

## Supporting Information

### Single Atom Detachment from Cu Clusters, Diffusion and Trapping on CeO<sub>2</sub>(111): Implications in Ostwald Ripening and Atomic Redispersion

*Qiang Wan,<sup>1</sup> Fenfei Wei,<sup>1</sup> Yingqi Wang,<sup>2</sup> Feiteng Wang,<sup>3</sup> Linsen Zhou,<sup>2</sup>*

*Sen Lin,<sup>1,2,\*</sup> Daiqian Xie,<sup>3,\*</sup> and Hua Guo<sup>2,\*</sup>*

*<sup>1</sup>State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry,*

*Fuzhou University, Fuzhou 350002, China*

*<sup>2</sup>Department of Chemistry and Chemical Biology, University of New Mexico, Albuquerque,*

*New Mexico 87131, USA*

*<sup>3</sup>Institute of Theoretical and Computational Chemistry, Key Laboratory of Mesoscopic*

*Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing*

*210023, China*

\*: corresponding authors: [slin@fzu.edu.cn](mailto:slin@fzu.edu.cn), [dqxie@nju.edu.cn](mailto:dqxie@nju.edu.cn) and [hguo@unm.edu](mailto:hguo@unm.edu)

Table S1. Binding energies (eV) of  $\text{Cu}_n$  ( $n = 2-10, 12, 14, 16, 18,$  and  $20$ ) clusters on  $\text{CeO}_2(111)$  and CO on  $\text{Cu}_n/\text{CeO}_2(111)$ .

<b>Cluster size</b>	<b><math>E_b(\text{Cu}_n)</math></b>	<b><math>E_b(\text{CO})</math></b>
2	-2.02	-2.15
3	-4.31	-1.14
4	-4.48	-1.50
5	-4.38	–
6	-4.59	–
7	-4.06	-0.50
8	-4.40	-1.02
9	-5.95	-0.89
10	-6.72	-1.43
12	-7.98	-1.37
14	-4.93	-1.01
16	-6.08	-0.94
18	-5.84	-0.57
20	-5.48	-1.31

Table S2. Detachment energies (eV) of  $\text{Cu}_8/\text{CeO}_2$  and  $\text{CO-Cu}_8/\text{CeO}_2$  calculated by DFT+ $U$  with  $U$  equal to 2 and 4.5 eV.

	Detachment Energy	
	CO	no CO
$U=4.5$ eV	0.30	0.92
$U=2$ eV	0.23	0.94

Table S3. Detachment energies (eV) calculated by placing Cu or Cu<sub>1</sub>-CO at the most favorable adjacent site away from its original position in the Cu<sub>n-1</sub> cluster. The

detachment energies are calculated via  $E(\text{Cu}_{n-1} + \text{Cu}_1\text{-CO/CeO}_2) - E(\text{Cu}_n/\text{CeO}_2)$ ,  $E(\text{Cu}_{n-1} + \text{Cu}_1/\text{CeO}_2) - E(\text{Cu}_n/\text{CeO}_2)$  and  $E(\text{Cu}_{n-1} + \text{Cu}_1\text{-CO/CeO}_2) - E(\text{Cu}_n/\text{CeO}_2) - E(\text{CO})$ , respectively. The adsorption energy is included for Cu detachment with CO by following equation  $E(\text{Cu}_{n-1} + \text{Cu}_1\text{-CO/CeO}_2) - E(\text{Cu}_n/\text{CeO}_2) - E(\text{CO})$ .

n	$E_{\text{det}}(\text{CO})$	$E_{\text{det}}(\text{no CO})$	$E_{\text{det}}(\text{including CO adsorption energy})$
2	-0.12	0.31	-2.27
3	1.02	1.34	-0.13
4	0.38	0.81	-1.12
5	-	-0.48	-2.00
6	-	-0.30	-1.82
7	-0.70	0.23	-1.20
8	0.65	1.41	-0.37
9	-0.35	0.54	-1.24
10	0.42	0.91	-1.00
12	0.61	0.89	-0.76
14	-0.04	0.42	-1.05
16	0.72	0.78	-0.76
18	0.26	1.22	-0.31
20	0.56	0.73	-0.75

Table S4. Detachment energies (eV) for removing a single Cu atom or  $\text{Cu}_1\text{-CO}$  complex from different configurations of the  $\text{Cu}_8$  cluster adsorbed on ceria. A and B

in the notation A\_B represent the configuration of Cu<sub>8</sub> adsorbed on ceria and the adsorption site for the CO molecule, respectively. The corresponding configurations can be seen in Figure S3.

