Density functional study of O₂ molecule and O atom adsorption on α -U(001) surface

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Abstract:

First-principle calculations have been performed to study both O₂ molecule and O atom adsorption on α -U(001) surface and subsurface. The results show that the long-bridge site is the most stable adsorption site for O₂-U(001) and O-U(001) surface adsorption. The tetrahedral (Tet) 1 site is the most stable adsorption site for O-U(001) subsurface adsorption. The partial electronic density of states (PDOSs) of O₂-U(001) and O-U(001) shows the hybridization of U and O atoms orbitals causes the electrons of 5f/6d of U more non-local and leads to the formation of O-U bond. The O-U bond is partly ionic and partly covalent. The analysis of the diffusion path of O atom on U(001) shows that O atom can easily transfer from hollow (hol) 1 site to hollow 2 site with no energy barrier. O atom can hardly transfer from surface to the subsurface.

Key word: First-principle. α -U(001) surface. hybridization. O atom transfer

Introduction

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Uranium (U) oxidizing is one of the most important processes in surface corrosion, which has received considerable attentions for years [1-7]. Uranium's large atomic radius and special 5f/6d electronic state have shown its distinctively active reactivity, making it easily corrode under an aerobic environment. Thus, increasing efforts have been devoted to reducing the surface corrosion [8-10], which is not only of fundamental interest but also technologically important in the manufacture and storage of nuclear fuel.

Comprehensive experimental research is available on study the uranium corrosion at different aspects. An early experimental work performed by McLean *et al* [11] used X-ray photoelectron spectroscopy, Auger electron spectroscopy and second ion mass spectroscopy showed that the oxygen remained on the surface, forming an oxide. They also mentioned that the uranium at saturation oxygen coverage closely resembles that of UO_2 . Bloch *et al* [12] reached the same conclusion. This group showed that the chemisorbed oxygen formed islands on the uranium surface, which later spreading over the surface. Gouder *et al* [13] used ultraviolet photospectroscopy to study the adsorption of O_2 on the uranium surface and showed that O_2 adsorption resulted in a decrease of Fermi level emission and an increase of the U 5f and O 2p emission, which means that the withdrawal of the 5f electrons from the Fermi level and their transfer into O 2p.

Due to the radioactive nature of uranium dioxide and the high cost of related experimental work, computer modeling and simulation have become critical for the research of uranium oxidizing processes. Density functional theory (DFT) is a well established computational approach to study the structures and electronic properties of metal substrate systems, especially to elucidate complex surface process, such as surface adsorptions, catalytic reactions, and diffusions. The interactions

between uranium surface and most gases (O_2 , H_2 , CO , CO_2 , H_2O) have been investigated by DFT methods [14-19]. G. Li and W. Luo used DFT methods to study the hybridization effects of O_2 adsorption on α -U (001) surface [14]. Z. Xiulin et al investigated the ab initio study on molecular geometries, electronic structure and energies of the U- O_2 interaction. However, there have not been any comprehensive computational studies on the molecular geometries, electronic structure and energies of the interactions of O_2 molecule and O atom with α -U(001) surface. The α -U (orthorhombic, Figure 1) to uranium oxide phase transformation (often referred to as uranium oxidation) involved both a change in chemical composition and structure. In the process, it can be generally divided into six unique phenomena: (1) surface phenomena, (2) absorption, (3) transport, (4) trapping, (5) saturation and finally, (6) phase transformation [20]. In the present study, we calculated the adsorption of O_2 molecule adsorption on the α -U(001) surface and O atom adsorption on the α -U(001) surface and subsurface. With employing DFT calculations, the O_2 molecule decomposition on U(001) surface, atomic O adsorption/absorption/immigration on U(001) surface and subsurface are systematically investigated. Hope to provide more insight thinking for the future uranium oxidation research.

