge ( e )	mag. (μ <sub>B</sub> )	E <sub>bind</sub> (eV)	E <sub>diss</sub> (eV)	E <sub>a</sub> (eV)
Au/Ti <sub>5c</sub> -Ti <sub>5c</sub>	1.429	0.92	0.00	-1.64	-0.70	0.50
Ti <sub>5c</sub> -Ti <sub>5c</sub>	1.401	0.82	0.00	-1.31	0.04	1.16
Au-Ti <sub>5c</sub>	1.370	0.72	0.00	-1.05	-0.13	—
Au-Au	1.278	0.32	0.62	0.04	0.18	—
Ti <sub>5c</sub> -Ti <sub>5c</sub> bare TiO <sub>2</sub>	1.261	0.00	1.98	-0.06	3.53	—

indicated by the blue arrow in Figure 2b. Charge transfer from Au to the stoichiometric TiO<sub>2</sub> support is also observed in experimental measurements by photoelectron spectroscopy.<sup>49,50</sup> Beside charge transfer caused by the work function difference of the metal and the oxide, polarization effects at the interface also contribute to the band alignment. In order to resolve the polarization effect, the charge redistribution upon interface formation is shown in Figure 2c. It can be seen that electron density is depleted from the space between Au and O<sub>br1</sub> and populated into the space between Au and Ti<sub>5c</sub>, as a result of the polarization of metal electrons induced by the electrostatic field of the substrate, or equivalently, the image charge effect. Consequently, Au atoms of two different charge states can be identified along the interface boundary. The Bader charges in Figure 2d show that cationic Au is present at the Au/O<sub>br1</sub> site and anionic Au is present at the Au/Ti<sub>5c</sub> site.

In summary, the interface established between the Au rod and the TiO<sub>2</sub> substrate gives rise to two main effects. First, excess electrons appear on the TiO<sub>2</sub> substrate as a result of the charge transfer from the Au rod. Second, both cationic and anionic Au species appear at the interface depending on their registry with the substrate due to the image charge effect. These two effects, caused by interface formation, will be shown to have significant consequences for the catalytic properties.

**3.3. O<sub>2</sub> Adsorption and Dissociation at the Au/TiO<sub>2</sub> Interface.** To investigate the catalytic properties of the Au/TiO<sub>2</sub> interface, we start by studying O<sub>2</sub> adsorption. Four unique

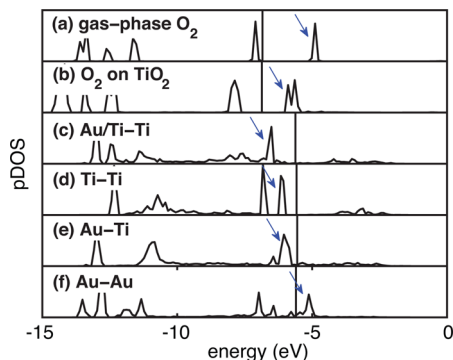
O<sub>2</sub> adsorption sites (Au/Ti<sub>5c</sub>-Ti<sub>5c</sub>, Ti<sub>5c</sub>-Ti<sub>5c</sub>, Au-Ti<sub>5c</sub>, Au-Au) are recognized at the interface perimeter, as well as a Ti<sub>5c</sub>-Ti<sub>5c</sub> site on bare rutile TiO<sub>2</sub>(110) surface, for comparison. The O<sub>2</sub> adsorption structures are shown in Figure 3, and their corresponding properties are summarized in Table 1.

The O<sub>2</sub> molecule adsorbs strongly at the interface with binding energies greater than 1 eV. This is in sharp contrast with the weak O<sub>2</sub> adsorption on the bare TiO<sub>2</sub> surface, illustrating the prominent role of the Au/TiO<sub>2</sub> interface. To understand the reason behind the binding strength enhancement at the interface, Bader charges and magnetic moments of the adsorbed O<sub>2</sub> are calculated. Adsorbed O<sub>2</sub> at the Au/Ti<sub>5c</sub>-Ti<sub>5c</sub>, Ti<sub>5c</sub>-Ti<sub>5c</sub>, and Au-Ti<sub>5c</sub> sites all feature a significant charge transfer to the LUMO (lowest unoccupied molecular orbital) 2π\* states of O<sub>2</sub> and a charge state similar to a peroxide (O<sub>2</sub><sup>2-</sup>) species. Charge transfer to the LUMO 2π\* states is also seen in the plots of charge density redistribution upon O<sub>2</sub> adsorption in Figure 3, where electrons populate the LUMO 2π\* orbital in a dumbbell shape when O<sub>2</sub> is adsorbed at the Au/Ti<sub>5c</sub>-Ti<sub>5c</sub>, Ti<sub>5c</sub>-Ti<sub>5c</sub>, and Au-Ti<sub>5c</sub> sites. In contrast, on the bare TiO<sub>2</sub> surface, no charge is transferred to O<sub>2</sub>, and it has a triplet spin state, which is a signature of the gas-phase O<sub>2</sub> molecule. The most pronounced charge transfer to O<sub>2</sub>, and also the strongest binding, occur at the Au/Ti<sub>5c</sub>-Ti<sub>5c</sub> site. At this adsorption state, O<sub>2</sub> not only accepts charge from the substrate, it also benefits from the electron-rich Au/Ti<sub>5c</sub> site. O<sub>2</sub> does not



