Dissociation of $O_2$ molecules on strained Pb(111) surfaces

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Abstract

By performing first-principles molecular dynamics calculations, we systematically simulate the adsorption behavior of oxygen molecules on the clean and strained Pb(111) surfaces. The obtained molecular adsorption precursor state, and the activated dissociation process for oxygen molecules on the clean Pb surface are in good agreements with our previous static calculations, and perfectly explains previous experimental observations [Proc. Natl. Acad. Sci. U.S.A. 104, 9204 (2007)]. In addition, we also study the influences of surface strain on the dissociation behaviors of $O_2$ molecules. It is found that on the compressed Pb(111) surfaces with a strain value of larger than 0.02, $O_2$ molecules will not dissociate at all. And on the stretched Pb(111) surfaces, $O_2$ molecules become easier to approach, and the adsorption energy of the dissociated oxygen atoms is larger than that on the clean Pb surface.
I. INTRODUCTION

Oxygen molecules in the atmosphere are thermodynamically allowed to react with most metal surfaces, causing the formation of thin oxide films. This phenomenon has been widely taken advantage of during the fabrications of heterogeneous catalysts, gas sensors, dielectrics, and corrosion inhibitors. However, understanding the oxidation mechanisms from the atomic view, as well as artificially manipulating the oxide products are still not mature yet. Although the adsorption and dissociation processes of oxygen molecules on most metal surfaces have been studied widely and deeply, some more practical problems like the influences of surface morphology on the oxygen dissociation processes are still lacking attentions. With the latest development of surface science, experiment researchers are now able to manipulate surface morphologies at the nanometer level, which implies that by controlling the surface morphology, one may be able to manipulate the oxidation processes and the corresponding reaction products of metal surfaces. Recently, Thürmer et al. and Ma et al. studied the manipulation of surface impurity and quantum size effect on the oxidation of epitaxial Pb(111) crystallites, respectively. The former revealed that pure Pb(111) crystallites were resistant to oxidation, but once nucleated by surface impurities, monolayer films of lead oxide would grow on the Pb(111) surface in an autocatalytic process. The latter revealed that the adsorption rate of oxygen and oxidation rate of Pb were both modulated by the quantum size effect of ultrathin Pb(111) films, and showing even-odd oscillations. Therefore, studying the modulation of different surface morphologies on the oxidation of metal is very meaningful, and here in this paper, we study the influences of surface strain on the oxidation of the Pb(111) surface.

In addition, studying the influences of surface strain on oxidation is also practically very needed. The above two experimental studies about surface oxidation of Pb (Refs. and ) are both carried out on epitaxially growed Pb(111) terraces, which are deposited on the Ru(0001) and Si(111) surfaces respectively. Since there are 9% and 5% lattice mismatches between Pb and Si, Ru, the deposited Pb(111) terraces might contain some inherent strains. This fact also motivates our present study. More importantly, most experimental studies on surface oxidation of metals are also carried out on epitaxially deposited metal surfaces, which inevitably introduces strains on metal surfaces. In this way, studying the influences of strain on surface oxidation of metals has a broad significance. In the follow-
ing of the paper, we first build the atomistic model for oxygen dissociation on the Pb(111) surface, based on first-principles molecular dynamics (FPMD) simulations, and then study the relationship between surface strain and the dissociation processes of O$_2$ molecules on differently strained Pb(111) surfaces.