2. Computational Details

The calculations were performed using the CASTEP package. This program evaluates the total energy of periodically repeating geometries on the basis of density functional theory (DFT) and the pseudopotential approximation. The generalized gradient approximation (GGA) of Perdew and Wang known as PBE was employed for the exchange-correlation functional in the calculations. As for the isolated O_2 molecule, we obtained a bond length of 1.186Å, whereas the experimentally measured bond length for O_2 is 1.209 Å [21], which proved once more that the calculation method

is reliable. As shown in spin polarization test on O₂ system, the non-spin polarization O₂ ($E_{\text{tot}} = -868.950$ eV) is more stable than the spin polarization O₂ ($E_{\text{tot}} = -869.337$ eV). Therefore, the non-spin polarization of O-U(001) configurations and O-U(001) configurations are used in our paper.

In order to investigate on the process how the O₂ molecule and O atom react on the U(001) surface. Herein we choose α -U(001) surface with C(3*3) unit cells as the adsorption substrate due to its lowest surface energy out of all seven uranium low index cleavage plane surfaces [22]. In view of the quick convergence of the surface energy of the α -U(001) and the computational efficiency, a three-layers slab of α -U(001), periodically repeated in a supercell geometry with 16 Å of vacuum between any two successive metal slabs, was used to model the adsorbate-substrate system. The plane-wave cut-off energy is 400 eV. All degrees of freedom of the adsorbed O₂ molecule, O atom and the U layers were allowed to relax, except the last layer at the bottom. This model is consistent with other surface slabs for hydride surface in the literature [23]. In O₂ molecule adsorption model, one O₂ molecule approaches to four different high-symmetric adsorption sites (top, long-bridge, short-bridge and triangle centre) of the α -U(001) surface (Figure.1) in three ways (Par (parallel), “Inc (inclined), and Ver (vertical)). In the O atom adsorption model, one O atom interacts with the surface at seven different sites (Figure 2 and Figure 3).

For O₂ molecule and O atom adsorption configurations, the corresponding adsorption energies were calculated according to the expression: $E_{\text{ads}} = E_{(\text{A+slab})} - E_{\text{slab}} - E_{\text{A}}$, where $E_{(\text{A+slab})}$ is the total energy of the optimized adsorbate/slab system, E_{slab} is the total energy of the relaxed slab, and E_{A} is the energy of the optimized isolated O₂ molecule or O atom. The negative value for E_{ads} means

that the absorption system is stable.

3 Results and Discussion

3.1 Bulk properties of alpha uranium

Uranium is an orthorhombic crystal structure (Figure 1). We first benchmarked our calculation method by calculating the ground state properties of the alpha uranium crystal and comparing with previous first-principles calculations and experimental values [24-26]. The calculated lattice parameters and total energies of alpha uranium bulk were listed in Table 1. All the lattice parameters of the GGA methods (GGA-PBE, GGA-RPBE, GGA-PW91) are close to the experimental values ($a = 2.836 \text{ \AA}$, $b = 5.867 \text{ \AA}$, $c = 4.955 \text{ \AA}$). It also shows that the results of the GGA-PBE method ($a = 2.854 \text{ \AA}$, $b = 5.869 \text{ \AA}$, $c = 5.035 \text{ \AA}$, CASTEP) agree well with the experimental values, FP calculation ($a = 2.845 \text{ \AA}$, $b = 5.818 \text{ \AA}$, $c = 4.996 \text{ \AA}$) and PP calculation ($a = 2.809 \text{ \AA}$, $b = 5.447 \text{ \AA}$, $c = 4.964 \text{ \AA}$). The similar investigations also can be seen in Söderlind's research results [24]. After the original cell of the uranium being fully relaxed, the calculated total energy of the original cell is -5615.273 eV (GGA-PBE) which is the lowest total energy of all the three GGA methods. Therefore, the GGA-PBE method is a feasible method for the ground state properties of alpha uranium.