adsorb at Au–Au sites because the Au–O interaction is of a covalent nature, and there is no significant charge transfer to the  $2\pi^*$  state of  $O_2$ .

To understand why charge transfers to adsorbed  $O_2$ , the  $p$ -states of  $O_2$  in the gas-phase and various adsorbed states are shown in Figure 4. Initially, the LUMO  $2\pi^*$  state in the gas-

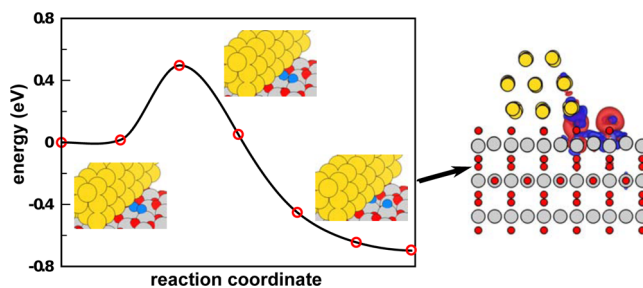


**Figure 4.** pDOS of an  $O_2$  molecule in (a) gas-phase and adsorbed at the (b) bare  $TiO_2$  surface, (c)  $Au/Ti_{5c}-Ti_{5c}$ , (d)  $Ti_{5c}-Ti_{5c}$ , (e)  $Au-Ti_{5c}$  and (f)  $Au-Au$  sites. The Fermi level of each system is denoted by a black vertical line. The LUMO  $2\pi^*$  orbital of  $O_2$  is indicated by a blue arrow.

phase  $O_2$  lies above the Fermi level of the  $Au/TiO_2$  interface. When  $O_2$  is brought into contact with the bare  $TiO_2$  surface, the LUMO  $2\pi^*$  state is shifted downward in energy because of the electrostatic interaction with the Ti cation. The energy shift of the  $O_2$  orbitals can be seen in Figure 4a,b. As a result of this shift, the charge transfer to the LUMO  $2\pi^*$  states is now possible because it drops below the Fermi level of the  $Au/TiO_2$  interface.

In addition, adsorbed  $O_2$  must be in contact with the Ti cation in order to gain access to the excess electron density on the substrate transferred from the Au rod. After charge transfer, the occupied LUMO  $2\pi^*$  state is further stabilized by the Ti cations in which  $O_2$  is in contact. The degree of stabilization positively correlates with the number of electrons transferred to the LUMO  $2\pi^*$  state, as can be seen in Figure 4c–e. This picture of charge transfer to the  $2\pi^*$  state is similar to that described in a previous study by Liu et al.<sup>20</sup>

The strong binding of  $O_2$  at the  $Au/TiO_2$  interface suggests the possibility of facile dissociation. The heats of  $O_2$  dissociation ( $E_{diss}$ ) and the activation energies ( $E_a$ ) at the  $Au/Ti_{5c}-Ti_{5c}$ ,  $Ti_{5c}-Ti_{5c}$ , and  $Au-Ti_{5c}$  sites are listed in Table 1. The dissociation process is exothermic by  $-0.7$  eV, and the energy barrier is  $0.5$  eV at the  $Au/Ti_{5c}-Ti_{5c}$  site, as can also be seen in the minimum energy path (MEP) in Figure 5. After dissociation, one O atom is further embedded into the space between the Au atom and the  $Ti_{5c}$  atom; the other O atom sits atop the  $Ti_{5c}$  atom. The dissociation of the  $O_2$  molecule adsorbed at the  $Ti_{5c}-Ti_{5c}$  site, on the other hand, is endothermic and has an energy barrier of  $1.16$  eV. At the  $Au-Ti_{5c}$  site,  $O_2$  dissociation is found to proceed in two steps; first,  $O_2$  diffuses to the  $Au/Ti_{5c}-Ti_{5c}$  site and then dissociates, as in Figure 5. The charge redistribution in the final state is shown in Figure 5, where charge transfer to the two adsorbed O atoms can be seen. A Bader analysis gives net charges on O at the  $Au/Ti_{5c}$  and  $Ti_{5c}$  sites of  $0.87e$  and  $0.74e$ , respectively. Both have zero magnetic moments as in a  $O^{2-}$  species. The source of the excess charge on the two O atoms is different, however. At



