A density functional theory study on the adsorption of CO and O_2 on Cu-terminated Cu_2O (111) surface*

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The adsorptions of CO and O_2 molecules individually on the stoichiometric Cu-terminated Cu_2O (111) surface are investigated by first-principles calculations on the basis of the density functional theory. The calculated results indicate that the CO molecule preferably coordinates to the Cu_2 site through its C atom with an adsorption energy of −1.69 eV, whereas the O_2 molecule is most stably adsorbed in a tilt type with one O atom coordinating to the Cu_2 site and the other O atom coordinating to the Cu_1 site, and has an adsorption energy of −1.97 eV. From the analysis of density of states, it is observed that Cu 3d transfers electrons to 2π orbital of the CO molecule and the highest occupied 5σ orbital of the CO molecule transfers electrons to the substrate. The sharp band of Cu 4s is delocalized when compared to that before the CO molecule adsorption, and overlaps substantially with bands of the adsorbed CO molecule. There is a broadening of the 2π orbital of the O_2 molecule because of its overlapping with the Cu 3d orbital, indicating that strong 3d-2π interactions are involved in the chemisorption of the O_2 molecule on the surface.

Keywords: adsorption, Cu_2O (111), density function theory

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1. Introduction

Despite numerous experimental and theoretical studies, many surface properties of metal oxides are not well understood. Metal–oxide surfaces behave as catalysts for reactions in gases or solutions, or in some cases, act as supports for catalysts. The challenge is to understand the factors controlling the adsorption and reactivity of the adsorbates on the surface. Recently, photocatalytic properties of Cu_2O have been studied extensively. It is demonstrated to be a promising photocatalyst in direct water splitting and organic contamination degradation under visible-light irradiation.[1,2] Additionally, Cu_2O can effectively adsorb an oxygen molecule which can scavenge the photogenerated electrons to restrain the recombination of electron–hole pairs and consequently improve the photocatalytic efficiency.[3] Furthermore, some researchers have studied the synthesis and growth mechanism of Cu_2O microcrystals, and found that the photocatalytic properties of different crystal faces were different. The Cu_2O (111) facet showed the highest photocatalytic activity, while its adsorption and photocatalytic ability were related to the nature of the crystal surface.[4,5]

The Cu_2O (111) surface belongs to class II of Tasker's classification of polar surfaces with a non-polar O termination (O–Cu_4–O–O–Cu_4–O–$\cdots$) and a polar Cu termination (Cu_4–O–O–Cu_4–O–O–$\cdots$).[6] Schulz and Cox[7] showed that the Cu_2O (111) surface could be prepared in a nearly stoichiometric non-reconstructed (1×1) form by ion bombardment and annealing in a vacuum, and found that the absence of reconstruction deduced the non-polar properties of the O-terminated Cu_2O (111) surface. So far, both theoretically and experimentaly, the non-polar stoichiometric O-terminated Cu_2O (111) surface has often been chosen as an ideal model system to investigate the properties of stability, structure, and ad-

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sorption. However, experimental and theoretical calculation studies showed that the polar Cu-terminated Cu_2O (111) surface can be stabilized by surface reconstruction or by surface hydroxylation.[8−11] The basic interaction and reaction of small molecules with the Cu_2O (111) surface, such as CO, O_2, H_2, NO, N_2O, H_2S, NH_3, and H_2O, are crucial to fundamentally understanding the mechanism of the catalytic processes.[12−27] Although the nature of the individual adsorption of CO and O_2 on the O-terminated Cu_2O (111) perfect surface and defect surface have been investigated by theoretical calculations,[14−21] to the best of our knowledge, no theoretical research has been carried out on the individual adsorption of CO and O_2 on the Cu-terminated Cu_2O (111) surface. Therefore, we hope that our theoretical study can provide instructive information for an experiment to further investigate the interaction of CO and O_2 with a Cu-terminated Cu_2O (111) surface.

In the present study, we conduct detailed density functional theory (DFT) calculations about CO and O_2 molecules individually adsorbed on the possible sites of the Cu-terminated Cu_2O (111) surface. We also investigate the electronic structural changes upon the CO and O_2 adsorptions by calculating the densities of states (DOSs) of the Cu 3d and Cu 4s of Cu-terminated Cu_2O (111) surface, respectively. According to the values of the adsorption energy, the CO molecule coordinates to Cu_2 through its C atom, and the O_2 molecule is adsorbed in a tilt type with one O atom coordinating to the Cu_2 site and the other O atom coordinating to the Cu_1 site. This should represent the most stable molecule adsorption states. From the analysis of the Mulliken population and DOS, we find that CO is positively charged, and there is a strong charge transfer from CO to the substrate, whereas the adsorbed O_2 molecule is polarized and negatively charged, indicating that the substrate donates electrons to O_2 molecule.

2. Calculation details

The computations were performed using the density functional theory (DFT) method. The first-principles DFT approach used here is based on the plane-wave basis set and the pseudopotential concept to describe the electron–ion interaction. All relaxation and total energy calculations are carried out by the CASTEP package on the basis of DFT within the ultrasoft pesudopotential approach.[28] The Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional based on the generalized gradient approximation (GGA) is employed.[29−32] In the calculations, the kinetic energy cutoff (450 eV) and the density of the Monkhorst–Pack k point mesh of $6 \times 6 \times 6$ are chosen which is sufficient to ensure the convergence of the computed bulk Cu_2O structure. Our calculated lattice constant for bulk Cu_2O is 4.30 Å (1 Å=0.1 nm) and Cu–O bond length is 1.86 Å, which are generally in agreement with both experimental measurements and other theoretical calculations.[11,18,33,34]

The calculations are performed with the slab model using 15 layers for the Cu-terminated Cu_2O (111) surface comprising of a 2-dimensional (1×1) surface unit. A vacuum layer of 12 Å is employed to separate each slab from its neighbouring images along the z direction. We do not execute a dipole correction, because neglecting the dipole correction for surface systems results in a small change of the binding energy by a few tens of meV.[35,36] The self-consistent convergence accuracy is set at 1.0×10^{-5} eV/atom. The convergence criterion of the largest force on atoms is 0.03 eV/Å, the maximum displacement is 1.0×10^{-5} Å. The convergence of the calculated total energy is examined with increasing k-point meshes by fixing kinetic energy cutoff $E_{\rm cut}$. We find that the calculated total energy converges with a $4 \times 4 \times 1$ Monkhoprst–Pack k-point grid. For the CO and O_2 molecules, all the relaxation calculations are performed under exactly the same calculation conditions as those on the Cu_2O (111) surface. In all calculations, the six topmost layers of our slab and the CO or O_2 molecule are allowed to fully relax, while the remaining layers are kept fixed.

The adsorption energy is defined as $E_{\rm ads} = E_{\rm adsorbate/substrate} - (E_{\rm adsorbate} + E_{\rm substrate})$, where $E_{\rm adsorbate/substrate}$, $E_{\rm adsorbate}$, and $E_{\rm substrate}$ are the total energies of adsorbate/substrate, isolated adsorbate molecules (CO, O_2), and substrate, respectively. A negative value corresponds to a stable adsorbate/substrate system. One adsorbate molecule per unit cell is included in the calculation for the individual adsorptions of the CO and O_2 molecules.

3. Results and discussion

3.1. Surface relaxation

The stoichiometric Cu-terminated Cu_2O (111) surface has three different surface atoms,[11] namely the oxygen atom (O_1), the copper atom (Cu_1), which is laterally bonded to the oxygen atom, and the copper atom (Cu_2), which is perpendicularly bonded to

the next oxygen layer. The relaxed geometry for the Cu-terminated Cu_2O (111) surface is shown in Fig. 1. The calculated geometry parameters for the Cu-terminated Cu_2O (111) surface are in good accordance with the optimized geometry of Islam *et al.*[11] Upon relaxation, the Cu-terminated surface shows a considerable geometrical rearrangement. The oxygen atom of the second layer moves towards the topmost copper layer, and the three Cu_1 atoms and the oxygen atoms of the second layer tend to become planar. The bond lengths increase from 1.87 Å to 2.03 Å and 1.90 Å for O_1–Cu_1 and O_2–Cu_2, respectively. Islam *et al.* have reported that geometrical rearrangement was indicative of a possible surface reconstruction stabilizing the polar Cu-terminated Cu_2O (111) surface.[11]

