

First-principles study of the adsorption behavior of O₂ on the γ -U(100) surface doped with Nb atom

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Abstract

In this paper, the adsorption behavior of O₂ on the surface of uranium-niobium alloy (5at.%) has been studied by first-principles calculation method with the framework of density functional theory (DFT) and periodic plate model. The results show that physical adsorption takes place when oxygen molecules are vertically adsorbed at the top of Nb atom, while dissociative chemical adsorption takes place in other configurations. When Nb doping is in the first layer of the surface, the most stable adsorption configuration of oxygen molecule is vacancy parallel adsorption, and the adsorption energy is -21.382eV. The essence of the interaction between oxygen molecule and uranium-niobium surface after adsorption is that the O/2p orbital electrons and U/6d, U/5f, Nb/4p, Nb/5s, Nb/4d orbital hybridization, forming relatively stable ionic bonds. When Nb doping is on the second layer of the surface, the most stable adsorption configuration of oxygen molecule is the top parallel adsorption, and the adsorption energy is -22.378eV. The essence of the interaction is the hybridization between O/2p orbital electrons and U/6d and U/5f electrons, and between O/2s orbital electrons and U/6p orbital electrons, forming a relatively stable ionic bond.

Keywords

Adsorption behavior; Density functional theory; γ -U(100) surface; Density of states; Nb doping.

1. Introduction

Three solid phases of uranium are known to exist: the orthogonal α phase with four uranium atoms per cell, the body-centered tetragonal β (bct) phase, and the body-centered cubic γ (bcc) phase. The α , β , and γ phases are stable in the range of 0~940K, 940~1050K, and 1050~1407K, respectively, at atmospheric pressure^[1]. γ -U is widely used in the nuclear industry because of its good performance and excellent structural stability. Adding Nb, Ti, Mo, Zr and other elements into uranium can make the γ phase of uranium stable under room temperature, and scientists have done a lot of research on this^[2-3].

Adding a small amount of Nb into uranium can greatly improve the density and corrosion resistance of uranium^[4]. Xiang et al.^[5] studied the doping form of Nb atom in γ -U. By comparing the formation energy of three doping forms, the results showed that when Nb atom exists in the form of substitution doping, the formation energy is the lowest, which theoretically proved the doping form of Nb element in U metal.

In this paper, the adsorption mechanism of O₂ on uranium-doped niobium surface has been studied by constructing Nb doping models at different positions on γ -U(100) surface and using first-principles calculation. The research focus of this paper is on the stable adsorption configuration, adsorption energy, Bader charge transfer and work function of O₂ during

hydrogen adsorption, aiming to reveal the mechanism of hydrogen reaction on the surface of uranium-niobium alloy, and provide some reference for the corrosion prevention of uranium materials.

2. Calculation Method

2.1. Methods

The Vienna AB-Initio Simulation package based on Density Functional Theory (DFT) was used for all calculations in this study. VASP5.4.4)^[6-7], first-principle calculations were made using the projected augmented wave (PAW) pseudopotential method^[8-9].

Firstly, the structure of O₂ molecule was optimized by placing it in A cubic box with side length of 15 Å and optimizing the ion position. The grid parameters of k point were set as 1×1×1. The structure of γ-U cell was optimized, the ion position, cell shape and cell volume were optimized, and the grid parameters of K point were set as 6×6×6. The slab model with 5 layers was set on γ-U (100) plane, and the structure optimization was carried out. The shape and volume of cell were not changed, the lower two layers were fixed, and the upper three layers were optimized. Then, the uranium-niobium alloy model was established. Two conditions were considered: Nb replaced a U atom in the first layer, Nb replaced a U atom in the second layer, and then the slab model after Nb doping was optimized without changing its shape and volume, the lower two layers were fixed, and the upper three layers were optimized. Finally, when the structure of (O₂)/U-Nb adsorption system is optimized, the bottom two U atoms are fixed, the top three atoms and the O₂ molecules on the surface are optimized without changing their shape and volume. The k point grid parameters of γ-U (100) surface, Nb doped surface and (O₂)/U-Nb adsorption system are set as 6×6×1. For structural optimization of all the above models, the normal accuracy was adopted, the projection was carried out in inverted space, and the proportional coefficient on the force was 0.5. N-order MethfessSL-Paxton method was adopted. When the total energy difference was less than 0.5 meV/ Atom, the plane wave truncation energy was selected as 420 eV. The convergence criterion of force was no more than 0.02 eV/Å, and the convergence criterion of electron total energy was less than 10⁻⁵eV.