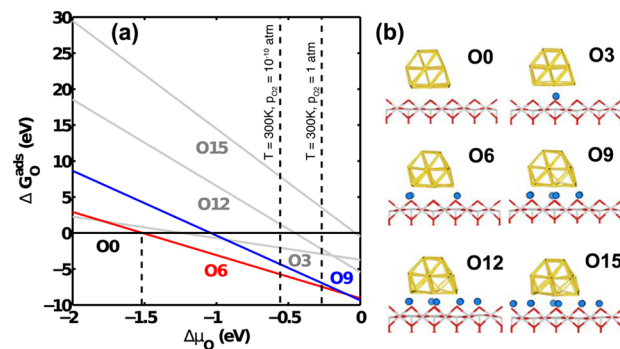
**Figure 5.** MEP of  $O_2$  dissociation at the  $Au/Ti_{5c}-Ti_{5c}$  site of the  $Au/TiO_2$  interface boundary. The insets show the atomic structure of the initial, transition, and final states. The right panel shows the charge redistribution upon adsorption of the two atomic O atoms.

the  $Au/Ti_{5c}$  site, the Au electrons that initially populated the space between Au and  $Ti_{5c}$  now populate the O  $p$ -states. The excess electron density on the O atom atop the  $Ti_{5c}$  site comes from the oxide substrate initially transferred from the Au rod. The additional interaction between the adsorbed O and Au at the  $Au/Ti_{5c}$  site makes its binding energy lower than that of the adsorbed O atop the  $Ti_{5c}$  site by  $0.4$  eV.

**3.4. Oxidation of  $Au/TiO_2$  Interface.** Interfacial oxidation is expected under catalytically relevant conditions because of facile  $O_2$  dissociation. To account for the oxidation, we have conducted ab initio thermodynamics calculations to determine the Gibbs free energy of O adsorption ( $\Delta G_{O}^{ads}$ ) as a function of the O chemical potential ( $\mu_O$ ), calculated as<sup>51</sup>

$$\Delta G_{O}^{ads} \approx E_{Au/TiO_2+N_O,O} - E_{Au/TiO_2} - N_O \left( \frac{1}{2} E_{O_2} + \Delta\mu_O \right) \quad (1)$$

where  $E_{Au/TiO_2+N_O,O}$  is the total energy of the oxidized  $Au/TiO_2$  interface with  $N_O$  oxygen atoms adsorbed around the interface perimeter,  $E_{Au/TiO_2}$  is the total energy of the  $Au/TiO_2$  interface,  $E_{O_2}$  is the total energy of gas-phase  $O_2$  molecule, and  $\Delta\mu_O$  is the free energy contribution to  $\mu_O$ . In these calculations, various O adsorption sites are considered including the  $Au/Ti_{5c}$  site at the interface, the  $Au/Ti_{5c}$  site at the interface boundary, and  $Ti_{5c}$  sites away from the interface. Based on these different O adsorption sites, six oxidized  $Au/TiO_2$  structures are examined in the ab initio thermodynamics calculation. The Gibbs free energy of oxygen adsorption as a function of O chemical potential is shown in Figure 6, along with the adsorption structures.

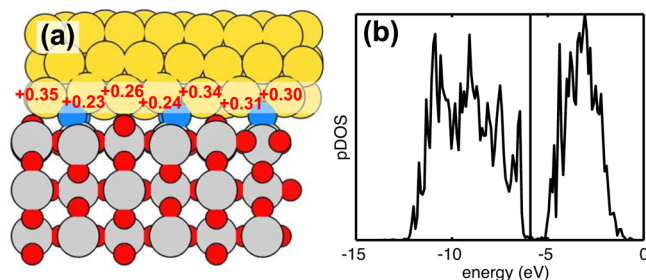


**Figure 6.** (a) Gibbs free energy of adsorption is plotted as a function of oxygen chemical potential. (b) O adsorption structures at the  $Au/TiO_2$  interface perimeter.

Structures with a reduced TiO<sub>2</sub> substrate containing oxygen vacancies are not included because our calculations, as well as previous theoretical studies,<sup>52</sup> have shown that the reduced structures are unstable under an oxygen-rich environment. We also note that a reduced TiO<sub>2</sub> slab with Ti interstitials could have a strong influence on the interfacial oxidation, because Ti interstitials induced donor-like gap states and provide the electrons required for O<sub>2</sub> adsorption and dissociation, as pointed out in ref 53. In this study, however, we focus on the interfacial oxidation of pristine TiO<sub>2</sub> slab.