A_B	$E_{\text{ads}}(\text{cluster})$	$E_{\text{det}}(\text{CO})$	$E_{\text{det}}(\text{no CO})$	$\Delta E = E_{\text{det}}(\text{CO}) - E_{\text{det}}(\text{no CO})$
0_1	-4.40	0.30	0.92	-0.62
1_1	-3.09	-1.64	-0.69	-0.94
1_2		-1.66	-0.70	-0.96
2_1	-4.60	0.10	0.98	-0.88
2_2		0.46	1.27	-0.81
3_1	-4.62	0.01	1.18	-1.17
3_2		0.58	1.40	-0.83
4_1	-3.24	-1.43	-0.51	-0.91
4_2		-1.29	-0.38	-0.91
5_1	-4.21	0.07	0.66	-0.58
5_2		0.22	0.72	-0.50
6_1	-4.21	0.30	1.01	-0.70
6_2		0.05	0.71	-0.66

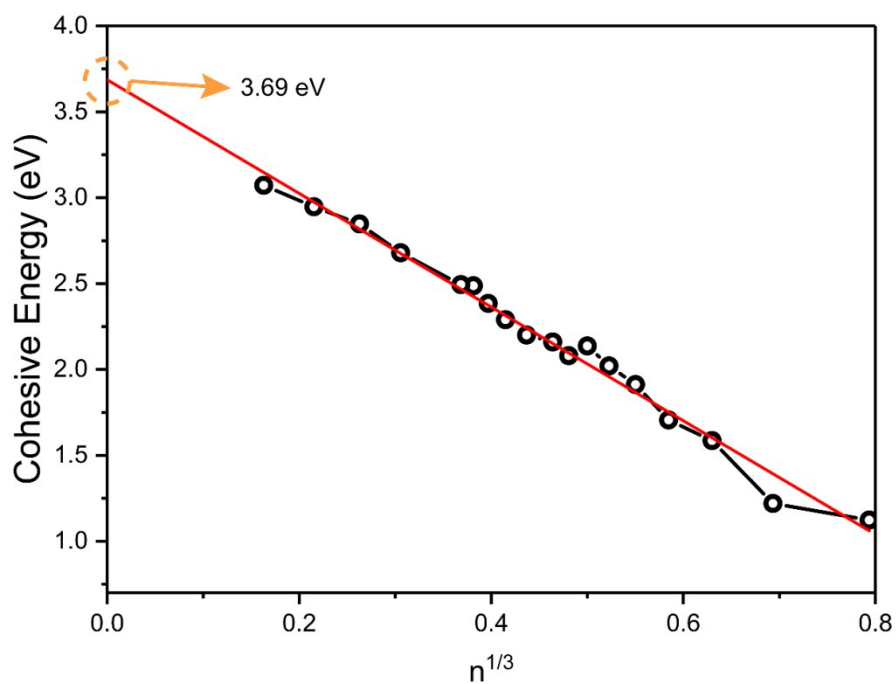
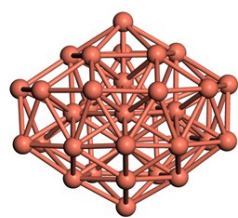
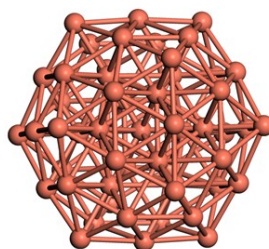


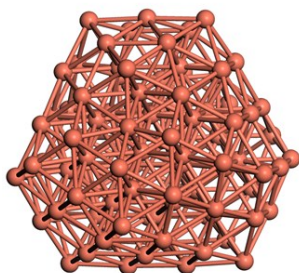
Figure S1. Cohesive energy of  $\text{Cu}_n$  cluster, with  $n = 2-10, 12, 14, 16, 18, 20, 35, 55, 100$  and  $230$  as a function of  $n^{-1/3}$ .<sup>1</sup> The total energies for the  $\text{Cu}_{35}$ ,  $\text{Cu}_{55}$ ,  $\text{Cu}_{100}$ , and  $\text{Cu}_{230}$  clusters were calculated using the same DFT protocol in a box of  $30 \times 30 \times 30 \text{ \AA}^3$ . The optimized structures for  $\text{Cu}_{35}$ ,  $\text{Cu}_{55}$ ,  $\text{Cu}_{100}$ , and  $\text{Cu}_{230}$  are displayed in Figure S2.



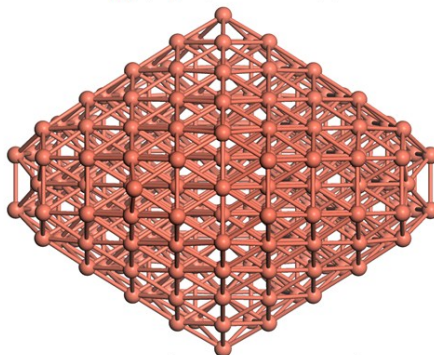
Cu<sub>35</sub> (C<sub>s</sub> symmetry)



Cu<sub>55</sub> (C<sub>1</sub> symmetry)



Cu<sub>100</sub> (C<sub>s</sub> symmetry)



Cu<sub>230</sub> (C<sub>1</sub> symmetry)

Figure S2. Optimized structures of Cu<sub>35</sub>, Cu<sub>55</sub>, Cu<sub>100</sub>, and Cu<sub>230</sub>.

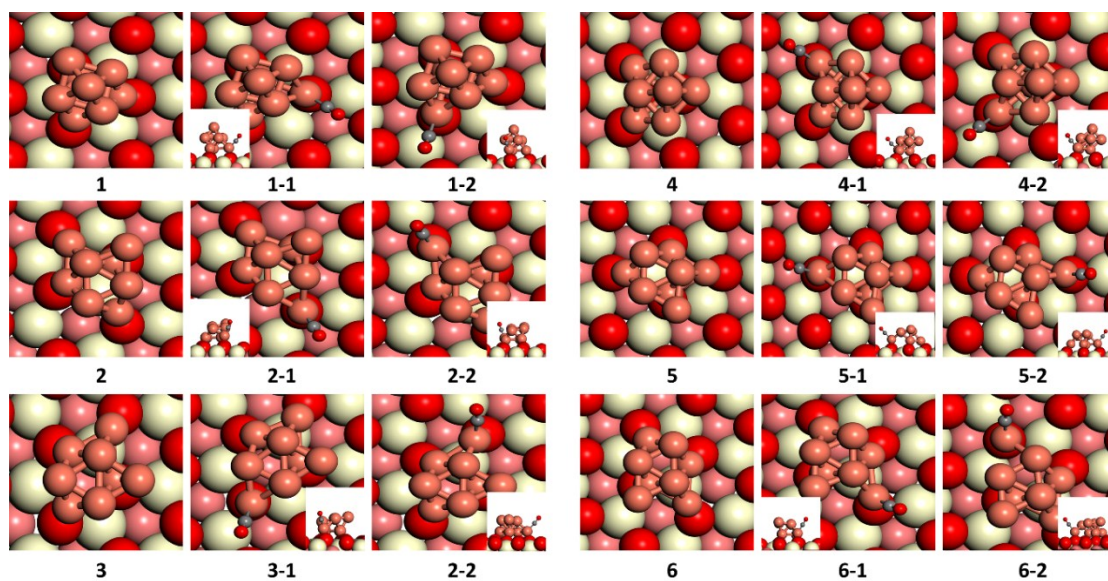


Figure S3. Different configurations for  $\text{Cu}_8/\text{CeO}_2$  with CO absorbed at different sites, as discussed in Table S4.



