Supporting Information

Molecular-Scale Mechanistic Investigation of Oxygen Dissociation and Adsorption on Metal Surface-Supported Cobalt Phthalocyanine

Duc Nguyen,[‡,¶] Gyeongwon Kang,[‡,¶] Mark C. Hersam,[‡,†,§] George C. Schatz,[‡,*] and Richard P. Van Duyne[‡,†,*]

[‡]Department of Chemistry, [†]Applied Physics Graduate Program, and [§]Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, United States

1. Calculation of the formation energy for different configurations

Formation energy of each configuration was calculated in comparison to the CoPc/Ag(111), CoPc/Cu(111) or CoPc/Au(111) and gas phase O_2 or adsorbed atomic O on metal surfaces (O_x/M). Here we define the energy of each species using the Methfessel-Paxton thermal smearing scheme.[1] Nuclear entropy was not considered. The following chemical equations were used to obtain the formation energy from gas phase O_2. On each metal surface (M):

$$CoPc + M \rightarrow CoPc/M$$

$$CoPc/M + O_2 \rightarrow O_2/CoPc/M$$

$$CoPc/M + \tfrac{1}{2}O_2 \rightarrow O/CoPc/M$$

$$CoPc/M + O_2 \rightarrow (O)_2/CoPc/M$$

$$CoPc/M + O_2 \rightarrow CoPc/(O)_2/M$$

For adsorbed atomic O on metal surfaces (O_x/M), oxygen coverage was varied by changing number of O atoms in the slab structure. For the formation energy calculations from O_x/M, the desorption energy of an

O atom from O_x/M was used. The free energy difference between O_x/M and O_{x-1}/M is constant regardless of the coverage due to the linearity in the energy as shown in Figure S1 and S2. Therefore, the reference energy is obtained according to the following chemical reaction:

$$O_x/Ag \rightarrow O_{x-1}/Ag + O \quad \Delta E = 72.4 \text{ kcal/mol}$$

$$O_x/Cu \rightarrow O_{x-1}/Cu + O \quad \Delta E = 96.7 \text{ kcal/mol}$$

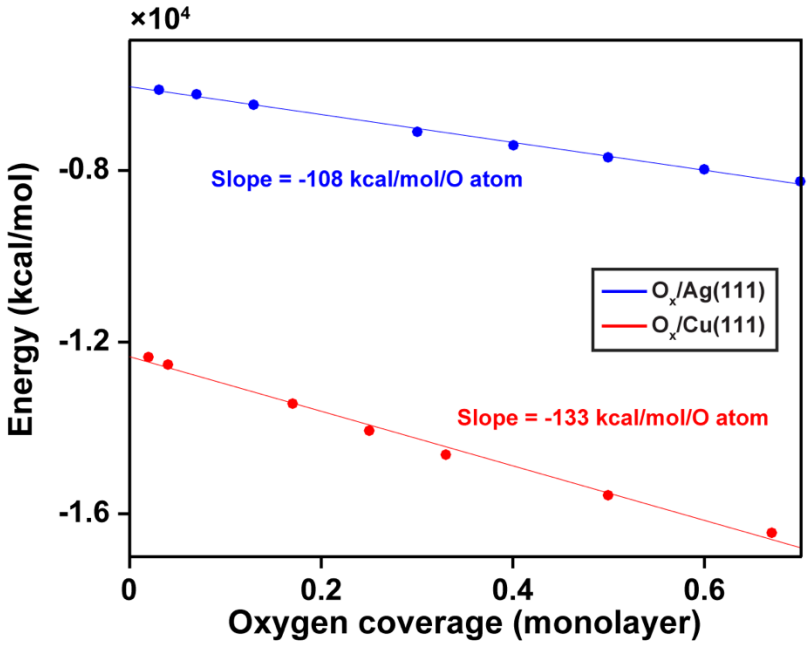

Figure S1. Calculated free energy plots of Ag(111) (blue) and Cu(111) (red) surfaces with respect to the oxygen coverage. The free energy values show a linear trend against the coverage with the slopes of -108 and -133 kcal/mol/O atom for O_x/Ag(111) and O_x/Cu(111), respectively. Note that the free energy of O atom is included in the energy values.