Surface energy is defined as:

$$E_{\text{sur}} = (E_{\text{slab}} - NE_{\text{bulk}}) / 2A$$

Where A is the upper and lower surface area of slab crystal cells, E_{slab} is the total energy of slab, N is the number of atoms in the slab model, and E_{bulk} is the energy of U atoms in the bulk phase.

The adsorption energy of O₂ is defined by E_{ads} as:

$$E_{\text{ads}} = E_{[\gamma\text{-U}(100)+\text{Nb}/\text{O}_2]} - E_{\text{O}_2} - E_{\gamma\text{-U}(100)+\text{Nb}}$$

Where E_{ads} is the adsorption energy of O₂ on the surface of slab model; $E_{[\gamma\text{-U}(100)+\text{Nb}/\text{O}_2]}$ is the total energy of the system after O₂ adsorption; E_{O_2} is the energy of O₂ molecule, and $E_{\gamma\text{-U}(100)+\text{Nb}}$ is the basal energy before adsorption. The energy before and after adsorption is obtained under the same calculation method and accuracy. If the adsorption energy is less than 0, the adsorption structure is stable and the smaller the adsorption energy is, the more stable the adsorption energy is.

2.2. Model

In the establishment of adsorption model, slab model with layers 3, 4, 5 and 6 under p(2×2) γ-U supercell was taken into account respectively, and the corresponding surface energy was calculated, as shown in Table 1.

Table 1 Surface energy of 3, 4, 5, and 6-layer slab models under p(2×2) supercell

Slab	$E_{sur}/(eV \cdot \text{\AA}^{-2})$	E_{slab}/eV	E_{bulk}/eV	$A/\text{\AA}^2$	$a/\text{\AA}^2$	$b/\text{\AA}^2$	N
U1003c	0.1060	-120.3306	-10.3605	47.1378	6.8657	6.8657	12
U1004c	0.1108	-163.3229	-10.3605	47.1378	6.8657	6.8657	16
U1005c	0.1070	-207.1200	-10.3605	47.1378	6.8657	6.8657	20
U1006c	0.1073	-250.5333	-10.3605	47.1378	6.8657	6.8657	24

The difference of surface energy between layers 3 and 4, 4 and 5, and 5 and 6 is $0.0048 eV \cdot \text{\AA}^{-2}$, $0.0024 eV \cdot \text{\AA}^{-2}$ and $0.0011 eV \cdot \text{\AA}^{-2}$, respectively. Therefore, we choose the slab model with 5 layers for Nb atom substitution and calculate the binding energy of the doping system. The adsorption sites were divided into three types: top, bridge and hole. The approach of O_2 molecule in each adsorption model was divided into horizontal and vertical conditions, and a total of 14 highly symmetrical adsorption configurations were obtained.

3. Results and discussion

3.1. Adsorption configuration and adsorption energy

Structural optimization was carried out for the high-symmetry adsorption model under the two doping forms until the structure tended to be stable, and the stable adsorption configurations as shown in Fig.1 and Fig.2 were obtained respectively. In order to facilitate differentiation, each adsorption configuration was defined as follows: In the case of Nb doping on the first surface layer, the vertical adsorption of O_2 molecule at the top is expressed as 1-T-ver; in the case of Nb doping on the second surface layer, the parallel adsorption of O_2 molecule at the vacancy is expressed as 2-H-hor. The structural parameters and adsorption energy of O_2 adsorption configuration optimized on γ -U(100) surface are shown in Table 2.