Figure 6a shows that over a wide range of  $\mu_{\text{O}}$  values, the O6 structure is most stable, in which O atoms adsorb at the Au/Ti<sub>5c</sub> sites along the interface boundary. More importantly, the O6 stability region extends to the experimental low-temperature oxidation reaction conditions ( $T = 300$  K,  $p_{\text{O}_2} = 10^{-10}$ – $1$  atm), as indicated in Figure 6a by vertical dashed lines. At extremely high  $\mu_{\text{O}}$ , close to the point of O<sub>2</sub> condensation ( $\Delta\mu_{\text{O}} = 0$ ), the oxidation of the entire Au/TiO<sub>2</sub> interface can occur; the corresponding structure is shown as O9. In contrast, O atoms occupying Ti<sub>5c</sub> sites at the interface perimeter are energetically favorable over the whole range of  $\Delta\mu_{\text{O}}$  examined. Most importantly, the adsorbed O atoms at the Au/TiO<sub>2</sub> interface boundary are the most abundant O species under reaction conditions. Interfacial oxidation at the Au/Ti<sub>5c</sub> site has been recognized in previous theoretical studies.<sup>52,54</sup> More recently, using an evolutionary global optimization algorithm, full interfacial oxidation structures (like the O9 structure) are predicted to be the most stable under catalytically relevant conditions.<sup>27,55</sup> This discrepancy may be related to the different optimization algorithm employed (global vs local).

**3.5. Promoting Effect of Interfacial Oxygen on TiO<sub>2</sub> Reduction.** In the most catalytically relevant O6 structure, the previously mentioned anionic Au species above the Ti<sub>5c</sub> site along the interface boundary is oxidized and turned into cationic Au. The net Bader charges on the Au atoms along the interface boundary are shown in Figure 7a. Another effect of



**Figure 7.** (a) Net Bader charges and (b) pDOS of the Au atoms along the oxidized Au/TiO<sub>2</sub> interface perimeter of the O6 structure.

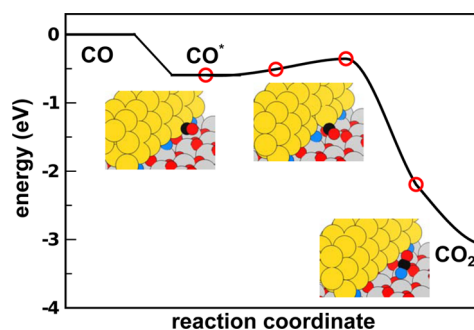
the oxidation of the interface boundary is that additional electronic states appear in the band gap, as shown in Figure 7b. The additional states leads to a shift of the Fermi level from the CBM in Figure 2b to slightly above the VBM. As a result of the Fermi level shift, we found that reduction of the TiO<sub>2</sub> slab is promoted.

At the Au/stoichiometric TiO<sub>2</sub> interface boundary (the O0 structure), the vacancy formation energy of a surface lattice oxygen ( $O_{\text{bri}}$ ) is calculated to be 3.18 eV. Compared to the vacancy formation energy of 2.33 eV on the bare TiO<sub>2</sub> surface, Au is found to stabilize  $O_{\text{bri}}$ . At the oxidized Au/TiO<sub>2</sub> interface (the O6 structure), the oxygen vacancy formation energy of  $O_{\text{bri}}$  is reduced to 1.57 eV. Similarly, TiO<sub>2</sub> reduction is also

enhanced by the presence of Ti interstitials. The Ti interstitial formation energy is calculated to be 0.98 and  $-0.71$  eV for the O0 and O6 structures, respectively, by placing a Ti atom into an O-octahedral site between the first and second layer of the TiO<sub>2</sub> slab. Metallic Ti is used as the reference for the Ti interstitial defect, and the chemical potential of Ti with respect to this reference is taken to be 0. Based upon the spin density, the charge state of the Ti interstitial defect is 0 and +3 at the stoichiometric and oxidized interfaces, respectively. This decrease in the oxygen vacancy and the Ti interstitial formation energy can be explained by the shift of Fermi level between stoichiometric Au/TiO<sub>2</sub> and oxidized Au/TiO<sub>2</sub>, as shown in Figure 7. Experimental observations and theoretical calculations indicate that oxygen vacancy and Ti interstitial defect produce a localized state right below the conduction band.<sup>53,56</sup> At the stoichiometric Au/TiO<sub>2</sub> interface, the localized defect states are occupied, because the Fermi level is located around the CBM. In contrast, at the oxidized Au/TiO<sub>2</sub> interface, it is energetically favorable for the electrons to be released from the high-energy defect states and occupy states near the Fermi level around the VBM, resulting in a stabilization of the vacancy. These states at the Fermi level around VBM of the oxidized Au/TiO<sub>2</sub> interface are  $p$ -states of the adsorbed Au/O/Ti<sub>5c</sub> oxygen species.

