Supporting Information:

Electronic Storage Capacity of Ceria: Role of Peroxide in Au_x Supported on CeO_2 (111) Facet and CO adsorption

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The structure or spin density of CeO_2 (111) facet containing single O vacancy is shown Figure S1, two excess electrons are localized at two Ce ions, which is consistent with our previous calculation.[S1]

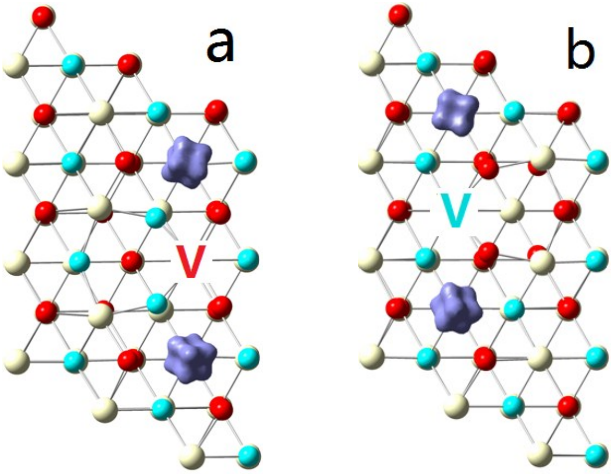


Figure S1. Calculated structures (top view) of the CeO_2 (111) facet containing single O vacancy: (a) top-surface O vacancy, and (b) sub-surface O vacancy. (The isosurface (0.005 e/Å^3) of calculated spin charge densities are in dark blue).

The structures of O_2^{2-} (peroxide) and O_2^- (superoxide) species adsorbed on the CeO_2 (111) facet were studied as the reference.[S1] Peroxide formed by O_2 adsorbing at oxygen vacancy on CeO_2 (111) facet with a single top-surface O vacancy, in which O_2 in the surface oxygen vacancy bind with its neighbor Ce ions, and the O-O bond changed to 1.44Å from 1.21Å in natural O_2 molecular, as shown in Figure S2a, and superoxide resulted from O_2 adsorbed at the second-neighbor Ce^{3+} site on CeO_2 (111) containing single subsurface O vacancy is shown Figure S2b. The charge density difference analysis of these two configurations also was calculated and shown in Figure S2. Like the result predicted by Teng *et al.*,[S2] no electron is located at Ce atom on the surface with peroxide, and one electron is located at Ce atom by bonding with O_2^- on the surface with superoxide. The structure and the charge density difference for CeO_2(111) containing peroxide and an oxygen vacancy ($(PO_2)_1$-V_1) are also calculated and shown in Figure 2Sc. The O-O bond length is 1.44 Å, which is consistent with that on PO_2. And there are two reduced Ce^{3+} ions on the $(PO_2)_1$-V_1 surface.