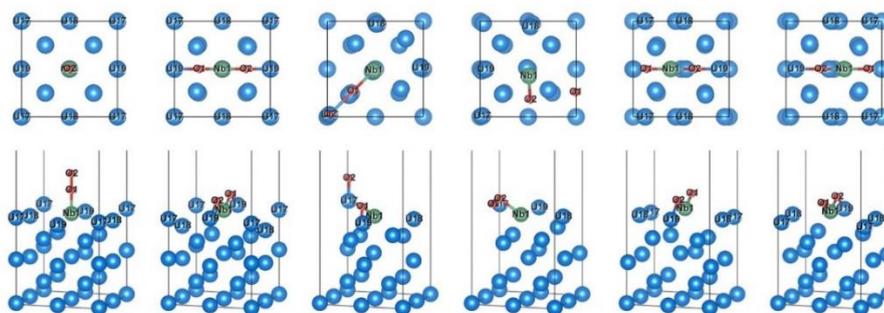


Fig.1 The top view and side view of the optimized adsorption model of O_2 on the γ -U(100) surface (Nb doped in the first layer): (a) Top vertical (b) Top horizontal (c) Hollow vertical (d) Hollow horizontal (e) Bridge vertical (f) Bridge horizontal

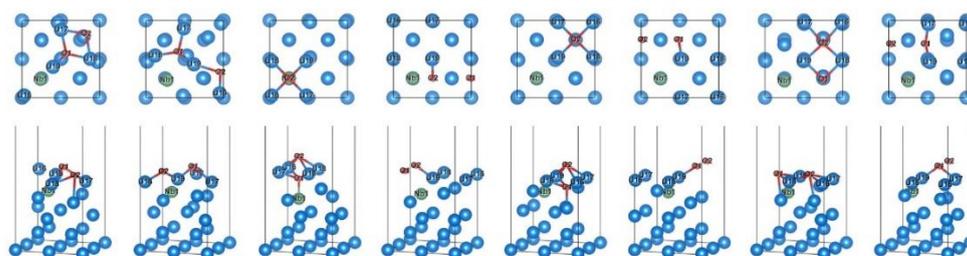


Fig.2 The top view and side view of the optimized adsorption model of O_2 on the γ -U(100) surface (Nb doped in the second layer): (a) Top vertical (b) Top horizontal (c) Hollow vertical 1 (d) Hollow horizontal 1 (e) Hollow vertical 2 (f) Hollow horizontal 2 (g) Bridge vertical (h) Bridge horizontal

Table 2 Optimized geometrical and energy parameters of O₂ adsorption on surface

Nb doped	Configuration	E _{ads} ^a /eV	d _{O1-O2} ^b /nm	Bond ₁ ^c	d _{bond} ^d /nm	h _{O1-s} ^e /nm	Bond ₂ ^f	d _{bond} ^g /nm	h _{O2-s} ^h /nm
first layer	T-ver	-11.735	0.131	O-Nb	0.188	0.188	-	-	-
	T-hor	-19.014	0.334	O-Nb	0.196	0.117	O-Nb	0.195	0.116
	H-ver	-20.156	0.305	O-Nb	0.215	0.034	O-U ₁₇	0.183	0.197
	H-hor	-21.382	0.329	O-U ₁₇	0.201	0.122	O-Nb	0.202	0.112
	B-ver	-19.940	0.347	O-Nb	0.200	0.136	O-Nb	0.194	0.135
	B-hor	-19.938	0.347	O-Nb	0.200	0.136	O-Nb	0.194	0.135
second layer	T-ver	-20.500	0.253	O-U ₁₉	0.203	0.117	O-U ₁₈	0.244	0.072
	T-hor	-22.378	0.413	O-U ₁₉	0.207	0.113	O-U ₁₆	0.218	0.114
	H-ver 1	-17.220	0.218	O-Nb	0.201	-	O-U ₁₈	0.257	0.129
	H-hor 1	-20.997	0.334	-	-	0.114	O-U ₁₉	0.208	0.114
	H-ver 2	-17.006	0.220	O-U ₁₅	0.205	-	O-U ₁₉	0.260	0.140
	H-hor 2	-21.055	0.319	O-U ₁₉	0.207	0.115	-	-	0.115
	B-ver	-20.911	0.320	O-U ₁₈	0.240	0.045	O-U ₁₈	0.233	0.055
	B-hor	-21.031	0.305	O-U ₁₉	0.204	0.118	-	-	0.118

^aadsorption energy, ^b bond distance between the O–O atoms, ^c bond of O₁ and neighbor surface atoms, ^d binding length between O₁ and neighbor surface U or Nb atoms, ^e adsorption height of O₁ atom with respect to the first layer, ^f bond of O₂ and neighbor surface atoms, ^g binding length between O₂ and neighbor surface U or Nb atoms, ^h adsorption height of O₂ atom with respect to the first layer.