II. CALCULATION METHOD

Our calculations are performed using the Vienna *ab-initio* simulation package\textsuperscript{19}. The PW91\textsuperscript{20} generalized gradient approximation and the projector-augmented wave potential\textsuperscript{21} are employed to describe the exchange-correlation energy and the electron-ion interaction, respectively. The cutoff energy for the plane wave expansion is set to 400 eV. The molecular dynamics (MD) simulations are performed using the Verlet algorithm with a time step of 1 fs within the microcanonical ensemble. In our present study, the Pb(111) surface is modeled by a periodically repeated slab of four Pb layers separated by a vacuum region correspondent to six metal layers. We consider a (3\times3) surface unit cell with 9 Pb atoms in each atomic layer. The surface Brillouin zone is sampled by a 3\times3 $k$-point distribution using the Monkhorst-Pack scheme\textsuperscript{22}. The calculated lattice constant of bulk Pb and the bondlength of isolated O$_2$ are 5.03 Å and 1.24 Å, respectively, in good agreements with the experimental values of 4.95 Å\textsuperscript{23} and 1.21 Å\textsuperscript{24}. The O$_2$ is placed on one side of the slab, namely on the top surface, whereas the bottom Pb layer is fixed. All other Pb atoms as well as the oxygen atoms are free to move during the geometry optimizations and MD simulations.

III. RESULTS AND DISCUSSION

Before simulating the adsorption of O$_2$ molecules, we firstly optimize the geometry of the clean Pb(111) surface. During the surface relaxation, the Pb atoms at the outmost layer tend to relax inward, because of the asymmetry of the electron density at the surface. In contrast, Pb atoms at the second layer tend to relax outward\textsuperscript{25}. With respect to the interlayer spacing along the [111] direction of bulk Pb, the first interlayer spacing of the Pb(111) surface is compressed by 2.26\%, whereas the second interlayer spacing is expanded by 4.35\%. We also perform geometry optimizations for the compressively and stretchingly strained Pb(111) surfaces. The surface strains are simultaneously added on the $x$ and $y$ directions, with plus
and minus values representing for stretched and compressed surfaces respectively. The Pb atoms are free to relax during the geometry optimizations of the compressed or stretched surfaces. From the optimized geometries, we find that within the surface strains between ±0.1, no obvious structure transformation happens for the studied Pb(111) surface.

We then perform our FPMD simulations to study oxygen dissociation on the Pb(111) surface, which are started with different orientations of an O$_2$ molecule placed over different surface sites. There are four high symmetry sites on the Pb(111) surface, namely the top (T), bridge (B), fcc- (FH), and hcp-hollow (HH) sites, and the adsorbed O$_2$ molecule has three high-symmetry orientations ([0\bar{1}1], [2\bar{1}1], and [111] directions). Thus in total, we consider 12 high-symmetry trajectories for the adsorption of O$_2$. At the beginning of all these trajectories, the mass center of the O$_2$ molecule is initially set to be 4 Å away from the metal surface. The substrate Pb atoms are initially set at rest while the adsorbed oxygen atoms are initially with a kinetic energy.

Figure 1 shows the free electronic energy evolutions for two FPMD simulations of an parallel O$_2$ molecule adsorbing at the surface hcp hollow site of Pb. The initial kinetic energy of the O$_2$ molecule is 0.2 and 0.6 eV respectively. We can see clearly that the free electronic energy before t=300 fs evolves similarly for the two O$_2$ molecule with different initial kinetic energies. As we will discuss in the following, the energy evolution at this period corresponds to the repulsion of surface electrons to the O$_2$ molecule. After t=300 fs, the two O$_2$ molecules show different adsorption behaviors. The adsorption system of the O$_2$ molecule with an initial kinetic energy of 0.6 eV experiences an energy reduction of about 1.6 eV. As we will see later, this reduction of energy corresponds to the dissociative adsorption of O$_2$. At meantime, the adsorption system with the O$_2$ molecule with an initial kinetic energy of 0.2 eV has few changes in the free electronic energy. This results clearly indicate that the dissociative adsorption of O$_2$ molecules on the clean Pb(111) surface needs to overcome an energy barrier, with the value of between 0.2 and 0.6 eV.