After optimizing and comparing the lattice constants via the GGA methods, the elastic and bulk moduli were also calculated using the GGA methods (PBE, RPBE and PW91 (CASTEP)). The calculation results were compared with the experimental data [24] and other works [27] (Table 1, Table 2). The determination of elastic constants is important because these constants

contain detailed information about the chemical bond and provide a very sensitive test of the DFT methods. As presented in Table 1, the values of bulk modulus of our calculation are very close to experimental value (115 GPa). Especially for the GGA-PBE method (CASTEP), the bulk modulus is 114.524 GPa and deviates only 1% from the experimental value. The same trend also can be seen in the elastic constants results of alpha uranium (Table 2). The elastic constants by GGA-PBE method are close to the experimental value and agree well with the those in literature. It is further certificated that the GGA-PBE method (CASTEP) is a suitable method in predicting the ground state properties of alpha uranium bulk. In the following work, we will use GGA-PBE method only (CASTEP) to calculate the non-spin polarization of O-U(001) configurations and O-U(001) configurations.

3.2 Surface adsorption of O₂ molecule on α -U(001) surface

Here in this section, the relative stabilities of one O₂ molecule adsorbed on α -U(001) surface has been discussed. Four high symmetry adsorption sites (denoted as A: Top, B: Short-bridge, C: Long-bridge, D: Triangle-centre) were considered, as shown in Figure 2. The adsorption energies and structural parameters for O₂-U(001) adsorption configurations are given in Table 3. The experimental value of R_{U-O} is 0.231 nm, which is well consistent with our results of 0.225 nm [23]. As shown in Table 3, the d_{O-O} of all the O₂-U(001) configurations are much larger than the experimental distance of O-O bond [21], indicating that the O₂ molecules are broken into two O atoms. As can be seen in Figure 4, all the O₂ molecules of these twelve O₂-U(001) configurations broken down into two O atoms, and most O atoms prefer to interact with the uranium atoms of top layer of surface (Figure 4a and 4b). However, one oxygen atom penetrates the top layer and

interacts with the first and second layers for the D-Ver O₂-U(001) adsorption configuration, one O atom preferred the uranium atoms of subsurface (Figure 4c).

In Table 3, the adsorption energies of O₂-U(001) are in the range from -8.792 to -9.990 eV, indicating a strong chemical adsorption. The long-bridge sites (denoted as C site) have the largest adsorption energies, which indicate that the long-bridge site is the most stable adsorption site. The adsorption energy of D-Ver O₂-U(001) adsorption configuration is -8.792 eV, which is the smallest adsorption energy of all these twelve O₂-U(001) configuration and far less than the surface adsorption energies. This indicates that the decomposed O atom can penetrate into the subsurface of α -U(001), and the penetration process is endothermic.

In Table 3, $\Delta d_{12}/d_0$ and $\Delta d_{23}/d_0$ represent the relaxation of the first and second interlayer spacing of the U slab with respect to the bulk value d_0 . The layer distances in O₂-U(001) system decrease greatly as compared to the pure U(001) surface. This manifested that the structure of U(001) changed greatly when the O₂ molecule adsorbs on the U(001) surface. In the same adsorption configurations, the $\Delta d_{12}/d_0$ has much larger shrinkage than the $\Delta d_{23}/d_0$ due to the interaction of O atoms with the uranium atoms, which strengthens the interaction between the surface and subsurface, and finally narrows the distances between all the uranium layers. Furthermore, this phenomenon is consistent with other surface slab calculations performed for oxygen on metallic surfaces [23]. For the D-Ver O₂-U(001) configuration, the decreases of subsurface distance ($\Delta d_{23}/d_0$) is much larger than the other eleven O₂-U(001) adsorption configurations. This phenomenon ascribes to that the O atom penetration process produces a stronger effect on the geometric structure of U(001) than the O surface migration.