According to the data in Figure 1, 2 and Table 2, the adsorption state of oxygen molecules and geometric structure parameters of the adsorption model show that when Nb atoms are doped in the first layer of the surface, oxygen molecules are activated at the top position occupied by Nb atoms, the O–O bond becomes slightly longer (0.131nm, experimental value 0.121nm), and O₂ is adsorbed on the uranium-niobium surface in molecular form. Weak chemisorption. In the other five adsorption positions, the distance between two oxygen atoms is greater than 0.3nm(0.305-0.347 nm), the O–O bond is completely broken, and the oxygen molecule is split into two oxygen atoms to adsorb on the surface of uranium-niobium, which shows the dissociation chemical adsorption. Four of them (T-hor, H-hor, B-ver, B-hor) are in the configuration. The dissociated oxygen occupies the bridge, and in the H-Ver configuration, the oxygen occupies the hole. By analyzing the adsorption configuration, the distance between oxygen atom and the nearest atom on the surface is about 0.2nm (0.188-0.217 nm), which is slightly smaller than the bond length of U–O in UO₂ (0.237nm), indicating that a stable chemical bond has been formed between oxygen atom and uranium or niobium atom on the surface. In addition, the vertical distance between oxygen atom and the nearest uranium atom or niobium atom on the surface is stable within 0.2nm, and the adsorption has reached stability. At this time, the atomic position on the surface of the slab model changes slightly, but the overall relative position is basically unchanged, and the first layer on the surface has a slight fluctuation. When Nb atoms are doped on the second layer of the surface, oxygen molecules are completely dissociated into two oxygen atoms, which are adsorbed on the surface of uranium-niobium. After adsorption, oxygen atoms tend to occupy the hole site. When the vacancy is vertically adsorbed (H-ver1 and H-ver2), oxygen atoms migrate to the inner layer. The distance between

oxygen atom and the nearest uranium atom on the surface is more than 0.2nm (0.201~0.260nm), which is close to the bond length of U-O in UO₂. The vertical distance between oxygen atom and the nearest uranium atom or niobium atom on the surface is less than 0.14nm (0.045~0.140nm), and the surface atom has a small fluctuation. The overall relative position is pretty much the same.

3.2. Bader charge distribution

The Bader charge distribution of (O₂)/γ-U(100)+Nb adsorption system was calculated in this paper, as shown in Table 3.

Net charge is defined as:

$$q_{\text{atom}} = q_{\text{Bader}} - q_{\text{valence}}$$

In the formula, q_{atom} , q_{Bader} and q_{valence} represent net charge, Bader charge and valence electron number respectively.