We have previously studied in depth the molecular and atomic adsorption of oxygen on the Pb(111) surface, by using static first-principles calculations\textsuperscript{25,26}. It has been revealed that O$_2$ adsorbs barrierlessly into the molecular adsorption precursor state on the clean Pb(111) surface. In these precursor states, the O$_2$ molecule adsorbs at surface hcp or fcc hollow sites, with no spin any more because of the electronic hybridizations with surface electrons, and the precursor state at surface hcp hollow site is the most stable one\textsuperscript{25}. In
our recent studies, we find that the dissociation energy barrier for \( \text{O}_2 \) from the molecularly adsorbed precursor states is much smaller than that directly from the gas-like molecules, and the minimum energy dissociation path is from the most stable precursor adsorption state of \( \text{O}_2 \) on the Pb(111) surface\(^{27} \). Here through FPMD simulations, we find that the \( \text{O}_2 \) molecule along the top and bridge trajectories will firstly move to the hcp or fcc hollow sites before its adsorption, and the energy evolutions along the hcp and fcc trajectories are very similar to each other. Therefore, we will mainly discuss the results of the hcp-hollow trajectory at subsequent discussions, which already contains most of the related information during the adsorption and dissociation of \( \text{O}_2 \) molecules.

At another side, although the ground electronic state of an \( \text{O}_2 \) molecule is the spin-triplet state, the adsorption system in both the molecular adsorption precursor state\(^{25} \) and the atomic adsorption states are found to be nonmagnetic\(^{26} \). These results suggest that spin polarization has little importance to the adsorption behavior of \( \text{O}_2 \) on the Pb(111) surface. Our test FPMD calculation also proves this result, as the spin of \( \text{O}_2 \) quickly quenches to be zero when approaching the Pb(111) surface. Therefore, to simplify the calculations and discussions, our FPMD calculations are all spin-nonpolarized.

Our ensemble for the adsorption system of \( \text{O}_2 \) on the Pb(111) surface is a microcanonical one, thus the total energy (i.e. summation of free electronic energy, Madelung energy of ions, and kinetic energy of ions) is conserved. This fact is clearly shown in Fig. 2(a), where the free electronic energy of the adsorption system at \( t=0 \) fs is set to zero. The obtained free electronic energy of the adsorption system during the adsorption process of an \( \text{O}_2 \) molecule at the surface hcp hollow site is shown in Fig. 2(b). Figures 2(c) and 2(d) show the molecule bond length (\( d_{\text{O}-\text{O}} \)) and the height of the \( \text{O}_2 \) center of mass (\( h_{\text{O}_2} \)), respectively. We can see from Fig. 2(b) that when the \( \text{O}_2 \) molecule approaches the Pb(111) surface, the free electronic energy of the adsorption system goes down. This result is in agreement with our previous static calculations finding that \( \text{O}_2 \) molecule enters into the molecular adsorption state without any energy barriers\(^{25} \), and accords well with the previous experimental observation that \( \text{O}_2 \) molecules adsorb on the Pb(111) surface at very low temperatures\(^{17} \). The energy reduction when approaching the metal surface is different from that has been found for the \( \text{O}_2/\text{Be}(0001) \) system, where the free electronic energy of the adsorption system goes up when \( \text{O}_2 \) approaches the Be surface\(^{28} \). As shown in Fig. 2(b), when the \( \text{O}_2 \) molecule approaches too close to the Pb(111) surface (after \( t_1=90 \) fs), the
free electronic energy goes up sharply, because of the electronic repulsion from the surface electrons of Pb to the O$_2$ molecule. And the free electronic energy of the adsorption system reaches a local maximum at $t_2=107$ fs. From $t_2=107$ fs to $t_3=127$ fs, the O$_2$ molecule moves back from the Pb(111) surface, and the free electronic energy reduces again. The geometries of the adsorption system at $t_1$, $t_2$, and $t_3$ are shown in Figs. 3(a)-3(c). We can see from both Fig. 2(c) and Fig. 3 that the molecular length does not change much from $t_1$ to $t_3$. 