As can be seen in Table 4, for all the O₂-U(001) configurations, O atoms accept electrons

from the uranium atoms. As a result, the oxygen atoms are negatively charged, and the first α -U(001) surface positively charged, the subsurface negatively charged. For the D-Ver O₂-U(001) configuration, the charge distributions of O atom and uranium slabs are different greatly from the other O₂-U(001) adsorption configurations. The first layer of D-Ver configuration loses more charge and the second layer gains more charge than the other non-penetrated O₂-U(001) configurations. It can be put forward that the O atom penetrating has a great effect on the charge distribution of O₂ molecule adsorption on α -U(001). The thermionic experiments described in Ref 27 report a work function for polycrystalline uranium of 3.47 eV, which is close to the 3.46 eV obtained for the α -U(001) single crystal surface examined in this work. The other Mulliken work function analysis [22] also shows that the Mulliken work function of U(001) surface is 3.721 eV. As can be seen in Table 4, the values of work functions are in the range of 2.609 to 2.764 eV for all the non-penetrated O₂-U(001) configuration. The work function of the D-Ver configuration is 3.452 eV. All the work function values of the O₂-U(001) configurations are smaller than that of the U(001) surface. This indicates that the charge transfer between the surface and O₂ molecule affects the Fermi level and lowers the Milliken work function.

To understand the O₂-U(001) adsorbate-substrate interaction, the projected density of states (PDOSs) were studied. As shown in Figure 5, we presented the PDOSs of U(001) (a) O₂-U(001) configurations with the largest surface adsorption energy (b), smallest surface adsorption energy (c), O atom penetration process adsorption (d). In Figure 5(a), there exist large energy bands that pass through the Fermi surface, which possess of a large proportion in the total DOS. This indicates that the uranium atoms have a strong metallic character. As can be seen in Figure 5(b)-(d), there are overlap between 2p orbital of O₂ and the 5f/6d orbital of the U(001) surface.

The 2p states have extended toward the Fermi level and mixed with the 5f/6d orbital to form interaction peaks, which is much more complex than the U(001) surface. For Figure 5b and 5c, there are only one interaction peak of 2p orbital of O₂ with 5f/6d orbital of the U(001) in the region of -6 to -4.5 eV (Figure 5b) and -6 to -4 eV (Figure 5c). For the Figure 5(d), there is two interaction peak of 2p orbital of O₂ with 5f/6d orbital of the U(001) in the region of -7 to -4.5 eV, which is more complicate than these two non-penetrated O₂-U(001) configurations (with largest surface adsorption energy (b), smallest surface adsorption energy (c)). It can be manifested that the hybridization of 2p orbital of O with 5f/6d orbitals of U causes the electrons of 5f/6d of U to be more non-local. It also indicates that the hybridization between 5f/6d of U and 2p of O₂ leads to the covalent part of O-U bonding and contributes to the dissociation adsorption. Thus, the ionic part of U-O bonding plays a significant role in the dissociative adsorption, along with the covalent part. The hybridization between 5f/6d orbitals of U and 2p orbital of O₂ of penetrated O₂-U(001) configurations is stronger than the non-penetrated O₂-U(001) configurations.

3.3 Surface adsorption of O atom on the α -U(001) surface and subsurface

Four high symmetry surface adsorption sites (Figure 2: denoted as A: Top, B: Short-bridge, C: Long-bridge, D: Triangle-centre) and three subsurface adsorption sites (Figure 3: denoted as E: octahedral (Oct), F: tetrahedral (Tet) 1, G: Tet 2) were considered. The adsorption energies and structural parameters are given in Table 5. The experimental value of R_{U-O} is 0.231 nm [22]. As shown in Table 5, the value is consistent with our results. As shown in Figure 6, the O atom finally relocates at the hollow, indicating that there were only two preferred adsorption sites (Figure 6. hollow 1 and hollow 2) at surface, which is the same with the N atom adsorption on the α -U(001)

surface [29]. This can be attributed to the different U-U distance of α -U(001) surface, together with the strong reaction between the uranium atoms and the O atoms. In Figure 7, the O atoms have only one preferred adsorption site (oct site) which is different from the case of the N atom adsorption on the α -U(001) surface [29]. Su et al. report that the N atom has two preferred adsorption site. This phenomenon can be attributed to the small space around the subsurface, together with the strong reaction between the uranium atoms with the O atoms.