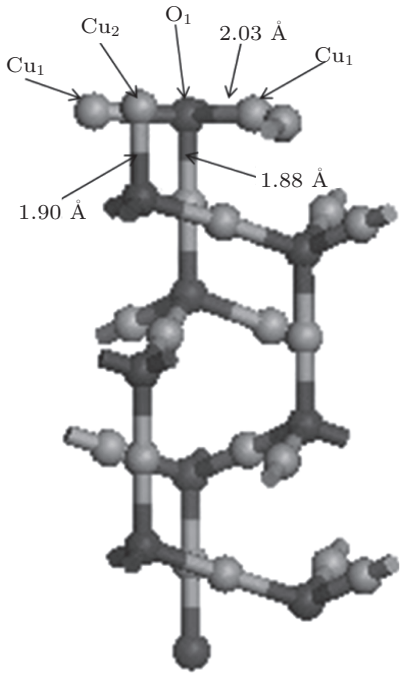


Fig. 1. Relaxed structure of the stoichiometric Cu-terminated Cu_2O (111) surface. The optimized bond is labeled. Copper atoms are shown as grey spheres and oxygen atoms as black spheres.

3.2. Adsorption of CO on stoichiometric Cu-terminated Cu_2O (111)

The adsorption of the CO molecule on the Cu-terminated Cu_2O (111) surface is theoretically investigated. The CO molecule is set to be C-down and O-down, perpendicular to three distinct sites, i.e., the Cu_1, Cu_2, and O_1 sites respectively. The equilibrium configuration parameters and adsorption energies for the CO molecule on the Cu-terminated Cu_2O (111) surface are listed in Table 1.

Table 1. Properties of the CO molecule adsorbed at different adsorption sites on the Cu-terminated Cu_2O (111) surface. The distances and angles between the adsorption site and the adsorbate are represented by R_e and α. Bond length and adsorption energy are in units of Å and eV, respectively.

Mode	R_{C-O}	R_e	α	E_{ads}
Cu_1–CO	1.162	1.848	178°	–0.81
Cu_2–CO	1.158	1.782	180°	–1.69
O_1–CO	1.152	3.545	178°	–0.23
Cu_1–OC	1.155	3.419	136°	–0.22
Cu_2–OC	1.243	2.066	178°	–0.29
O_1–OC	1.242	3.373	180°	0.001

From Table 1, we find, as expected, that the C-down orientation is more favoured than the O-down one. The adsorption energy is larger for the CO adsorbed with C-down over the Cu_2 site than that at the Cu_1 and O_1 sites, indicating that CO prefers to be adsorbed at the Cu_2 site through its C atom as shown in Fig. 2(a). The calculated adsorption energy is −1.69 eV which indicates that the adsorption is chemisorption and a strong bond is formed between the CO and Cu_2 sites. The bond length of the C–O is elongated from 1.141Å to 1.158 Å, which indicates that the C–O bond in the adsorbed CO molecule gains a little activation. From the structural analysis, we can see that the CO molecule is still perpendicular to the surface after optimization (the angle of O–C–Cu_2 is 180°). For the CO molecule with C-down toward the surface Cu_1 site configuration, the adsorption energy is −0.81 eV, which is smaller than that at the Cu_2 site. However, this adsorption configuration is also chemisorption. For CO with O-down toward the surface O_1 site configuration, the adsorption energy is bigger than zero and this structure is found to be endothermic. As for other adsorption models their adsorption energies are relatively small which is

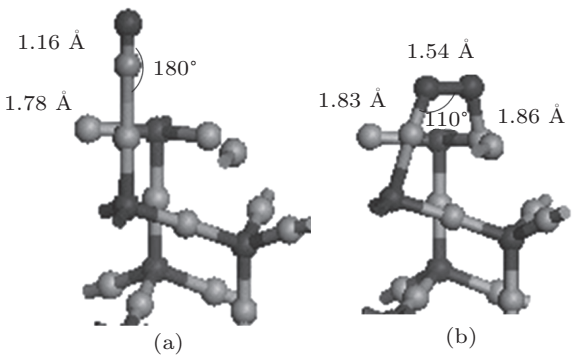


Fig. 2. The optimized stable configurations: (a) CO adsorption on Cu_2 of the Cu-terminated Cu_2O (111) surface, (b) O_2 adsorption on Cu_2 of the Cu-terminated Cu_2O (111) surface.

indicative of physisorption. As is well known, the shorter the adsorbed distance, the more stable the adsorption system is. From the analysis of adsorbed distances R_e, we know that the CO molecule coordinates preferably to the Cu_2 site through its C atom which is consistent with the results from the adsorption energy.

