## **Supporting Information**

# Exchange between Sub-surface and Surface Oxygen Vacancies on

# CeO<sub>2</sub>(111): A New Surface Diffusion Mechanism

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#### 1. Calculation details

The calculations were performed with the GGA-PW91 functional using the VASP code<sup>s1</sup>. The project-augmented wave (PAW) method was used to represent the core-valence interaction. The valence electronic states were expanded in plane wave basis sets with energy cut-off at 500 eV. It was reported that the standard DFT calculation might lead errors due to the electron self-interaction of the 4f states for the reduced ceria surface. Therefore, to correctly describe the localization of 4f electrons, the so-called DFT+U methodology has been extensively used for ceria and it has been already shown that the approach can accurately reproduce the electronic and structural properties of  $CeO_2^{s2-s9}$ . Therefore, in this study the DFT+U method was used, in which the value of U was set to be 5 eV as tested in many previous works<sup>s3,s8,s9</sup>. The CeO<sub>2</sub>(111) surface was modeled as a periodic slab with 9 atomic layers and the vacuum between slabs is ~15 Å. The bottom one layer are fixed, and all other atoms are fully relaxed as in other previous studies of  $CeO_2(111)$  surface<sup>89</sup>. A p(3×4) surface cell which is rather large (11.64×15.52 Å<sup>2</sup>) with corresponding  $1 \times 1 \times 1$  k- point mesh was used in order to fully take the relaxation effects into account. The k-point sampling was checked <sup>s9</sup>. For example, using  $2 \times 2 \times 1$  k-point mesh the formation energies of the sub-surface and surface O vacancies are 0.02 eV and 0.00 eV higher than those using  $1 \times 1 \times 1$  k-point mesh. The nudged elastic band (NEB) method<sup>s10</sup> was applied to locate the diffusion transition states (TS), and potential energy surfaces (PESs) were constructed accordingly. The STM images

were calculated according to the Tersoff-Hamman method in VASP. The height of the simulated tip was placed at  $\sim 0.6$ Å with the conscant-height mode in p4VASP.

#### 2. The top-surface vacancy structure

It is worth discussing the structure in the presence of a top-surface O vacancy, shown in S-Figure 1, in order to understand STM images and 4f electron localization. The existence of the two excess electron localization on Ce ions breaks the hexagonal symmetry of the (111) surface around the defect, which induces the following structural modifications: (i) Three sub-surface oxygen atoms (O1, O2 and O3 defined in Figure 1) move upwards (0.17 Å for O1 and 0.27 Å for O2 and O3 compared to the second surface oxygen atoms of clean surface, indicated by three arrows in Figure 1(a)) and also contract significantly towards the O vacancy (2.543 Å for O1-Ce6, 2.610 Å for O2-Ce5 and 2.592 Å for O3-Ce4 compared to the general surface O-Ce bond length of 2.375 Å). (ii) Four of the six surface O atoms in the second neighbors of the vacancy (from O4 to O7) move slightly upwards (0.02 Å). However, two of them (O8 and O9) have almost no change in their positions (S-table 1). To check the validity of the structure, we also calculated the filled-state STM image from the DFT results and the calculated STM image is shown in Figure 1(c), which agrees well with the experimental work: Because two cerium ions are reduced from  $Ce^{4+}$  to  $Ce^{3+}$ , the original hexagonal symmetry of the surface is broken, as shown by the simulated filled-state STM images (four bright dots). In addition, it is clear from S-table 1 that the relaxation of the first neighbor O anions is much more significant than that of the second nearest neighbor O anions.

The main distances between Ce and O around the top-surface and sub-surface vacancies are listed in S-Table 2. It can be seen from the table that the average Ce-O distance between the second-neighbor Ce ions (Ce4 and Ce5) and the oxygen ions which are directly bonded to these Ce ions is longer than those between the first-neighbor Ce ions (Ce1, Ce2 and Ce3) and the corresponding oxygen ions. The relaxation is so significant that the two second-neighbor Ce ions (Ce4 and Ce5) become the localization sites for the excess electrons<sup>s9</sup>, as shown in Figure 1.

	Zi	n the sec	ond C	) layer	Z in	the first O layer	Z in the third O layer
top-surface	04	0.028	O7	0.007	01	0.164	
vacancy	05	0.031	08	-0.002	O2	0.256	
structure	06	0.024	09	0.024	03	0.259	
sub-surface	01	-0.216	O4	0.095			0.092
vacancy	O2	-0.206	05	0.081			0.090
structure	03	-0.200	06	0.070			0.093

S-Table 1. The distances of oxygen atoms moved upwards sub-surface oxygen atoms, compared to the same position atom of clean surface (Å).