Table 3 Bader charge distribution in O₂/γ-U(100)+Nb adsorption system

Nb doped	Configuration	Atoms		q_{total}^i	Layers					q_{total}^2
		q_{O1}	q_{O2}		q_{1st}	q_{2nd}	q_{3rd}	q_{4th}	q_{5th}	
first layer	free O ₂	0.1414	-0.1414	0						
	free surface	-	-	-	-0.3544	0.3933	-0.1786	0.7193	-0.5797	-0.0001
	T-ver	0.6063	0.1382	0.7445	-1.2041	0.4469	-0.1779	0.8541	-0.6635	-0.7445
	T-hor	1.1214	1.1213	2.2427	-2.7488	0.3061	0.1768	0.6849	-0.6616	-2.2427
	H-ver	1.1162	1.1096	2.2258	-2.7362	0.5331	-0.1164	0.8630	-0.7694	-2.2258
	H-hor	1.2559	1.0030	2.2589	-2.5360	0.2700	-0.0819	0.8562	-0.7671	-2.2589
	B-ver	1.1343	1.1133	2.2476	-2.7410	0.5026	0.0336	0.6749	-0.7177	-2.2476
	B-hor	1.1355	1.1113	2.2468	-2.7353	0.5116	0.0194	0.6745	-0.7171	-2.2468
second layer	free surface	-	-	-	-0.7888	0.8563	-0.3434	0.9719	-0.6960	0
	T-ver	1.1138	1.1589	2.2727	-1.9942	-0.2156	-0.1164	0.8597	-0.8062	-2.2727
	T-hor	1.3019	1.2479	2.5498	-2.1518	-0.3609	-0.2613	1.0144	-0.7902	-2.5498
	H-ver 1	1.1835	1.1936	2.3771	-2.3948	0.0647	-0.2304	1.0923	-0.9089	-2.3771
	H-hor 1	1.1146	1.1146	2.2292	-2.0931	-0.0728	-0.3523	1.1171	-0.8280	-2.2292
	H-ver 2	1.2399	1.1734	2.4133	-2.0120	-0.2404	-0.3365	0.9802	-0.8048	-2.4133
	H-hor 2	1.1239	1.1239	2.2478	-2.1307	-0.0403	-0.2642	0.9529	-0.7655	-2.2478
	B-ver	1.1809	1.1936	2.3745	-2.3803	0.1181	-0.2204	0.8618	-0.7537	-2.3745
B-hor	1.1044	1.0948	2.1992	-2.0612	-0.1447	-0.1304	0.9121	-0.7750	-2.1992	

q_{total} is the total net charge of two oxygen atoms. q_{1st} , q_{2nd} , q_{3rd} , q_{4th} and q_{5th} respectively represent the total net charge of the first to fifth layers on the surface of uranium-niobium, in unit e.

According to the data in Table 3, from the point of view of charge transfer, the charge of the whole adsorbed configuration is redistributed. Due to the strong electronegativity of O atoms, electrons transfer from the surface layer of Uranium-niobium to O atoms. When Nb atoms are doped in the first layer of the surface, except for t-Ver configuration, In T-hor, H-ver, H-hor, B-ver and B-hor, the net charge number redistributed on oxygen atom is greater than 2e, which is 2.2427e, 2.2589e, 2.2258e, 2.2476e and 2.2468e, respectively. The difference of charge transfer of the five configurations is very small. However, in H-hor configuration, the two oxygen atoms bond with adjacent uranium and niobium atoms in the largest number, and the adsorption energy is the smallest and the charge transfer amount is the largest. Therefore, the structure is the most stable by comprehensive comparison. From the charge distribution of each layer of uranium-niobium, it can be seen that the total charge of the first layer on the surface changes the most, from -0.354e to -1.204e to -2.736e, the total charge of the second

layer changes the next, from 0.3933e to 0.2700-0.5331e, and the change of the third, fourth and fifth layers is smaller. It is less than 0.15e, indicating that the dissociated oxygen atom mainly interacts with the first layer atoms on the surface, and the electrons gathered around the oxygen atom are mainly provided by the surface layer, while the second layer has weak effect, and the last three layers almost have no effect

When Nb atoms are doped on the second layer of the surface, the net charge numbers on oxygen atoms are all above 2e (2.1992~2.5498e), and the charge transfer numbers of atoms on the first layer of the surface slightly decrease on the whole, while the charge changes of atoms on the second layer increase, which may be caused by Nb doping. The change of charge of the last three layers is similar to that of Nb doping in the first layer, which almost has no effect, indicating that oxygen adsorption is mainly the interaction between O and surface and subsurface atoms. It is reasonable to select Nb atoms doped in the first and second layers of γ -U surface to simulate the adsorption system of Uranium-niobium alloy.

3.3. Electronic structure analysis

Through charge-density difference, the aggregation of electrons outside each nucleus in the system can be intuitively reflected, so as to judge the bonding characteristics of O₂, U and Nb atoms. By analyzing the interaction mechanism between atoms, the differential charge density is defined as:

$$\Delta\rho = \rho[(O_2)/\gamma-U_{(100)+Nb}] - \rho(O_2) - \rho(\gamma-U_{(100)+Nb})$$

In the equation, $\rho[(O_2)/\gamma-U_{(100)+Nb}]$, $\rho(O_2)$ and $\rho(\gamma-U_{(100)+Nb})$ represent (O₂)/ $\gamma-U_{(100)+Nb}$ adsorption system, O₂ molecule and $\gamma-U_{(100)+Nb}$ surface charge density, respectively.