After being repulsed by the Pb(111) surface, the O$_2$ molecule suspends on the Pb(111) surface. Until $t_4=551$ fs, it enters into the molecular adsorption state. In the precursor state, the molecular bond length is enlarged to be 1.43 Å, indicating that the adsorbed O$_2$ molecule is superoxide-like$^{29,30}$. It is because that in the molecular adsorption precursor state, a certain number of electrons transfer from bonding orbitals to Pb, while more electrons transfer back from Pb to the antibonding orbitals of O$_2$.$^{25}$ After climbing an energy barrier of 0.31 eV (from $t_4=551$ fs to $t_5=601$ fs), the O$_2$ molecule then dissociates into two adsorbed oxygen atoms. As shown in Fig. 2(b), the atomic adsorption of the two oxygen atoms causes the free electronic energy of the adsorption system to reduce 2.29 eV at $t_6=684$ fs. The geometries of the adsorption system from the molecular adsorption precursor state to the atomic adsorption final state are shown in Figs. 3(d)-3(f). We can see from Fig. 3(f) that the final state of the dissociation process is the adsorption state of two oxygen atoms in two neighboring hollow sites. These results are in agreements with our recent static calculations$^{27}$. 

After dissociation, the distance between the two oxygen atoms is rapidly enlarged by 3 Å within 150 fs, as shown in Fig. 2(c), which is very similar to the dissociated oxygen atoms on the Al(111) surface, where the fast moving oxygen atoms are called as “hot” oxygen atoms, and the dissociation mechanism is described into a “Hot-Atom” picture$^{4}$. This result indicates that the oxidation mechanisms of Al and Pb are similar. After $t=800$ fs, the O$_2$/Pb(111) adsorption system begins to vibrate in its intrinsic frequencies. 

The molecular height $h_{O_2}$ of O$_2$ after dissociation (i.e. after $t=700$ fs) is found to fluctuate around 1.25 Å, indicating that the oxygen atoms do not penetrate into the Pb(111) surface, and the underlying Pb layers hardly take part in the interactions with oxygen. We can also see from Fig. 3 that during the dissociation process, the topmost Pb atomic layer is distorted. However, the second Pb layer almost does not change at all, with a negligible distortion. So, the interaction between O$_2$ molecules and the Pb(111) surface is very localized on the
surface. This result is also in agreement with our previous difference charge density analysis for the molecular adsorption of O\(_2\) on the Pb(111) surface\(^{25}\).

The evolution of the electronic structure during the adsorption and dissociation of O\(_2\) molecules on metal surfaces is of great theoretical importance and thus has been widely studied\(^{28,31}\). We here also calculate and analyze the projected density of states (PDOS) of the O\(_2\) molecule during its dissociation process on the unstrained Pb(111) surface. The PDOS of the O\(_2\) molecule in the molecular adsorption, transition, and atomic adsorption states are shown in Figs. 4(a)-(c) respectively. As shown in Fig. 4(a), there are four peaks in the s- and p-PDOS of the molecularly adsorbed O\(_2\), corresponding to the four molecular orbitals, \(\sigma_{2s}\), \(\sigma^*_{2s}\), \(\sigma_{2p}\), and \(\pi_{2p}\) from low to high energies respectively. The half-filling \(\pi^*_{2p}\) molecular orbital of O\(_2\) is broadened into several energy bands through electronic hybridizations with p electrons of Pb\(^{25}\). At \(t=601\) fs, the O\(_2\) molecule evolves into the transition state, with its \(\pi_{2p}\) molecular orbital further vanished through hybridizations with p electrons of Pb, as shown in Fig. 4(b). In the transition state, because the two oxygen atoms are not far away from each other, then the \(\sigma_{2s}\), \(\sigma^*_{2s}\), and \(\sigma_{2p}\) molecular orbitals still keep their localization characters. After dissociation, all the molecular orbitals of O\(_2\) are broken. The s1 and s2 states shown in the s-PDOS of oxygen in Fig. 4(c) distribute around the two oxygen atoms, representing for their atomic orbitals. The energy levels are different for the two oxygen s orbitals because the two oxygen atoms are at different surface sites [as shown in Fig. 3(f)]. We can see from the PDOS evolution that only the p states of Pb and oxygen atoms take part in the electronic hybridizations, during the dissociation process.