To summarize, we argue that the TiO<sub>2</sub> support can be more easily reduced under catalytically relevant conditions due to the presence of interfacial oxygens at Au/Ti<sub>5c</sub> sites. Evidence from experiments support this prediction. In situ electrical conductance measurements<sup>57</sup> have shown that the electrical conductance of the Au/TiO<sub>2</sub> catalyst increases immediately after the introduction of the reaction mixture, which is attributed to the generation of oxygen vacancies at the perimeter of the interface boundary. Ti interstitial ions are found to exist at the interface of Au/TiO<sub>2</sub> from TEM images, whereas they are deficient in a peripheral region of the gold nanoparticles.<sup>58</sup> This observation can be explained by the Ti interstitials in the bulk diffusing to the Au/TiO<sub>2</sub> interface because of the low defect formation energies.

**3.6. O Species Active for CO Oxidation.** As shown in the previous sections, O<sub>2</sub> can readily overcome the 0.5 eV dissociation barrier at the Au/Ti<sub>5c</sub>–Ti<sub>5c</sub> adsorption site at room temperature. Additionally, the dissociated atomic O is stable at the Au/Ti<sub>5c</sub> site under reaction conditions, as demonstrated by our ab initio thermodynamic calculations. Finally, we consider the ability for O adsorbed at the Au/Ti<sub>5c</sub> site to oxidize CO, which in turn readily adsorbs to the Au nanoparticle. Figure 8 shows the MEP of this reaction and that the process is highly exothermic with a calculated activation

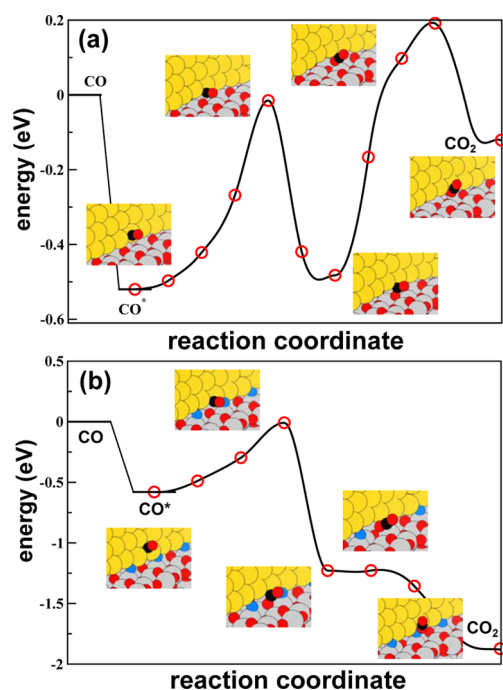


**Figure 8.** MEP of adsorbed O at the Au/Ti<sub>5c</sub> site reacting with a CO adsorbed on the Au rod. The insets show the atomic structure of the initial, transition, and final states.

energy of 0.24 eV. The low activation energy indicates that the adsorbed O at the Au/Ti<sub>5c</sub> site is highly active toward CO oxidation.

Previous experimental studies using TAP<sup>25</sup> have assigned the active oxygen species to be surface lattice oxygen (O<sub>brl</sub>) at the perimeter of Au nanoparticle. Our computational results, however, suggest that the active role of adsorbed O at the Au/Ti<sub>5c</sub> site (Au/O/Ti<sub>5c</sub>) at the interface boundary has been overlooked in the interpretation of the experimental results, because the criteria for the active oxygen species summarized from the experimental observation are met by the Au/O/Ti<sub>5c</sub> species. First, deposition of Au/O/Ti<sub>5c</sub> is fast through facile O<sub>2</sub> dissociation at Au/Ti<sub>5c</sub>-Ti<sub>5c</sub> site. Second, Au/O/Ti<sub>5c</sub> is stable provided that the average adsorption energy of Au/O/Ti<sub>5c</sub> is -1.51 eV/O in the O6 structure. Third, Au is indispensable in O<sub>2</sub> dissociation and stabilizing Au/O/Ti<sub>5c</sub>.