Through calculation, differential charge density diagrams (Isosurface value = 0.005e/bohr) of the three configurations of Nb doping parallel adsorption (1-H-hor) and vertical adsorption (1-T-ver) at the first surface layer and parallel adsorption at the top (2-T-hor) at the second surface layer were obtained 0.005e/bohr³, as shown in Fig.3. Contrast figure 3 (a) and (b), you can see that after the charge redistribution, electronic main gathered around in the dissociation of O atom, with the core part of the area O charge density increases, the surface layer of uranium and niobium atom lose after lose electron charge density decreases, and it shows that the oxygen and ionic bond is the main way of bonding between surface atoms, However, the charge distribution around the undissociated oxygen molecule is more uniform, mainly the O-O covalent bond. The charge transfer of surface atoms is not obvious, and the ionic bond between oxygen molecule and surface layer is weak, showing a weak chemical adsorption state. By comparing (a) and (b), it can be found that when Nb is doped at the second layer, the volume of yellow region is larger, and the uranium atom on the surface loses more electrons, which indicates that the activity of uranium atom on the surface is obviously stronger than that of uranium atom doped with a niobium atom on the surface. Therefore, all oxygen molecules are dissociated at the second layer when Nb is doped.

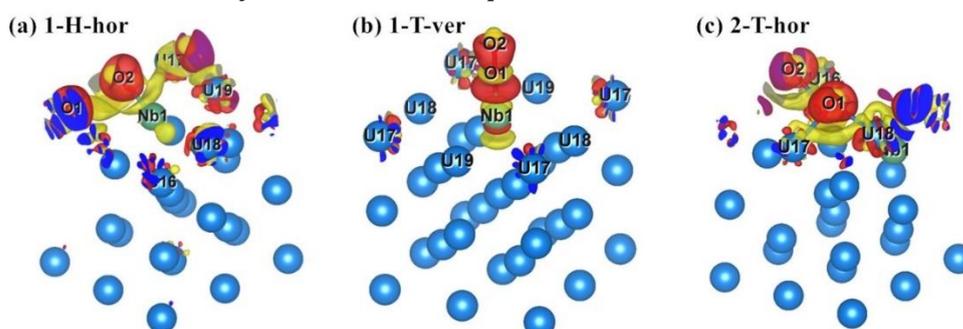


Fig. 3 Charge density differential isosurface

In order to further study the interaction between the dissociated oxygen atom and the surface atom, and reveal the overlap of electrons in the orbital outside the nucleus, the state densities of the two most stable adsorption configurations, 1-H-hor and 2-T-hor, were calculated and analyzed, and the total state density and state-density plots were obtained

As can be seen from Fig.4, the electron energy of 2s and 2p orbital of oxygen atom is distributed around -20eV and -5eV. Near -5eV, the electronic states of 4p orbital, 5s orbital and 4d orbital of Nb atom are split, forming a new orbital peak. These results indicate that there are hybridization between the orbital electrons of Nb-4p, Nb-5s and Nb-4d and the orbital electrons of O-2p, and a stable bond is formed between oxygen and niobium atoms. In the vicinity of -22eV, overlapping and hybridization occur between Nb-4p, Nb-5s and O-2s orbitals, but the peak intensity of state density is weak in this range, indicating that the chemical bond strength formed by oxygen and niobium atoms is weak. After analyzing the interaction between O-Nb and O-U, the electron state density peak of 6d orbital of U atom is obviously split near -5eV, and the electron state of U-7s, U-6p and U-5f orbital is also weak near here, which indicates that the interaction between oxygen atom and uranium atom. It's mainly the hybridization between the 2p of O and the 6d of U. And in the position of energy is 0, namely in the Fermi energy, near U/5f of the peak intensity decrease, U/5f electronic information of O-U bonding contribution is bigger also, near the low level -45eV, U/6s electronics and O, there is no overlap between Nb extranuclear electron orbit, can therefore be seen as the inner electrons and the valence electrons, so comprehensive, When Nb is doped in the first layer of the surface, the nature of the interaction between oxygen molecules and the surface layer of uranium-niobium after adsorption is that the 2p orbital electrons of O atoms hybridized with the electron orbitals of U-6d, U-5f, Nb-4p, Nb-5s and Nb-4d, forming relatively stable ionic bonds.