By performing a series of FPMD simulations, we find that compressive and stretching strains influence the oxygen dissociation on the Pb(111) surface in quite different ways. Once the Pb(111) surface is compressed over 2\%, we find that oxygen molecules will not dissociate at all on the Pb(111) surface. As clearly shown in Fig. 5(a), the free electronic energy of the adsorption system for the compressed Pb(111) surface does not reduce after the surface repulsion to the adsorbing O\(_2\) molecule, indicating that no chemisorption happens. In contrast, O\(_2\) molecules can also dissociate on the stretched Pb(111) surfaces. We can see from Fig. 5(a) that the free electronic energy of the adsorption system for the stretched Pb(111) surface reduces by about 2.65 eV after \(t=500\) fs, because of the dissociative chemisorption of O\(_2\). After that, the distance between the dissociated oxygen atoms on the 2\% stretched Pb(111) surface is rapidly enlarged to be 4 Å within 100 fs, as shown in Fig. 5(b). This result
indicates that stretching strain does not change the “Hot-Atom” dissociation mechanism of \( \text{O}_2 \) molecules on the Pb(111) surface. The molecular height of \( \text{O}_2 \) from the Pb surface \( (h_{\text{O}_2}) \) on the stretched surface, as shown in Fig. 5(c), is always smaller than that on the clean Pb(111) surface, indicating that the chemisorbed oxygen atoms are nearer to the stretched surface than to the unstrained Pb(111) surface.

As we have discussed, charge transfer from the Pb surface to the antibonding orbital of the \( \text{O}_2 \) molecule is very important for the adsorption interaction between them. Thus we can understand the above results from the charge density view. On the compressed Pb surface, surface electrons of Pb are more dense and so their repulsion to the \( \text{O}_2 \) molecule becomes stronger. This explains why the \( \text{O}_2 \) molecule does not dissociate on the 2\% compressed Pb surface. As a proof to the stronger repulsion, the lowest molecular height during the repulsion process on the compressed Pb surface is larger than on the unstrained and stretched Pb surfaces, as shown in Fig. 5(c). On the stretched Pb surface, surface electrons become looser, and thus become easier to transfer into the antibonding \( \text{O}_2 \) orbital. This causes that the repulsion force to the \( \text{O}_2 \) molecule is smaller from the stretched Pb surface than from the unstrained Pb surface, and the dissociated oxygen atoms bond stronger with Pb atoms of the stretched surface than with that of the unstrained surface. The smaller molecular height on the stretched Pb surface also confirms our theory.

To make the influences of stretching strain more clear, we simulate the adsorption process of \( \text{O}_2 \) molecules on different stretching Pb surfaces. The free electronic energies correlated with the repulsion process, i.e., \( E_{t1}, E_{t2}, \) and \( E_{t3} \) can be easily read from the free electronic energy evolutions of FPMD simulations. The equilibrium energy of the adsorption system after atomic adsorption of oxygen \( (E_{\text{finale}}) \) can be obtained by averaging the free electronic energy in a time period of 200 fs. Based on these quantities, we can define \( E_{\text{rep}}=E(t2)−E(t1) \) to scale the repulsion strength of the Pb(111) surface to the impinging \( \text{O}_2 \) molecule, and \( E_{\text{ad}}(\text{atom})=E_{\text{O}_2}+E_{\text{Pb surf}}−E_{\text{finale}} \) to scale the binding strength between dissociated oxygen atoms and the Pb(111) surface, where \( E_{\text{O}_2} \) and \( E_{\text{Pb surf}} \) are the free electronic energies of an isolated \( \text{O}_2 \) molecule and the stretched Pb surface, respectively.

The calculated \( E_{\text{rep}} \) and \( E_{\text{ad}}(\text{atom}) \) on different stretching Pb(111) surfaces are shown in Fig. 6. One can see that the more stretched the Pb(111) surface is, its repulsion to \( \text{O}_2 \) molecules becomes weaker, indicating that \( \text{O}_2 \) molecules are easier to approach the stretched Pb(111) surface. It is because that surface electrons of Pb become more dilute.
after stretching, and so their repulsion becomes weaker. The reduction of surface electron density also makes the electronic interactions between oxygen and Pb more easier on the stretched Pb(111) surfaces. And correspondingly, the binding energy between oxygen atoms and the stretched Pb(111) surface becomes larger. Therefore, after the Pb(111) surface being stretched, O\textsubscript{2} molecules are easier to approach the Pb surface before dissociation, and oxygen atoms bind stronger with Pb atoms after dissociation.