A further issue in the assignment of Au/O/Ti<sub>5c</sub> as the active oxygen species is a comparison with the activity of the O<sub>brl</sub> species at the interface boundary. As demonstrated in the previous section, interfacial oxygen at the Au/Ti<sub>5c</sub> site reduces the O vacancy formation energy of O<sub>brl</sub>. To further illustrate the role of the Au/O/Ti<sub>5c</sub> oxygen species in activating surface lattice oxygens (O<sub>brl</sub>), MEPs for the CO oxidation involving an O<sub>brl</sub> at the interface boundary with and without the adsorbed Au/O/Ti<sub>5c</sub> oxygen species were calculated and the results are shown in Figure 9. The MEP of CO oxidation can be



**Figure 9.** MEP of a surface O<sub>brl</sub> reacting with an adsorbed CO on the Au rod in (a) O0 and (b) oxidized O6 structures.

considered consisting of two parts. In the first step, adsorbed CO on the Au rod diffuses toward the O<sub>brl</sub> and then forms an intermediate bent CO<sub>2</sub> species. To complete the CO oxidation, in the second step, the bent CO<sub>2</sub> desorbs from the interface boundary leaving behind an oxygen vacancy. In the bent CO<sub>2</sub> formation process, the barrier is about 0.55 eV at both the oxidized and stoichiometric interface boundaries. The activation of the interfacial O<sub>brl</sub> species is manifested in the CO<sub>2</sub> desorption step. At the Au/stoichiometric TiO<sub>2</sub> interface

boundary, the desorption is endothermic with a barrier 0.65 eV, due to the high vacancy formation energy of O<sub>brl</sub>. In sharp contrast, the CO<sub>2</sub> desorption process is exothermic and barely activated at the oxidized interface boundary. Hence, we have shown that surface lattice oxygen (O<sub>brl</sub>) is also active toward CO oxidation under reaction conditions. The activation of O<sub>brl</sub> relies on the presence of adsorbed Au/O/Ti<sub>5c</sub> oxygen species. In experiments, the activity of surface lattice oxygens toward CO oxidation is confirmed by in situ electrical conductance measurement.<sup>57</sup> It was found the electrical conductance of the Au/TiO<sub>2</sub> catalyst immediately increased just after the introduction of the reaction mixture, which is attributed to the generation of oxygen vacancies at the perimeter of the interface boundary.

In this study, we have proposed a new picture of the CO oxidation reaction mechanism over a Au/TiO<sub>2</sub> catalyst. Both the Langmuir-Hinshelwood (LH) and Au-assisted MvK mechanisms are calculated to be active at the Au/TiO<sub>2</sub> interface boundary. Briefly, adsorbed CO on the Au rod can either react with an adsorbed Au/O/Ti<sub>5c</sub> oxygen species via a LH mechanism or react with a surface lattice oxygen O<sub>brl</sub> via a Au-assisted MvK mechanism at the oxidized Au/TiO<sub>2</sub> interface boundary. Although the LH mechanism has been extensively explored theoretically, in contrast to this work, most previous calculations predict that CO reacts with molecular O<sub>2</sub> forming an intermediate CO·O<sub>2</sub> complex from which CO<sub>2</sub> forms and desorbs.<sup>18,20,21,59,60</sup> This mechanism of CO oxidation could be active at low temperatures, but it is not consistent with recent experiments showing that the active oxygen species is atomic oxygen, due to its superior stability at room temperature and above.<sup>25</sup> More recently, Hammer's group highlighted the role of the Au/Ti<sub>5c</sub> site for adsorbing oxygen species and explicitly proposed that adsorbed O<sub>2</sub> and O are active for CO oxidation.<sup>27</sup> This reaction mechanism is similar to our LH mechanism, but the activity of O<sub>brl</sub> was not examined. For the Au-assisted MvK mechanism, the activity of O<sub>brl</sub> was investigated and confirmed in a recent ab initio molecular dynamics study using the small Au<sub>16</sub> cluster model.<sup>61</sup>

**3.7. Role of Au/Ti<sub>5c</sub> Site in CO Oxidation.** The Au/Ti<sub>5c</sub> site at the interface boundary of Au/stoichiometric TiO<sub>2</sub> is electron-rich and oxophilic due to the polarization effect of Ti cations on the metallic Au orbitals. We have demonstrated that O<sub>2</sub> adsorption, dissociation, and Au/TiO<sub>2</sub> interface oxidation can take place at this Au/Ti<sub>5c</sub> site. In terms of CO oxidation via the LH mechanism, the Au/Ti<sub>5c</sub> site stores oxygen for CO to react with. During the course of the CO oxidation process via the LH mechanism, the Au atom alternates between anionic and cationic state. For the Au-assisted MvK mechanism, the Au/Ti<sub>5c</sub> site participates in the reaction only indirectly in that the adsorbed O at the site works as an electron reservoir which facilitates oxygen vacancy generation.