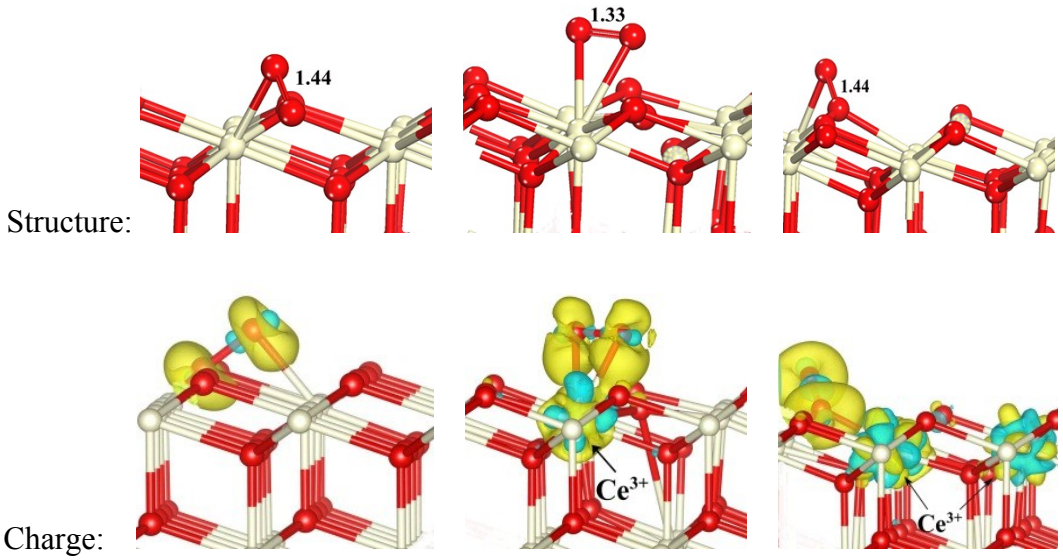
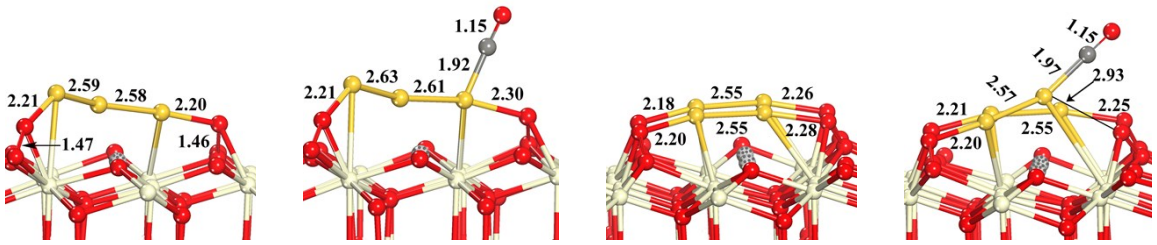


Figure S2. Calculated structures of the CeO_2 (111) facet containing (a) peroxide, (b) superoxide, and (c) peroxide and O vacancy simultaneously, and the corresponding charge density difference. (The isosurface value was set as 0.005 e/Å^3).

Au_3 supported on CeO_2-$(PO_2)_2$-V_1 and Au_4 supported on CeO_2-$(PO_2)_4$-V_2 and corresponding CO adsorption on these Au_x/CeO_2 surfaces were calculated and their structures were displayed in Figure S3. As shown in Figure S3a, when three Au atoms lie linearly on the CeO_2 surface with the central Au atom bound to the O vacancy, it can be anchored by two peroxides. For this configuration, the lengths of two Au−O-peroxide bonds are 2.21Å and 2.20Å respectively. The corresponding adsorption energy of Au_3 cluster on CeO_2 is 2.32 eV. CO can adsorb on the Au_3-$(PO_2)_2$-V_1 surface (Figure S3b) to form a C-Au bond with the bond length of 1.92Å, and the corresponding adsorption energy is 0.43eV. For Au_4-$(PO_2)_4$-V_2 configuration (Figure S3c), all Au atoms lie on the surface with two structures of Au_2-$(PO_2)_2$-V_1-L. The Au_4 adsorption energy is 5.00 eV. CO can chemically adsorb on the supported Au_4 (Au_4-$(PO_2)_4$-V_2) with the adsorption energy of 0.57 eV.



(a) Au_3-$(PO_2)_2$-V_1; (b) CO-Au_3-$(PO_2)_2$-V_1; (c) Au_4-$(PO_2)_4$-V_2; (d) CO-Au_4-$(PO_2)_4$-V_2

Figure S3. Calculated structures of Au_3-$(PO_2)_2$-V_1 and Au_4-$(PO_2)_4$-V_2 and CO oxidation on them.

References

S1. Li, H.-Y.; Wang, H.-F.; Gong, X.-Q.; Guo, Y.-L.; Guo, Y.; Lu, G. Z.; Hu, P. Multiple Configurations of the Two Excess 4f Electrons on Defective CeO_2 (111): Origin and Implication. Phys. Rev. B. 2009, 79 (19), 193401

S2. Zhao, Y.; Teng, B.-T.; Wen, X.-D.; Zhao, Y.; Chen, Q.-P.; Zhao, L.-H.; Luo, M.-F. Superoxide and Peroxide Species on CeO_2 (111), and Their Oxidation Roles. J. Phys. Chem. C 2012, 116, 15986-15991.