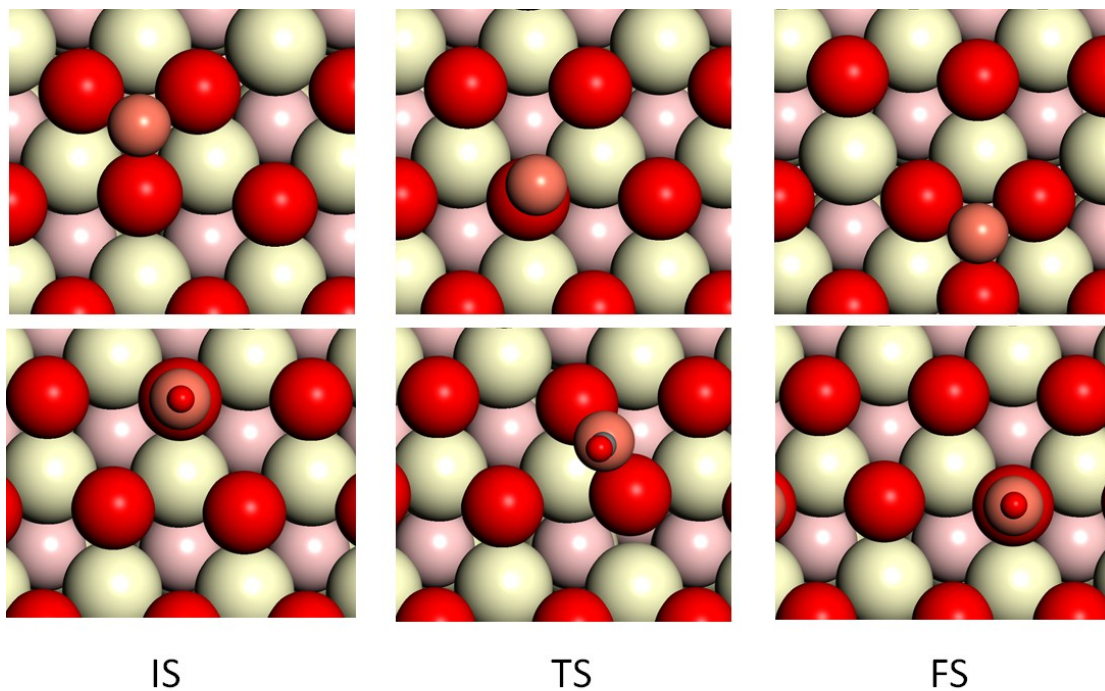


Figure S4. Stationary point structures along the diffusion path (IS, TS and FS) for the migration of the single Cu atom from the oxygen hollow site to an adjacent oxygen hollow site and Cu<sub>1</sub>-CO complex from the oxygen top site to an adjacent oxygen top site on CeO<sub>2</sub>(111). Color scheme: Ce, yellow; surface O, red; subsurface O, coral; Cu, bronze; C, grey.

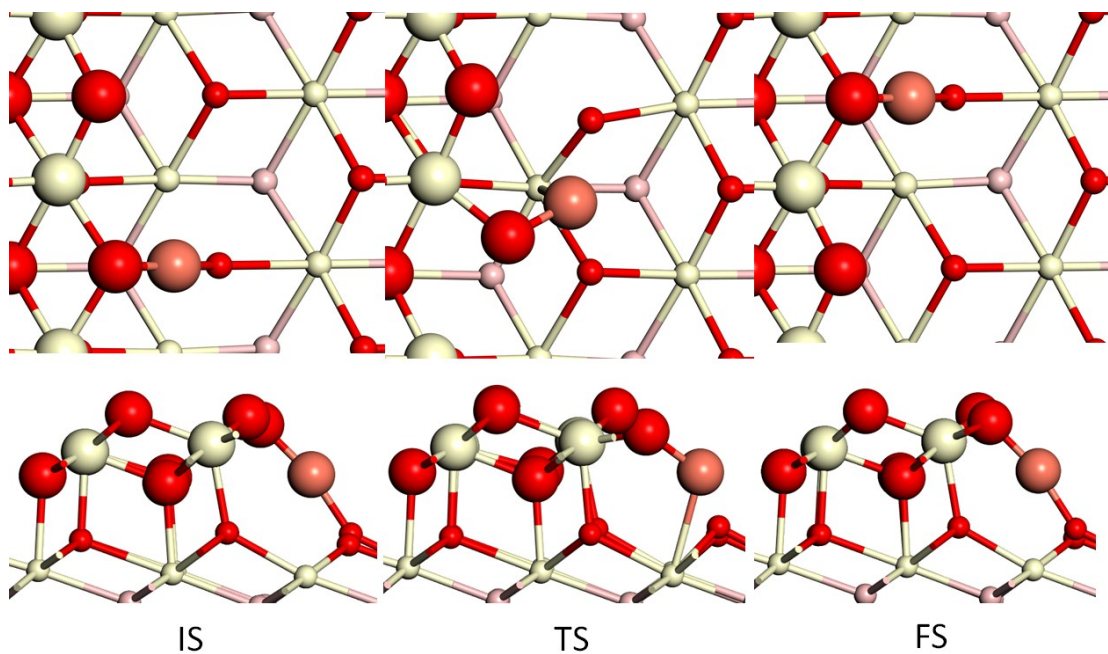


Figure S5. Stationary point structures (IS, TS and FS) for the diffusion of the Cu atom along the step edge on CeO<sub>2</sub>(111). Color scheme: Ce, yellow; surface O, red; subsurface O, coral; Cu, bronze; C, grey.

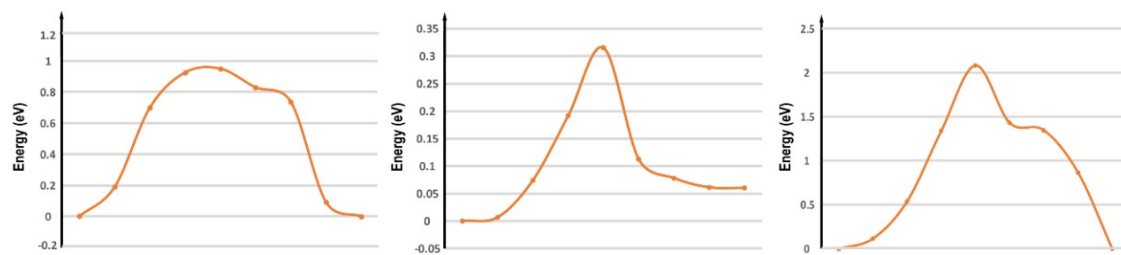
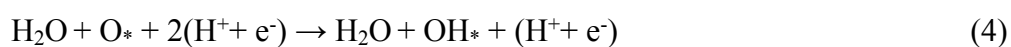
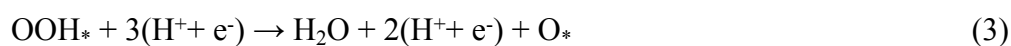


Figure S6. CI-NEB minimal energy paths for migration of single Cu atom on  $\text{CeO}_2(111)$ ,  $\text{CO-Cu}_1$  complex on  $\text{CeO}_2(111)$  and single Cu atom at  $\text{CeO}_2$  step, respectively.

Computational details for ORR on Cu-CeO<sub>2</sub> SAC:

ORR is supposed to take place at the single Cu site following four-electron pathways as below:



The thermochemistry of these electrochemical reaction step was obtained by using DFT calculations in conjunction with SHE model developed by Nørskov and co-workers.<sup>2</sup> The free energy of O<sub>2</sub> was obtained from the free energy change of the reaction  $\text{O}_2 + 2\text{H}_2 \rightarrow 2\text{H}_2\text{O}$  ( $G_{\text{O}_2} = 2G_{\text{H}_2\text{O}} - 2G_{\text{H}_2} + 4.92$ ). The free energy of (H<sup>+</sup> + e<sup>-</sup>) in solution at standard conditions equal to that of hydrogen atom in gaseous H<sub>2</sub> ( $1/2G_{\text{H}_2}$ ).  $\Delta G = \Delta E + \Delta ZPE - T\Delta S$ , which  $\Delta ZPE$  is the difference in zero point energies,  $T$  is the temperature (298.15 K), and  $\Delta S$  is the change in entropy. All of the parameters have been taken from DFT calculations or standard tables for gas-phase molecules. More details can be seen in the work by Nørskov *et al.*<sup>2</sup>

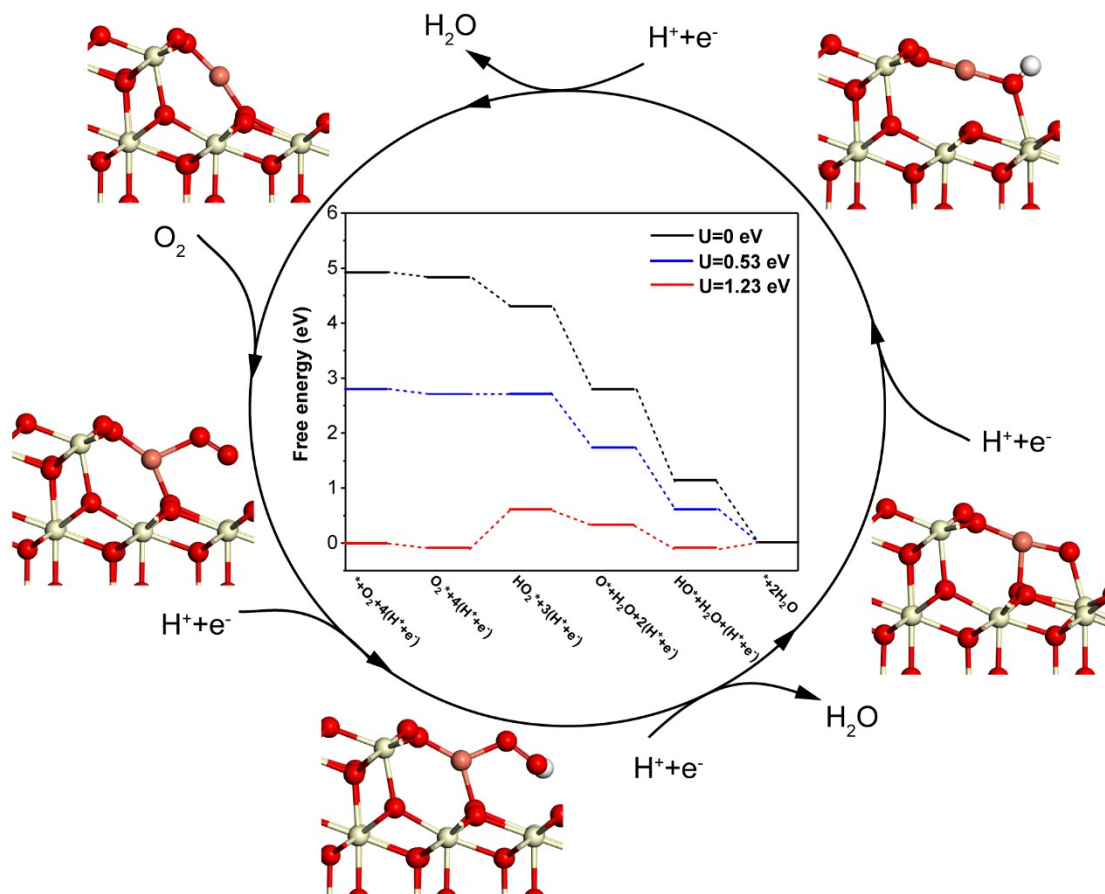


Figure 7. The proposed reaction pathway for complete oxygen reduction reaction (ORR) on the CeO<sub>2</sub>-supported Cu SAC discussed in this work. The inset in cycle (a) shows the free energy diagram for ORR on the Cu SAC catalyst in an acidic medium.

**Reference:**

1. P. Nava *et al.*, *Phys. Chem. Chem. Phys.*, 2003, **5**, 3372–3381.
2. J. K. Nørskov *et al.*, *J. Phys. Chem. B*, 2004, **108**, 17886–17892