## 4. CONCLUSION

We have employed DFT calculations to investigate CO oxidation at the Au/TiO<sub>2</sub> interface perimeter along the TiO<sub>2</sub> [110] direction. Further understanding has been gained regarding the exceptional catalytic activity of CO oxidation at room temperature. We have identified the Au/Ti<sub>5c</sub> site at the interface boundary as being active for O<sub>2</sub> dissociation. At the Au/Ti<sub>5c</sub> site, O<sub>2</sub> dissociatively adsorbs with an energy barrier of 0.5 eV. Under reaction conditions, the Au/Ti<sub>5c</sub> site is found to be oxidized. Interfacial oxygen atoms facilitate the reduction of the TiO<sub>2</sub> support either by oxygen vacancy



formation or Ti interstitial formation. The adsorbed O atom at the Au/Ti<sub>5c</sub> is shown to be active toward CO oxidation with a low energy barrier of 0.24 eV. In contrast, surface lattice oxygen O<sub>bri</sub> at an unoxidized interface boundary is inactive. At the oxidized interface boundary, however, O<sub>bri</sub> is activated by adsorbed Au/O/Ti<sub>5c</sub> oxygen.

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### Notes

The authors declare no competing financial interest.

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## REFERENCES

- (1) Haruta, M.; Daté, M. *Appl. Catal., A* **2001**, *222*, 427–437.
- (2) Haruta, M. *CATTECH* **2002**, *6*, 102–115.
- (3) Bond, G. C.; Thompson, D. T. *Gold Bulletin* **2000**, *33*, 41–50.
- (4) Hashmi, A. S. K.; Hutchings, G. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7896–7936.
- (5) Haruta, M. *Faraday Discuss.* **2011**, *152*, 11–32.
- (6) Wu, Y. Y.; Mashayekhi, N. A.; Kung, H. H. *Catal. Sci. Technol.* **2013**, *3*, 2881–2891.
- (7) Yang, J. H.; Henao, J. D.; Raphulu, M. C.; Wang, Y.; Caputo, T.; Groszek, A. J.; Kung, M. C.; Scurrill, M. S.; Miller, J. T.; Kung, H. H. *J. Phys. Chem. B* **2005**, *109*, 10319–10326.
- (8) Kung, M. C.; Davis, R. J.; Kung, H. H. *J. Phys. Chem. C* **2007**, *111*, 11767–11775.
- (9) Fierro-Gonzalez, J. C.; Gates, B. C. *Chem. Soc. Rev.* **2008**, *37*, 2127–2134.
- (10) Miller, J.; Kropf, A.; Zha, Y.; Regalbutto, J.; Delannoy, L.; Louis, C.; Bus, E.; van Bokhoven, J. J. *Catal.* **2006**, *240*, 222–234.
- (11) Mavrikakis, M.; Stoltze, P.; Nørskov, J. K. *Catal. Lett.* **2000**, *64*, 101–106.
- (12) Lopez, N.; Janssens, T.; Clausen, B.; Xu, Y.; Mavrikakis, M.; Bligaard, T.; Nørskov, J. K. *J. Catal.* **2004**, *223*, 232–235.
- (13) Lopez, N.; Nørskov, J. K. *J. Am. Chem. Soc.* **2002**, *124*, 11262–11263.
- (14) Schubert, M. M.; Hackenberg, S.; van Veen, A. C.; Muhler, M.; Plzak, V.; Behm, R. J. *Catal.* **2001**, *197*, 113–122.
- (15) Kung, H. H.; Kung, M. C.; Costello, C. K. *J. Catal.* **2003**, *216*, 425–432.
- (16) Bond, G. C.; Thompson, D. T. *Catal. Rev.* **1999**, *41*, 319–388.
- (17) Green, I. X.; Tang, W.; Neurock, M.; Yates, J. T. *Science* **2011**, *333*, 736–739.
- (18) Molina, L. M.; Rasmussen, M. D.; Hammer, B. *J. Chem. Phys.* **2004**, *120*, 7673–7680.
- (19) Wang, J. G.; Hammer, B. *Phys. Rev. Lett.* **2006**, *97*, 136107.
- (20) Liu, Z.-P.; Gong, X.-Q.; Kohanoff, J.; Sanchez, C.; Hu, P. *Phys. Rev. Lett.* **2003**, *91*, 266102.
- (21) Wang, Y.-G.; Yoon, Y.; Glezakou, V.-A.; Li, J.; Rousseau, R. J. *Am. Chem. Soc.* **2013**, *135*, 10673–10683.
- (22) Stiehl, J. D.; Kim, T. S.; McClure, S. M.; Mullins, C. B. *J. Am. Chem. Soc.* **2004**, *126*, 1606–1607.
