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Supporting Information

Evidence of the O-Pd-O and Pd-O₄ Structure Units as Oxide Seeds and Their Origin on Pd(211): Revealing the Mechanism of Surface Oxide Formation

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Supplementary Figures



Supplementary Figure 1. A sketch of the three regions model. The bottom two layers are bulk region and the atoms in the bulk region are fixed. The atoms in the unreconstructed layer are relaxed but not involved in the structure evolution. The top layer atoms in the reconstructed surface region are subject to structure swarm evolution. The number of exterior O atoms is ranging from 1 to 9, corresponding to oxygen coverage from 0.11 monolayer to 1.0 monolayer.







Supplementary Figure 2. The surface O atom vacancy formation energy, Pd-O-Pd bond angle and charge difference of O_x/Pd (x=1,2,...,9) from (a) to (i). The charge difference of surface O atoms is calculated by substrate the charge value of chemisorbed O on 0.11 ML oxygen coverage surface.



Supplementary Figure 3. (a) illustrates the three and four coordinated surface O atom on PdO(101) surface. (b) illustrates the chemisorbed O atom on Pd(211) surface. (c) illustrates the four coordinated O atom in PdO crystal. The red and blue atoms are representing the O and Pd atoms, respectively. The E_v of O atoms is displayed, and the bonding energy of different O-Pd bonding types are also illustrated.

Supplementary Tables

Supplementary Table 1. The energy contribution of different O-Pd bonding types to the formation energy of surface O vacancy in the empirical equation.

O atom coordination Number	O bond Type	E_{O-Pd-x}/eV
2	O-Pd-Pd	-0.72
	O-Pd-O	-1.16
3	O-Pd-Pd	-0.51
	O-Pd-O	-0.95
4	O-Pd-Pd	-0.30
	O-Pd-O	-0.74

Supplementary Notes

Supplementary Notes 1

The application of CALYPSO code in this work

Our structure prediction is based on a global minimum search of the free energy surfaces obtained by ab initio total-energy calculation, through the crystal structure analysis by particle swarm optimization (CALYPSO) methodology. The feature of this methodology is the capability of predicting energetically stable/metastable structures at given chemical compositions for clusters, 2D layers, surfaces and 3D crystals, which was developed by Ma and co-workers. In this approach, an ensemble of surface structures were initially constructed unbiasedly by depositing a fixed number of atoms on an ideal surface. The atoms were randomly attached to the surface with bonds to at least one original surface atom. Symmetry operations of various space groups were applied while constructing the initial surface structures. Density functional theory was used to optimize the geometries and to obtain the total energies of those structures once the initial structures were generated. The structures then evolved towards lower-energy structure globally, through self- and swarm-structure learning.

We used a slab model (shown in Supplementary Figure 1) that consists of three regions: the bulk material region, the unreconstructed layer and the reconstructed layer. A vacuum layer was also needed to separate slabs in the supercell. In the unit cell, each layer contains nine Pd atoms and the number of surface O atoms was increased successively from 1 to 9, named as the O coverages of 0.11 to1.00 ML, respectively, for clarity. It should be noted that some O atoms might go to subsurface regions when the number of O atoms was high. The Pd atoms in the second layer were fully relaxed, and the bottom two layers were fixed. All the structures were optimized using the VASP code. The number of optimizations were chosen as 2 for the increase of converged calculation rate. Because the generated structures were often far from their local minima, a single fine structure optimization might lead to a non-converged result. The optimizations during the structure search were done with the conjugate gradients method and were stopped when total energy changes were smaller than 0.03 eV for the first optimization step (0.0001 eV for the second optimization step). The cut-off energies of the plane wave basis set were set at 300 eV and 380 eV for the first and second steps, respectively. The final structures were optimized using the cutoff energy of 400 eV. The 90% lowest-energy structures of each generation were used to produce the structures in the next generation by the PSO technique, and the remaining 10% structures were randomly generated within symmetry constraint to enhance the structural diversity. The evolutionary structure predictions were performed at 0 K and zero pressure. Each generation contained 16 structures, and typically 40 generations were generated to obtain the most stable (or relatively stable) structures. For our systems the most stable structures at different oxygen coverages were usually located between 10 to 20 generations. In the case of 1.00 ML oxygen coverage, the most stable structure appears at 38 generation, and thus we generated 10 more generations (50 generations in total) to see if a more stable structure would be located. Typically, the structure searching simulations for each structure were stopped after 640 to 800 structures were generated (e.g., about 40 to 50 generations).

Supplementary Notes 2

The derivation detail of the empirical equation for surface oxides O atom vacancy formation energy

The formation energy of O vacancy is contributed from different O-Pd bonding types, and the different O-Pd bond energies are obtained from chemisorbed O atom on Pd(211) and PdO bulk/(101) surface. The E_{ν} of the 3-fold coordinated O atom on Pd(211) is contributed evenly by three O-Pd-Pd bonds, and each O-Pd-Pd bond provides -0.51 eV energy (supplementary figure 3b). In Figure 3a, we can see that PdO(101) have both 3-fold and 4-fold coordinated O atoms, so we average their bonding energy based on their coordination number. The O-Pd-O bond contributes -0.95 eV bonding energy to 3-fold coordinated surface O atom, but it contributes -0.74 eV bonding energy to 4-fold coordinated surface O atom. To verify this result (supplementary figure 3c), we also calculated the 4-fold coordinated O atom in bulk PdO, and the O-Pd-O bond contributes -0.77 eV binding energy which is basically identical to the 4-fold coordinated O atom on the surface. From the above results, we know that the O atom E_{v} is quantitively related to the O-Pd bond type and the O atom coordination number, which can be explained from the bonding orbital perspective. Therefore, we assume that both O-Pd-Pd and O-Pd-O bond energy increases -0.21 eV for 2-fold coordinated surface O atoms and decrease 0.21 eV for 4-fold coordinated surface O atoms that based on the 3-fold coordinated O atom. The energy contribution of different O-Pd bond types to the surface O atom bonding energy is given in supplementary table 1. Based on the two parameters that affect the O atom bonding energy, we generated the empirical equation as shown in equation (1).

$$E_v = nE_{O-Pd-Pd} + mE_{O-Pd-O} \tag{1}$$