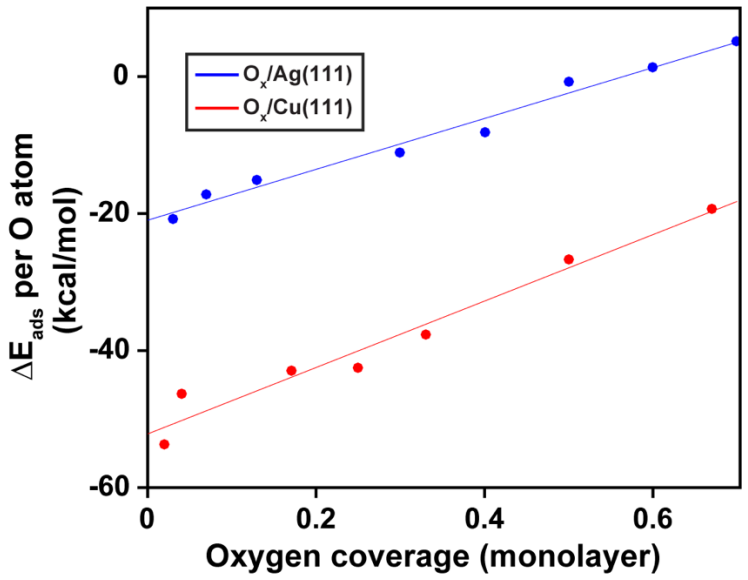

Figure S2. Calculated adsorption energy of oxygen per O atom on Ag(111) (blue) and Cu(111) (red) surfaces with respect to the oxygen coverage. The free energy values show a linear trend with respect to the coverage with the slopes of 36.8 and 48.2 kcal/mol/monolayer for O_x/Ag(111) and O_x/Cu(111), respectively.

2. Calculation details for atomic O diffusion on surfaces

Transition pathways for oxygen diffusion on each metal surface were studied using the nudged elastic band (NEB) procedure implemented in VASP.[2] An oxygen atom was placed on a fcc 3-fold hollow site as an initial state. The transitions pathways toward two neighboring hcp 3-fold hollow sites were calculated using 5 intermediate images in between the initial and final states. Spring constants between images were set to -5 eV/Å^2. The results are shown in Figure S3.

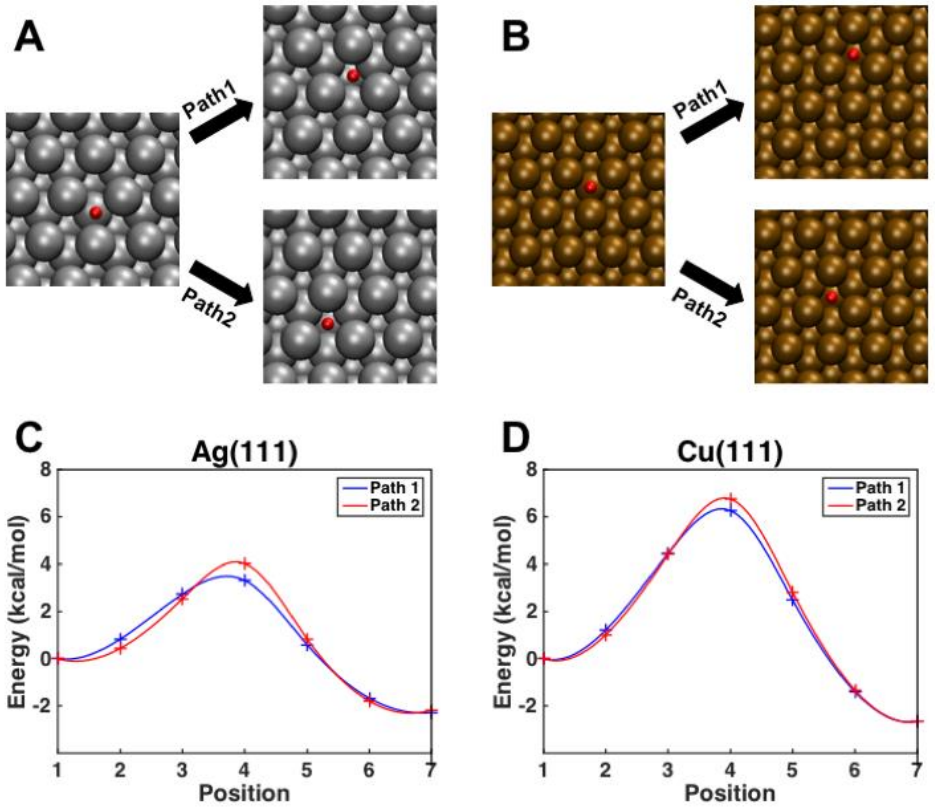

Figure S3. Initial (left) and final (right) geometries for NEB calculations for two different paths of oxygen diffusion on (A) Ag(111) and (B) Cu(111) surfaces. Energy profile along the diffusion paths are plotted in (C) and (D) for Ag(111) and Cu(111), respectively. O: red, Ag: silver, Cu: brown.

Relative diffusion coefficient (D_{Ag}/D_{Cu}) is estimated for atomic O on Ag(111) and Cu(111) surfaces at room temperature using the Arrhenius law, with the same pre-exponential factor and the above calculated energy barriers (lower pathways in Figure S3, ~5.6 kcal/mol for Ag(111) and 8.9 kcal/mol for Cu(111)). The relative diffusion coefficient (D_{Ag}/D_{Cu}) is found to be ~260.

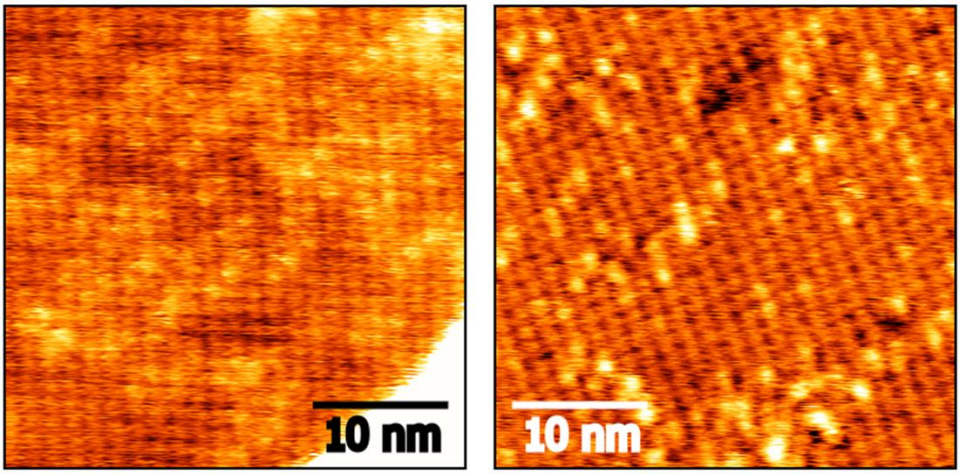

Figure S4. Typical STM images (areas mainly containing O_2/CoPc/Ag(111) and O/CoPc/Ag(111)) (left) ~2 hours and (right) ~9 hours after 1800 L O_2 dosing. Desorption of oxygen is observed in a timescale of several hours. Scanning conditions: -1.0 V, 0.5 nA.

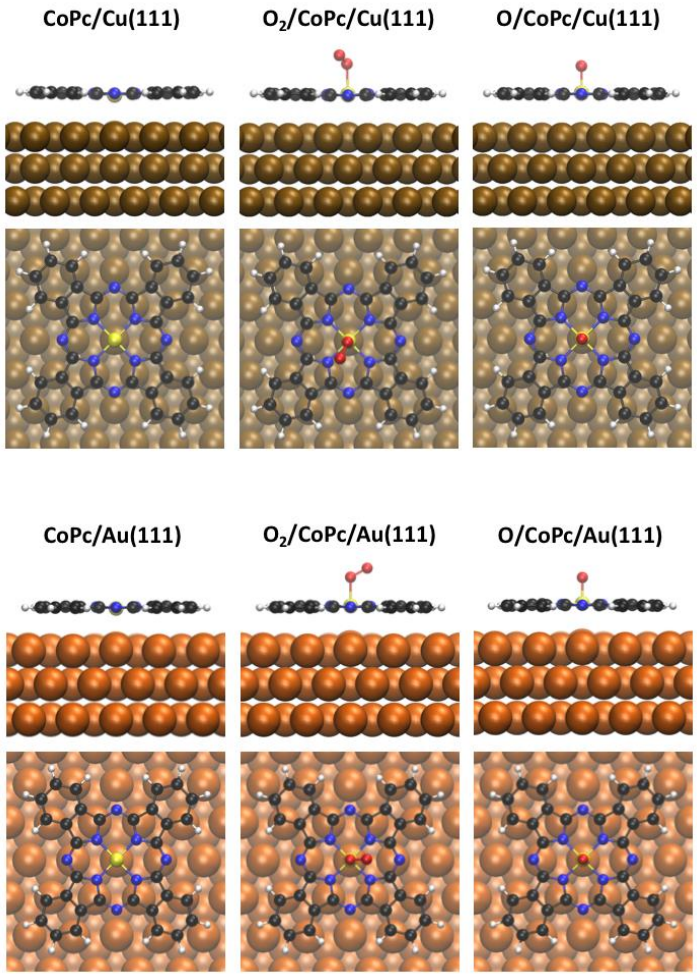

Figure S5. Though not observed in our experiments, oxygen adsorption on CoPc/Cu(111) and CoPc/Au(111) is stable in our calculations. Side and top views of calculated adsorption geometries of CoPc (left), O_2/CoPc (middle), and O/CoPc (right) on Cu(111) (top) and Au(111) (bottom) surfaces are shown. Cu: brown, Au: orange.

References

(1) Methfessel, M.; Paxton, A. T. High-precision sampling for Brillouin-zone integration in metals. *Phys. Rev. B* **1989**, *40*, 3616–3621.

(2) Jónsson, H.; Mills, G.; Jacobsen, K. W., Nudged elastic band method for finding minimum energy paths of transitions. In *Classical and quantum dynamics in condensed phase simulations*, World Scientific, **1998**, 385-404.