IV. CONCLUSION

In summary, we have systematically investigated the dissociative adsorption processes of O\textsubscript{2} molecules on the Pb(111) surface. By performing FPMD simulations, we find that the O\textsubscript{2} dissociation is an activated type on the Pb(111) surface, and the obtained molecular adsorption precursor states from the FPMD simulation are in agreements with with our previous static calculational results. Besides, we have also observed the repulsion process when the impinging O\textsubscript{2} molecule approaches too close to the Pb(111) surface. After a series of FPMD simulations for O\textsubscript{2} adsorption on the strained Pb(111) surfaces, we find that O\textsubscript{2} molecules will not dissociate at all on the compressed Pb(111) surfaces, while on the stretched Pb(111) surfaces, O\textsubscript{2} molecules can still dissociate, and the atomic bindings between the dissociated oxygen atoms and Pb atoms become stronger. Through the present studies, we expect to expand people’s knowledge on metal surface oxidation, by pointing out the specific role of surface strains.

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**Fig.1** (Color online). The free electronic energy of the adsorption system in two first-principles molecular dynamics (FPMD) simulations for the adsorption of O$_2$ molecule on the Pb(111) surface. The initial kinetic energy of the O$_2$ molecule is 0.2 and 0.6 eV respectively.

**Fig.2** (Color online). (a) and (b) Total energy and free electronic energy of the adsorption system in a FPMD simulation for the dissociative chemisorption of an O$_2$ molecule on the clean Pb(111) surface. The free electronic energy of an O$_2$ molecule plus that of the clean Pb(111) surface is set to energy zero. (c) and (d) Molecular bond length of O$_2$ ($d_{O-O}$) and height from the Pb(111) surface of the O$_2$ center of mass ($h_{O_2}$), in the same FPMD simulation. The t1-t6 are 90, 107, 127, 551, 601, and 684 fs, respectively.

**Fig.3** (color online). Snapshots from a FPMD simulation of the dissociative chemisorption of an O$_2$ molecule on the Pb(111) surface. Only the outermost two Pb layers are shown. Red balls represent oxygen atoms, while black and grey balls represent Pb atoms in the first and second atomic layer, respectively. (a)-(c) The repulsion process when an O$_2$ molecule approaches to the Pb surface. (d)-(f) The dissociation process for the O$_2$ molecule from its molecular adsorption precursor state. The molecular bond lengths ($d_{O-O}$) are 1.42, 1.44, 1.53, 1.43, 1.87, and 2.83 Å in (a)-(f), respectively.

**Fig.4** (Color online). The projected density of states of the oxygen molecule in the molecular adsorption (a), transition (b) and atomic adsorption states (c) on the unstrained Pb(111) surface. The Fermi energies are set to zero, and denoted by the dotted line.

**Fig.5** (a) Free electronic energy of the adsorption system in three FPMD simulations for the dissociative chemisorption of an O$_2$ molecule on the compressed, clean and stretched Pb(111) surfaces. The free electronic energy of an O$_2$ molecule plus that of the strained Pb(111) surface is set to energy zero. (b) and (c) Molecular bond length of O$_2$ ($d_{O-O}$) and height from the Pb(111) surface of the O$_2$ center of mass ($h_{O_2}$), in the three FPMD simulations.
Fig.6  The repulsion energy ($E_{\text{rep}}$) and atomic adsorption energy ($E_{\text{ad}}(\text{atom})$) for oxygen on the stretched Pb(111) surfaces.
FIG. 1:
FIG. 2:

(a) $E_{\text{tot}}$ (eV)

(b) $E_0$ (eV)

(c) $d_{\text{O-O}}$ (Å)

(d) $h_{\text{O}_2}$ (Å)

Time (fs)
FIG. 3:
FIG. 4:
FIG. 5:
FIG. 6: