Supporting Information:

Electronic Storage Capacity of Ceria: Role of Peroxide in Au\textsubscript{x} Supported on CeO\textsubscript{2} (111) Facet and CO adsorption

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The structure or spin density of CeO\textsubscript{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.\textsuperscript{S1}

**Figure S1.** Calculated structures (top view) of the CeO\textsubscript{2} (111) facet containing single O vacancy: (a) top-surface O vacancy, and (b) sub-surface O vacancy. (The isosurface (0.005 e/Å\textsuperscript{3}) of calculated spin charge densities are in dark blue).
The structures of $\text{O}_2^{2-}$ (peroxide) and $\text{O}_2^-$ (superoxide) species adsorbed on the CeO$_2$ (111) facet were studied as the reference.\textsuperscript{51} Peroxide formed by $\text{O}_2$ adsorbing at oxygen vacancy on CeO$_2$ (111) facet with a single top-surface O vacancy, in which $\text{O}_2$ 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 $\text{O}_2$ 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.,\textsuperscript{52} no electron is located at Ce atom on the surface with peroxide, and one electron is located at Ce atom by bonding with $\text{O}_2^-$ 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.

![Structure: PO$_2$, SO$_2$-SV, PO$_2$-V$_1$](image)

![Charge: PO$_2$, SO$_2$-SV, PO$_2$-V$_1$](image)

**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.

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