As shown in Table 5, the adsorption energies of O-U(001) for the surface are in the range from -4.786 to -4.871 eV, the adsorption energies of O-U(001) for the subsurface range from -3.400 to -3.456 eV, indicating a strong chemical adsorption. O atom penetration process is endothermic. It also can be seen in Table 5, the long-bridge site (denoted as C site) has the largest adsorption energies. The Tet 1 site (denoted as F site) has the largest adsorption energies of subsurface O-U(001) adsorption configurations. As can be seen in Table 5, the layer distances in O-U(001) system also decrease greatly as compared to the pure U(001) surface ($\Delta d_{12}/d_0$ and $\Delta d_{23}/d_0$). This can be manifested that the structure of U(001) changes greatly when one single O atom adsorbs on the U(001) surface. For subsurface O-U(001) configurations, the decreases of subsurface distance ($\Delta d_{23}/d_0$) are much bigger than the other surface O-U(001) adsorption configuration. This phenomenon also ascribed to the O atom penetration process can make stronger effect on the geometric structure of U(001) surface.

As can be seen in Table 6, for all the O-U(001) configurations, O atoms accept electrons from the uranium atoms, which makes O atoms negatively charged, the α -U(001) first surface greatly positively charged, the subsurface negatively charged, the third surface also negatively charged. Compared with the surface O-U(001) configuration(A: Top, B: Short-bridge, C: Long-bridge, D:

Triangle-centre), the subsurface O-U(001) configuration (E: Oct, F: Tet 1, G: Tet 2), the charges distribution of O atom and uranium slabs make the α -U(001) first surface more positively charged, the subsurface negatively charged, the third surface also negatively charged. As also can be seen in Table 6, the values of work functions are in the range from 2.708 to 2.742 eV for all the surface O-U(001) configuration. The values of work functions are in the range from 2.600 to 2.670 eV for all the subsurface O-U(001) configuration. All the work function values of the subsurface O-U(001) configurations are smaller than that of the surface O-U(001) configurations. It is indicated that the more charge transfer between the surface and O atom, the higher the Fermi level is but the lower the Milliken work function is.

Understanding the signature role of the 5f and 6d electrons in bonding and localization is one of the key issues for O-U(001) adsorption. Thus, we studied the PDOSs for a number of O-U(001) adsorption configurations (Figure 8). As can be seen in Figure 8(b)-(e), there are overlaps between 2p orbital of O and the 5f/6d orbital of the U(001) surface. The 2p states have extended toward the Fermi level and mixed with the 5f/6d orbital to form interaction peaks, which is much more complex than the U(001) surface. In Figure 8(b)-(e), the interaction peak of 2p orbital of O with 5f/6d orbital of the U(001) are in the region of -6 to -5.5 eV. For the Figure 8(f)-(h), the interaction peak of 2p orbital of O with 5f/6d orbital of the U(001) are -7.0 to -6.0 eV that is more complicated than those of oxygen atom on U(001). It can be manifested that the hybridization between 2p orbital of O with 5f/6d orbital of U causes the electrons of 5f/6d of U more non-local. The hybridization between 5f/6d of U and 2p of O leads to the covalent part of O-U bonding and contributes to the dissociation adsorption. Thus, the ionic part of U-O bonding plays a significant role in the dissociative adsorption, along with the covalent part. The hybridization between 5f/6d

of U and 2p of the surface O-U(001) adsorption process is stronger than the subsurface O-U(001) adsorption process.

3.4 Diffusion path way for O on α -U(001) surface

To gain more insights into the dynamical behavior of the chemisorbed O atom on the α -U(001) surface, the diffusion pathway for one O atom on α -U(001) surface has been investigated. Three diffusion pathways have been considered, i.e., diffusion from hol 1 site to its most nearby hol 2 site, from hol 1 site to its most nearby oct site, and from hol 2 site to its most nearby oct site (Figure 9). The calculated potential energies along these directions are presented in Figure 10. As O diffusion from hol 1 site to hol 2 site, there is no energy barrier, indicating that the O atom can easily diffuse to any triangle-centre place on U(001) surface. As shown in Figure 10, the O atom can hardly transfer from surface to the subsurface, the correspond energy barriers are in the range from 10.156 eV to 10.817 eV. The results are in accordance with the experimental researches [1, 2]. The uranium will form a dense oxide layer on the uranium surface at an initial oxidation process.