3.3. Adsorption of O_2 on stoichiometric Cu-terminated Cu_2O (111)

The adsorption of O_2 on Cu-terminated Cu_2O (111) is investigated in a manner similar to the one described for our previous studies about H_2 adsorption on Cu-terminated Cu_2O (111).[37] We consider two main adsorption configurations on the three distinct sites, Cu_1, Cu_2, and O_1 sites, respectively. The first type corresponds to end-on adsorptions at Cu_1, Cu_2, and O_1 sites, which can be denoted as M1, M2, and M3, respectively. The second one is a side-on adsorption type. The M4, M5, and M6 types represent O_2 adsorbed parallelly on the Cu_1, Cu_2, and O_1 sites, respectively. The calculated results of the O_2 molecule on Cu-terminated Cu_2O (111) are given in Table 2. For the end-on type, a feature of a bent structure is seen in M1 after being optimized. The angle of O–O–Cu_1 is 130° and the calculated adsorption energy is −0.15 eV. The O_2 molecule is most favourably adsorbed in a tilt type with one O atom coordinating to the Cu_2 site and the other O atom coordinating to the Cu_1 site after being optimized for the M2 and M4 types as shown in Fig. 2(b). The adsorption energy is −1.97 eV, which indicates a strong interaction between the O_2 molecule and Cu atom. The adsorption is chemisorption. The O–O bond length is 1.54 Å, and is elongated by 0.30 Å compared with the value of 1.24 Å in the free O_2 molecule. For the M3 type, the corresponding adsorption energy is bigger than zero and this structure is not thermodynamically favoured. For the side-on M5 type, the bond length of the O–O is elongated from 1.24 Å to 1.44 Å, and the calculated O1–Cu_2 and O2–Cu_2 bond lengths are 1.829 Å and 2.098 Å, respectively. The calculated adsorption energy is −1.46 eV. For the M6 type, the adsorption configuration is more stable than that of the M3 type, and has an adsorption energy of −1.42 eV which indicates that the adsorption of the O_2 molecule on the surface is chemisorption. In comparison with the adsorption on the O-terminated Cu_2O (111) surface,[20] the O_2 molecule adsorption on Cu-terminated Cu_2O (111) surface is more favourable.

Table 2. Properties of O_2 adsorbed at different adsorption sites on the stoichiometric Cu-terminated Cu_2O (111) surface, and bond length and adsorption energy are in units of Å and eV, respectively. For the M1 and M3 types, the angle of the O–O-adsorption site is α. For the M2 and M4 types, the angle of Cu_2–O–O is α. For the M5 and M6 types, the angle of the O-adsorption site-O is α.

Mode	D(O–O)	D(M–O1)	D(M–O2)	α	E_{ads}
M1	1.305	1.929	2.939	130°	–0.15
M2	1.540	1.830	1.860	110°	–1.97
M3	1.251	2.736	3.985	176°	0.39
M4	1.540	1.830	1.860	110°	–1.97
M5	1.440	1.829	2.098	42°	–1.46
M6	1.502	2.920	2.917	30°	–1.42

3.4. Electronic structural changes upon adsorption

To further obtain the details of CO adsorbed with C-down over the Cu_2 site and O_2 adsorbed on the Cu_2 site, the DOSs in the molecule-slab system are calculated as shown in Figs. 3 and 4.