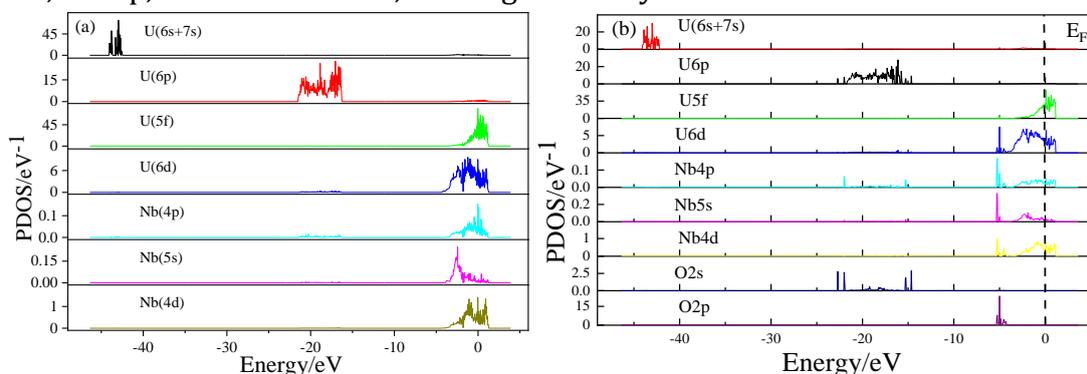


Fig.4 Separation density of pure γ -U(100)+Nb surface and the most stable configuration (1-H-Hor)

For Nb doping on the second layer of the surface, by comparing (a) and (b) in Fig.5, it can be found that the electronic energy of 2s and 2p orbital of oxygen atom is distributed around -20eV and -5eV. Near -5eV, the electronic states of 4p orbital, 5s orbital and 4d orbital of Nb atom are split, forming a new orbital peak. These results indicate that there are hybridization between the orbital electrons of Nb-4p, Nb-5s and Nb-4d and the orbital electrons of O-2p, and a stable bond is formed between oxygen and niobium atoms. In the vicinity of -22eV, overlapping and hybridization occur between Nb-4p, Nb-5s and O-2s orbitals, but the peak intensity of state density is weak in this range, indicating that the chemical bond strength formed by oxygen and niobium atoms is weak. After analyzing the interaction between O-Nb and O-U, the electron state density peak of 6d orbital of U atom is obviously split near -5eV, and the electron state of U-7s, U-6p and U-5f orbital is also weak near here, which indicates that the interaction between oxygen atom and uranium atom. It's mainly the hybridization between the 2p of O and the 6d of U. And in the position of energy is 0, namely in the Fermi energy, near U/5f of the peak intensity decrease, U-5f electronic information of O-U bonding contribution is bigger also, near the low level -45eV, U/6 s electronics and O, there is no overlap between Nb extranuclear

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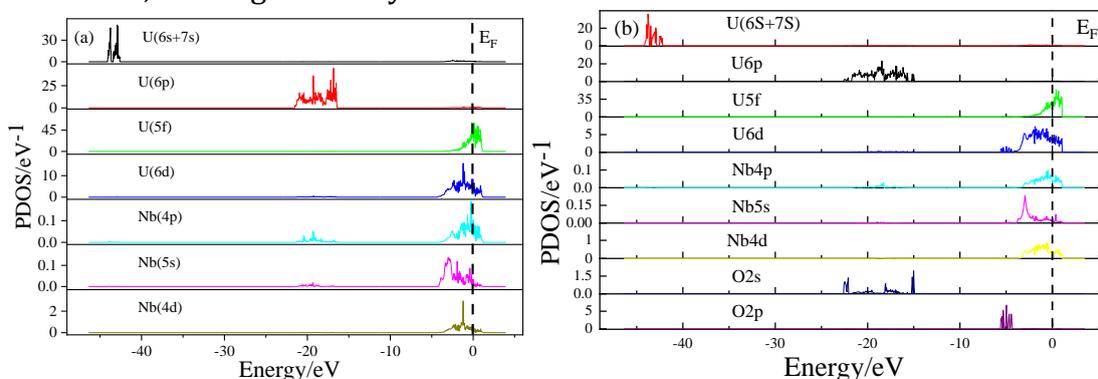