4. Conclusion

First-principle calculations have been performed to study the O₂ molecule adsorption on α -U(001) surface and O atom adsorption on on-surface and subsurface of α -U(001). The results show that the long-bridge site is the most stable adsorption site for O₂-U(001) and O-U(001) surface adsorption. The Tet1 site is the most stable adsorption site for subsurface O atom

adsorption. The adsorption energies of subsurface adsorption at the α -U(001) are found to be higher than the adsorption energies of O-U(001) surface adsorption configurations, which suggests that the adsorption at subsurface sites are less stable.

With the O₂ molecule or O atoms approaching to the U(001) surface, the O atom is attracted by uranium atoms and interacts with the most nearby uranium atoms and make its neighbor uranium atoms form a positive charged electric field on the U(001) surface which forces the other atoms of the surface to move toward the electric field, and changed the U(001) surface structures. There are three stable final geometric structures for the O₂-U(001) surface adsorption configurations, two stable final geometric structures for the O-U(001) surface adsorption configurations, only one stable final geometric structure for the O-U(001) subsurface adsorption configurations. The PDOSs of O₂-U(001) and O-U(001) shows the hybridization of U and O atoms cause the electrons at 5f/6d orbitals of U more non-local. It is also indicated that the hybridization between 5f/6d orbitals of U and 2p orbital of O leads to the covalent part of O-U bonding. The O-U bond is partly ionic and partly covalent.

The analysis of the diffusion path of O atom on U(001) shows that O atom can easily transfer from hol 1 site to hol 2 site with no energies barrier. O atom can easily transfer from one triangle-centre site to any other triangle-centre site. O atom can hardly transfer from surface to the subsurface, the correspond energy barriers are in the range from 10.156 to 10.817 eV. This research results are in accordance with the experimental research [1, 2].

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Table 1 Equilibrium lattice parameters (in Å), bulk modulus (in GPa) of uranium

Method	a	b	c	Bulk modulus (GPa)	Total Energy (eV)
GGA-PBE	2.854	5.869	4.955	114.524	-5615.273
GGA-RPBE	2.826	5.962	4.898	132.124	-5616.184
GGA-PW91	2.833	5.653	5.041	127.813	-5618.287
Expt [24]	2.836	5.866	4.936	115	—
PP [25]	2.809	5.447	4.964	—	—
FP [26]	2.845	5.818	4.996	130	—

Table 2 Experimental and calculated elastic constants of uranium (M bar)

Methods	C11	C22	C33	C44	C55	C66	C12	C13	C23
GGA-PBE	2.05	1.96	2.94	1.26	1.03	0.86	0.51	0.15	1.02
GGA-RPBE	1.91	1.86	3.33	1.33	1.11	1.04	0.55	0.40	0.98
GGA-PW91	2.39	2.05	3.18	1.34	1.23	0.35	0.53	0.36	1.41
GGA-PAW [24]	2.87	2.41	3.16	1.40	1.05	0.96	0.43	0.17	1.10
Expt [26]	2.15	1.99	2.67	1.24	0.73	0.74	0.46	0.22	1.08

Table 3 Geometric parameters and adsorption energies of the final calculated O₂-U(001)