As is well known, eigenstates characterize the main feature of a quantum system. In a molecule, the molecular orbitals are the eigenstates of the system, and this is the reason why molecular orbitals, such as 3σ, 4σ, 1π, 5σ, and 2π of the CO molecule, are essential to describing the bonding and the chemistry of the molecule. The occupied 5σ orbital of free CO is at the Fermi level as shown in Fig. 3(a). The 5σ orbital of free CO is mainly from the 2s and 2p orbitals of C, and the 2π orbital of free CO is mainly from the 2p orbital of C and O. As can be seen from Fig. 3(c), the CO bands are shifted towards lower energy after adsorption, and the 5σ orbital is also strongly stabilized upon adsorption, becoming almost degenerate with the 1π orbital. The peak of low intensity is due mainly to 4σ, 1π, and 5σ states of the CO molecule, while the peaks ranging from −2.5 eV to −4.0 eV are assigned to the 2π back donation of Cu_2 3d→CO. Figures 3(b) and 3(d) show the interaction between the CO molecule and the Cu_2 4s state. Before adsorption, the band seen at about 0.50 eV is due to the largely unpopulated Cu_2 4s. However, upon adsorption of CO, the sharp band of Cu_2 4s is delocalized. The overlapped peak can be seen at about −7.5 eV, which is assigned to the 5σ donation of CO→Cu_2 4s. For a better understanding of the above results, the Mulliken population of the CO molecule which is C-down toward the Cu_2 site is investigated. For the charge transfer, CO donates electrons to the surface, primary to the adsorption site. It indicates that the highest occupied 5σ orbital of the CO molecule transfers electrons to the substrate.

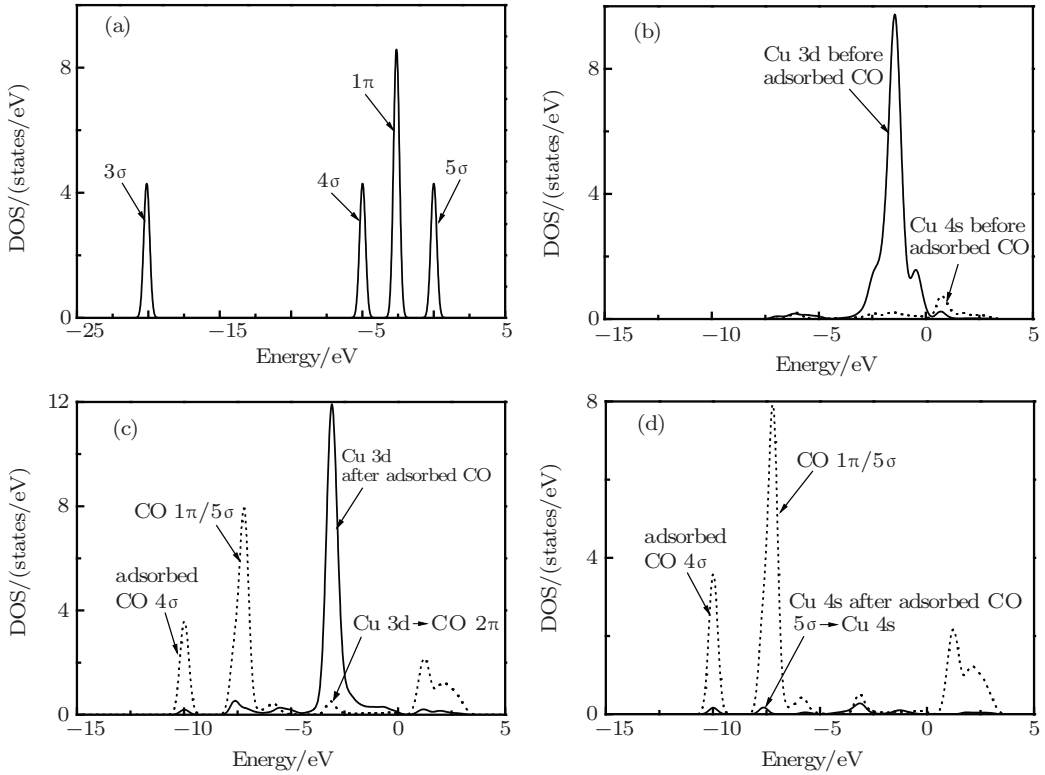


Fig. 3. DOSs of the Cu_2–C–O system before and after CO adsorption: (a) free CO molecule before adsorption, (b) DOSs of Cu_2 3d and Cu_2 4s before adsorption, (c) DOSs of Cu_2 3d and CO molecule after adsorption, and (d) DOSs of Cu_2 4s and CO molecule after adsorption. The zero energy is set at the Fermi level.