- (23) Stiehl, J. D.; Kim, T. S.; McClure, S. M.; Mullins, C. B. *J. Am. Chem. Soc.* **2004**, *126*, 13574–13575.
- (24) Kotobuki, M.; Leppelt, R.; Hansgen, D. A.; Widmann, D.; Behm, R. J. *J. Catal.* **2009**, *264*, 67–76.
- (25) Widmann, D.; Behm, R. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 10241–10245.
- (26) Widmann, D.; Behm, R. J. *Acc. Chem. Res.* **2014**, *47*, 740–749.
- (27) Vilhelmsen, L. B.; Hammer, B. *ACS Catal.* **2014**, *4*, 1626–1631.
- (28) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47*, 558.
- (29) Kresse, G.; Furthmüller, J. *Comput. Mater. Sci.* **1996**, *6*, 15–50.
- (30) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54*, 11169.
- (31) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.
- (32) Blöchl, P. E. *Phys. Rev. B* **1994**, *50*, 17953.
- (33) Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C. J.; Sutton, A. P. *Phys. Rev. B* **1998**, *57*, 1505–1509.
- (34) Morgan, B. J.; Watson, G. W. *Surf. Sci.* **2007**, *601*, 5034–5041.
- (35) Finazzi, E.; Di Valentin, C.; Pacchioni, G.; Selloni, A. *J. Chem. Phys.* **2008**, *129*, 154113.
- (36) Henkelman, G.; Jónsson, H. *J. Chem. Phys.* **2000**, *113*, 9978–9985.
- (37) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. *J. Chem. Phys.* **2000**, *113*, 9901–9904.
- (38) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: New York, 1990.
- (39) Henkelman, G.; Arnaldsson, A.; Jónsson, H. *Comput. Mater. Sci.* **2006**, *36*, 354–360.
- (40) Tang, W.; Sanville, E.; Henkelman, G. *J. Phys.: Condens. Matter* **2009**, *21*, 084204.
- (41) Kuwauchi, Y.; Yoshida, H.; Akita, T.; Haruta, M.; Takeda, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 7729–7733.
- (42) Louie, S. G.; Cohen, M. L. *Phys. Rev. B* **1976**, *13*, 2461–2469.
- (43) Bordier, G.; Noguera, C. *Phys. Rev. B* **1991**, *44*, 6361–6371.
- (44) Tung, R. T. *Phys. Rev. B* **2001**, *64*, 205310.
- (45) Goniakowski, J.; Noguera, C. *Interface Sci.* **2004**, *12*, 93–103.
- (46) Yeo, Y.-C.; King, T.-J.; Hu, C. *J. Appl. Phys.* **2002**, *92*, 7266–7271.
- (47) Goniakowski, J. *Phys. Rev. B* **1998**, *57*, 1935–1941.
- (48) Giordano, L.; Cinquini, F.; Pacchioni, G. *Phys. Rev. B* **2006**, *73*, 045414.
- (49) Okazawa, T.; Kohyama, M.; Kido, Y. *Surf. Sci.* **2006**, *600*, 4430–4437.
- (50) Jiang, Z.; Zhang, W.; Jin, L.; Yang, X.; Xu, F.; Zhu, J.; Huang, W. *J. Phys. Chem. C* **2007**, *111*, 12434–12439.
- (51) Reuter, K.; Scheffler, M. *Phys. Rev. B* **2001**, *65*, 035406.
- (52) Laursen, S.; Linic, S. *J. Phys. Chem. C* **2009**, *113*, 6689–6693.
- (53) Wendt, S.; Sprunger, P. T.; Lira, E.; Madsen, G. K. H.; Li, Z.; Hansen, J. Ø.; Matthiesen, J.; Blekinge-Rasmussen, A.; Lægsgaard, E.; Hammer, B.; Besenbacher, F. *Science* **2008**, *320*, 1755–1759.
- (54) Laursen, S.; Linic, S. *Phys. Chem. Chem. Phys.* **2009**, *11*, 11006–11012.
- (55) Vilhelmsen, L. B.; Hammer, B. *J. Chem. Phys.* **2013**, *139*, 204701.
- (56) Henrich, V. E.; Dresselhaus, G.; Zeiger, H. J. *Phys. Rev. Lett.* **1976**, *36*, 1335–1339.
- (57) Maeda, Y.; Iizuka, Y.; Kohyama, M. *J. Am. Chem. Soc.* **2013**, *135*, 906–909.
- (58) Tanaka, T.; Sumiya, A.; Sawada, H.; Kondo, Y.; Takayanagi, K. *Surf. Sci.* **2014**, *619*, 39–43.
- (59) Remediakis, I. N.; Lopez, N.; Nørskov, J. K. *Angew. Chem.* **2005**, *117*, 1858–1860.
- (60) Li, L.; Gao, Y.; Li, H.; Zhao, Y.; Pei, Y.; Chen, Z.; Zeng, X. C. *J. Am. Chem. Soc.* **2013**, *135*, 19336–19346.
- (61) Li, L.; Zeng, X. C. *J. Am. Chem. Soc.* **2014**, *136*, 15857–15860.