adsorption configurations

Configuration	E _{ads}	d _{O-O}	R _{O1-U}	R _{O2-U}	$\Delta d_{12}/d_0$	$\Delta d_{23}/d_0$
	(eV)	(nm)	(nm)	(nm)	(%)	(%)
A - Par	-9.403	0.312	0.225	0.233	-5.6%	-1.1%
A - Inc	-9.488	0.301	0.226	0.228	-5.2%	-2.4%
A - Ver	-9.419	0.373	0.225	0.226	-5.2%	0.1%
B - Par	-9.380	0.252	0.223	0.226	-5.6%	-2.6%
B - Inc	-9.320	0.249	0.222	0.225	-6.0%	-1.5%
B - Ver	-9.646	0.319	0.226	0.227	-5.6%	-2.3%
C - Par	-9.967	0.435	0.225	0.228	-5.6%	-1.8%
C - Inc	-9.979	0.614	0.227	0.228	-6.0%	-1.9%
C - Ver	-9.990	0.329	0.225	0.224	-6.0%	-1.5%
D - Par	-9.314	0.305	0.226	0.226	-5.6%	-2.4%
D - Inc	-9.462	0.304	0.224	0.227	-5.0%	-2.7%
D - Ver	-8.792	0.264	0.231	0.243	-5.6%	-4.4%

($\Delta d_{12}/d_0$ and $\Delta d_{23}/d_0$ represent the relaxation of the first and second interlayer spacing of the U slab with respect to the bulk value d_0 . d_{O-O} is the calculated equilibrium distances for the O₂ molecule adsorbed on the alpha U(001) surface at different sites. R_{O1-U} and R_{O2-U} represent the average length of the U-O bond of these two O atoms with the bonding U atoms.)

Table 4. Charge distribution and work function for the O₂ molecule adsorbed on the alpha U(001) surface at different sites.

Configuration	Φ (eV)	Q_{O1} (e)	Q_{O2} (e)	Q_1 (e)	Q_2 (e)	Q_3 (e)	Pop_{U-O1}	Pop_{U-O2}
A - Par	2.669	-0.57	-0.55	1.95	-1.25	0.42	0.26	0.267
A - Inc	2.718	-0.56	-0.56	1.95	-1.10	0.25	0.263	0.267
A - Ver	2.764	-0.57	-0.57	1.90	-1.08	0.31	0.263	0.273
B - Par	2.632	-0.56	-0.55	2.01	-1.15	0.24	0.257	0.267
B - Inc	2.695	-0.56	-0.56	1.97	-1.17	0.31	0.267	0.280
B - Ver	2.753	-0.58	-0.58	1.92	-1.14	0.37	0.283	0.307
C - Par	2.743	-0.56	-0.56	1.75	-1.10	0.46	0.27	0.277
C - Inc	2.627	-0.57	-0.56	2.15	-1.09	0.06	0.260	0.267
C - Ver	2.609	-0.58	-0.58	2.15	-1.13	0.12	0.253	0.257
D - Par	2.668	-0.56	-0.56	1.95	-1.08	0.24	0.27	0.280
D - Inc	2.644	-0.57	-0.55	1.91	-1.11	0.31	0.273	0.277
D - Ver	3.452	-0.59	-0.53	2.24	-1.06	-0.07	0.263	0.283

Q_1 , Q_2 and Q_3 denote total charge of the first, second and third U(001) layer, respectively.

Q_{O1} , Q_{O2} denotes charges of the O atoms. Pop_{U-O} denotes the average value of U-O bond population. A negative value represents charge gain, whereas a positive value corresponds to charge loss.

Table 5 Geometric parameters and adsorption energies of the final calculated O-U(001) adsorption configurations

Site	E_{ads}	$R_{\text{O-U}}$	$\Delta d_{12}/d_0$	$\Delta d_{23}/d_0$
	(eV)	(nm)	(%)	(%)
A	-4.786	0.227	-5.2%	-1.2%
B	-4.860	0.232	-5.6%	-1.4%
C	-4.871	0.227	-5.6%	-1.3%
D	-4.792	0.227	-5.6%	-0.8%
E	-3.400	0.228	-5.6%	-3.9%
F	-3.456	0.228	-5.6%	-3.5%
G	-3.412	0.228	-5.6%	-3.4%

($\Delta d_{12}/d_0$ and $\Delta d_{23}/d_0$ represent the relaxation of the first and second interlayer spacing of the U slab with respect to the bulk value d_0 . $R_{\text{O-U}}$ represents the average length of the U-O bond of O atom with the bonding U atoms.)