The density of state (DOS) of the Cu_2 3d, Cu_2 4s, and O_2 before and after adsorption is depicted in Fig. 4. The electronic configurations of the oxygen molecule are $(1\sigma)^2$ $(2\sigma)^2$ $(3\sigma)^2$ $(4\sigma)^2$ $(1\pi)^4$ $(5\sigma)^2$ $(2\pi)^2$. The 1π, 2π, and 5σ orbitals of free O_2 are mainly from the 2p orbital of O_2, and 3σ and 4σ orbitals of free O_2 are mainly from the 2s orbital of O_2. From the DOS curves of the free O_2 molecule (Fig. 4(a)), it can be easily seen that the 2π orbital is at the Fermi level and the strong oxygen peak below the Fermi level displays most characteristics of 1π and 5σ orbitals of the O_2 molecule. As shown in Fig. 4(b), there is a broadening of the 2π orbital of the O_2 molecule because of overlapping with the Cu_2 3d orbital, indicating that the charge loss of the Cu_2 occurs mainly in its 3d orbital, and the gained charges enter 2π orbital of the O_2 molecule. This means that strong 3d–2π interactions are involved in the chemisorption of O_2 molecule on the surface. The DOS curves for the Cu_2 4s orbital after adsorption show that a weak interaction occurs between the Cu_2 4s and the 1π and 5σ orbitals, implying that a small number of charges in the 1π and 5σ orbitals are transferred to the Cu_2 4s orbital.

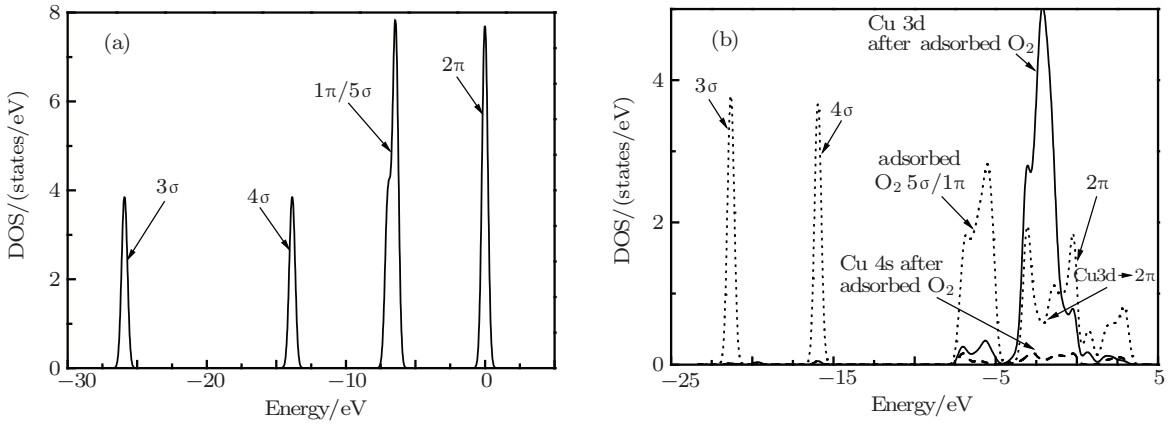


Fig. 4. DOSs of the Cu_2–O–O system before and after O_2 adsorption: (a) free O_2 molecule before adsorption, (b) DOSs of Cu_2 3d, 4s and O_2 molecule after adsorption. The zero energy is set at the Fermi level.

4. Conclusions

In this paper, we investigated CO and O_2 molecules individually adsorbed on the stoichiometric Cu-terminated Cu_2O (111) surface using DFT coupled with periodic slab models. Based on the analysis of the different adsorption structural types, we conclude that the CO molecule adsorbed at the C-down over Cu_2 site is the most stable adsorption configuration, and this absorption is chemisorption. The O_2 molecule adsorbed with one O atom coordinating to Cu_2 site and the other O atom coordinating to Cu_1 site is most favoured. A distinct stabilization of both the Cu 3d and molecule orbital 5σ of the CO is observed. The analysis of DOS for the chemisorption state of the Cu_2O (111)/O_2 system indicates that the charge loss of the Cu_2O (111) slab occurs mainly in its 3d orbital, and the gained charges in O_2 mainly go to 2p orbital. This means that the d–π charge transfer between the substrate and O_2 molecule occurs in the chemisorption process.

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