Fig.5 State density of pure γ -U(100)+Nb surface and the most stable configuration (2-T-Hor)

3.4. Surface work function analysis

Work function reflects the minimum energy required for electrons to move from the inside of a solid to the surface. The calculation formula is as follow:

$$\Phi = E_{\text{vacuum}} - E_{\text{Fermi}}$$

In the formula, Φ , E_{vacuum} and E_{Fermi} represent work function, vacuum level and Fermi level respectively, the unit is eV. The changes of surface work function before and after the adsorption of O_2 molecules on the γ -U(100)+Nb surface are shown in Table 4.

Table 4 Surface work function changes ($\Delta\Phi$) of different adsorption configurations.

Nb doped	Configuration	$E_{\text{vacuum}} / \text{eV}$	$E_{\text{Fermi}} / \text{eV}$	Φ / eV	$\Delta\Phi / \text{eV}$
first layer	Free surface	7.1037	3.8645	3.2392	-
	T-ver	8.7910	3.4174	5.3736	2.1344
	T-hor	7.7083	3.7733	3.9350	0.6958
	H-ver	8.1188	3.6191	4.4997	1.2605
	H-hor	7.6399	3.7627	3.8772	0.6380
	B-ver	7.8110	3.7163	4.0947	0.8555
	B-hor	7.8109	3.6920	4.1189	0.8797
second layer	Free surface	7.1037	3.8942	3.2095	-
	T-ver	7.4000	3.8571	3.5429	0.3334
	T-hor	7.4000	3.8935	3.5065	0.2970
	H-ver1	7.6399	3.8996	3.7403	0.5308
	H-hor1	7.5715	3.7920	3.7795	0.5700
	H-ver2	7.5373	3.9248	3.6125	0.4030
	H-hor2	7.5031	3.8399	3.6632	0.4537
	B-ver	7.2979	3.7687	3.5292	0.3197
	B-hor	7.5373	3.8254	3.7119	0.5024

The electronegativity of niobium is 1.6, the electronegativity of uranium is 1.38, the electronegativity of oxygen is 3.5, uranium and niobium uranium more electronegative than hydrogen, in the process of adsorption, charge transfer is more significant, and that part of the atomic charge on the surface of the uranium and niobium to oxygen transfer, from the

adsorbate layer was formed by pointing to the basal surface dipole moment, caused the work function to increase the whole system.

4. Conclusion

In this paper, the adsorption behavior of O₂ on γ -U(100)+Nb surface has been studied based on first-principles method. Results show that the oxygen adsorption, the adsorption configuration of all, the vertical adsorption oxygen atoms in Nb top level, the oxygen molecules is physical adsorption, dissociation oxygen molecules are happen in other configuration, which indicates that the doping of Nb will be weakened to some extent dissociation of oxygen, oxygen dissociation occurs in uranium and niobium system does not need to overcome the energy barrier. When Nb is doped in the first layer of the surface, the most stable adsorption configuration of oxygen molecule is vacancy parallel adsorption, and the adsorption energy is -21.382eV. The essence of the interaction between oxygen molecule and uranium-niobium surface after adsorption is that the 2p electrons of O atom are hybridized with U/6d, U/5f, Nb/4p, Nb/5s and Nb/4d electron orbitals, forming relatively stable ionic bonds. When Nb is doped on the second layer of the surface, the most stable adsorption configuration of oxygen molecule is the top parallel adsorption, and the adsorption energy is -22.378eV. The essence of the interaction between oxygen molecule and uranium-niobium surface after adsorption is the hybridization between 2p orbital electrons of O atom and U/6d and U/5f electrons, and between 2s orbital electrons of O atom and 6p orbital electrons of U, forming a relatively stable ionic bond.

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