Table 6 Work function and charge distribution for the O atom adsorbed on the alpha U(001) surface at different sites.

Site	Φ (eV)	Q_O (e)	Q_1 (e)	Q_2 (e)	Q_3 (e)	$Pop_{U-O}(e)$
A	2.708	-0.57	1.94	-1.04	-0.33	0.267
B	2.711	-0.56	1.99	-1.05	-0.38	0.277
C	2.742	-0.56	2.03	-1.09	-0.39	0.267
D	2.720	-0.57	1.98	-1.02	-0.37	0.257
E	2.637	-0.52	2.27	-1.19	-0.58	0.280
F	2.600	-0.52	2.23	-1.17	-0.62	0.273
G	2.670	-0.52	2.29	-1.17	-0.60	0.263

Q_1 , Q_2 and Q_3 denote total charge of the first, second and third U(001) layer, respectively. Q_O denotes charges of the O atom. A negative value represents charge gain, whereas a positive value corresponds to charge loss. Pop_{U-O} denotes the average value of U-O bond population.

Figure 1 Alpha uranium unit cell

Figure 2. Schematic illustration of the O_2 molecule adsorption sites (A: Top, B: Short-bridge, C: Long-bridge, D: Triangle-centre, uranium atoms of the first layer in green, uranium atoms of the second layer in blue)

Figure 3 Schematic illustration of the O atom adsorption sites inside the U(001) surface (E: Oct, F: Tet 1, G: Tet 2, the red sphere represent the O atom, the green sphere represent the uranium atoms of the first layer, the blue represent the uranium atoms of the second layer)

Figure 4 Side view of the final geometric structures of O_2 -U(001) (The red spheres represent the O atoms, the green sphere represent the uranium atoms of the first layer, the blue represent the uranium atoms of the second and third layer).

Figure 5 PDOS of O_2 molecule adsorption on the U(001) surface: (a) U(001); (b) O_2 -U(001) configurations of biggest surface adsorption energy; (c) smallest surface adsorption energy; (d) O atom penetration process adsorption.

Figure 6 Final geometric structures of O atom adsorption on the U(001) surface (The red spheres represent the O atoms, the green sphere represent the uranium atoms of the first layer, the blue represent the uranium atoms of the second and third layer).

Figure 7 Top view (a) and side view (b) of final geometric structures of O atom adsorption inside the U(001) subsurface (O atom in red, uranium on the first layer in green, and uranium on the second and third layers in blue).

Figure 8 PDOS of O atom adsorption on the U(001) surface: (a) U(001); (b) top O-U(001) surface configurations; (c) long-bridge O-U(001) surface configurations; (d) short-bridge O-U(001) surface configurations; (e) triangle-centre O-U(001) surface configurations; (f) oct O-U(001) subsurface configurations; (g) tet 1 O-U(001) subsurface configurations; (h) tet 2 O-U(001) subsurface configurations.

Figure 9 Schematic diagrams of the three different hopping processes that O atom can take (The red spheres represent the O atoms, the green sphere represent the uranium atoms of the first layer, the blue represent the uranium atoms of the second and third layer).

Figure 10 The energy profile for O atom diffusing on the U(001) surface.

First-principle calculations have been performed to study both O_2 molecule and O atom adsorption in on-surface and subsurface for α -U(001) surface. The results show that the long-bridge site is the most stable adsorption site for O_2 -U(001) and O-U(001) surface adsorption. The tetrahedral (Tet) 1 site is the most stable adsorption site for O-U(001) subsurface adsorption. The partial electronic density of states (PDOSs) of O_2 -U(001) and O-U(001) shows the hybridization of U and O atoms causes the electrons of 5f/6d of U more non-local and leads to the formation of O-U bond. The O-U bond is partly ionic and partly covalent. The analysis of the diffusion path of O atom on U(001) shows that O atom can easily transfer from hollow (hol) 1 site to hollow 2 site with no energy barrier. O atom can hardly transfer from surface to the subsurface.