#### 3. The sub-surface vacancy structure

Similar to the top-surface oxygen vacancy, the sub-surface oxygen vacancy in S-Figure 2 also induces a significant structural modification which can be summarized as follows: (i) The first neighbor surface oxygen ions on the top-surface (O1, O2 and O3) contract towards the vacancy and move downward by about 0.20 Å, while the second neighbor oxygen ions (O4, O5, and O6) on the top-surface move upwards by about 0.07-0.10 Å. This structural relaxation results in the characteristic triangular bright dots formed by the atoms with lower positions and the triangular dark dots formed by the atoms with higher positions in the filled-state STM image (Figure 2(c)), which is consistent with the experimental work [19]. (ii) The three oxygen atoms in the first neighbors to the vacancy in the third layer contract inward, increasing their heights by about 0.09 Å (indicated by the three arrows in Figure 2(a)). (iii) The two O atoms (O1 and O2) contract, leading to the Ce4-O1 and Ce5-O2 bond lengths to increase from the general surface Ce-O bond length of ~2.375 Å to 2.669 Å and 2.638 Å, respectively. Moreover, the average Ce-O bond length of Ce4 and Ce5 is the longest in the sub-surface structure. In fact, the relaxation is so significant that the Ce-O bonds of two second-neighbor Ce ions is broken, resulting in Ce4 and Ce5 being the localization sites for the excess electrons.

		Ce-O <sub>ave</sub> (Å)							
	Ce1	2.351	2.299	2.261	2.227	2.283	2.311		2.289
Top-surface	Ce2	2.350	2.312	2.259	2.225	2.299	2.300		2.291
vacancy	Ce3	2.314	2.25	2.243	2.266	2.328	2.32		2.287
structure	Ce4	2.485	2.463	2.525	2.592	2.516	2.471	2.419	2.496
	Ce5	2.610	2.519	2.467	2.498	2.455	2.533	2.420	2.500
	Ce1	2.304	2.252	2.328	2.317	2.317	2.264		2.297
Sub-surface	Ce2	2.268	2.274	2.314	2.282	2.321	2.320		2.296
vacancy	Ce3	2.259	2.302	2.336	2.253	2.323	2.318		2.298
structure	Ce4	2.669	2.483	2.478	2.473	2.512	2.421	2.407	2.492
	Ce5	2.638	2.482	2.477	2.506	2.418	2.492	2.416	2.490

S-Table 2. The main distances between Ce and O around the vacancy (Ce- $O_{sin}$ : the single Ce-O distance; Ce- $O_{ave}$ : the average Ce-O distance).

### 4. The transition state of hopping mechanism

The transition state is illustrated in Figure 2(a): the hopping oxygen atom is 0.45 Å above the top surface layer (the oxygen layer) with the Ce-O bond being 2.15 Å.

#### 5. The transition state of two step exchange mechanism

Although there are two transition states along the whole path, they are identical, which is shown in Figure 2(b): If a surface oxygen atom is linearly connected to a nearby subsurface oxygen atom, the diffusing oxygen atom is at the middle position of the linear path at the transition state. In other words, the oxygen atom is between the two Ce atoms and they are almost on the same Ce layer (the second layer). At the transition state, the diffusing Ce-O bond is around 2.23 Å.

#### 6. Why the sub-surface O vacancy is slightly more stable than the surface one

The result that the sub-surface O vacancy is slightly more stable than the surface one is against the common intuition: To create a sub-surface O vacancy, one has to break four Ce-O bonds while only three Ce-O bonds would be broken if a surface O vacancy is formed. Why should the surface O vacancy be slightly less stable the sub-surface one? In order to solve this puzzle, again we did energy decomposition

analyses. The O vacancy formation was decomposed into two steps: (i) moving the O atom to the gas phase with respect to O<sub>2</sub> without the structural relaxation and the corresponding energy cost is defined as the bond energy  $E_{bond}$ ; and (ii) allowing the structural relaxation to proceed, which gives rise to the relaxation energy gain  $E_{relax}$ . Namely,  $E_{formation} = E_{bond} - E_{relax}$ . For the surface and sub-surface O vacancies,  $E_{bond}$ were calculated to be 3.88 eV and 4.19 eV, respectively. This result is consistent with the common intuition that the sub-surface O directly bonds with four Ce<sup>4+</sup> while the surface O bonds with three  $Ce^{4+}$ . However,  $E_{relax}$  in the sub-surface O vacancy formation is 2.23 eV, larger than that of surface O vacancy (1.76 eV). It is this structural relaxation term that bring the stability of sub-surface O vacancy to the similar level of the surface one. The larger relaxation energy in the presence of sub-surface O vacancy than the surface one can be rationalized as follows: As shown in our previous work<sup>[18]</sup>, the relaxation energies are mainly determined by the relaxation of the first neighbour O ions. Around the sub-surface oxygen, three surface O ions and three O ions in the third layer are able to take part in the structural relaxation, while for the surface O vacancy only three sub-surface O ions are mainly available to be directly involved in the relaxation.



S-Figure 1. Isosurfaces of spin density for the  $CeO_2(111)$  in the presence of top-surface oxygen vacancy. The isosurface contours are 0.05 electrons/Å<sup>3</sup>. O atom is red, Ce is gray, and the vacancy is marked in a  $\Box$ .



S-Figure 2. Isosurfaces of spin density for the  $CeO_2(111)$  in the presence of sub-surface oxygen vacancy. The isosurface contours are 0.05 electrons/Å<sup>3</sup>. O atom is red, Ce is gray, and the vacancy is marked in a  $\square$ .

### **References and notes**

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