Supplementary Information for

Environmentally Adaptive Gold Single-Atom Catalyst with Variable Valence States

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1. Methodology

Due to insufficient consideration of the interactions between electrons, LDA and GGA are not very suitable for some highly localized and strongly correlated electronic systems, such as metal oxides, rare earth elements, and their compounds. Therefore, the Hubbard parameter U is added to the energy functional of LDA or GGA for correction, known as the DFT+U method. U is the strongly correlated repulsion energy of electrons with opposite spin. The U value in the article can be referred to in the literature: Tuning LDA+U for electron localization and structure at oxygen vacancies in ceria.

2. Supporting Figures (Figures S1-S11)

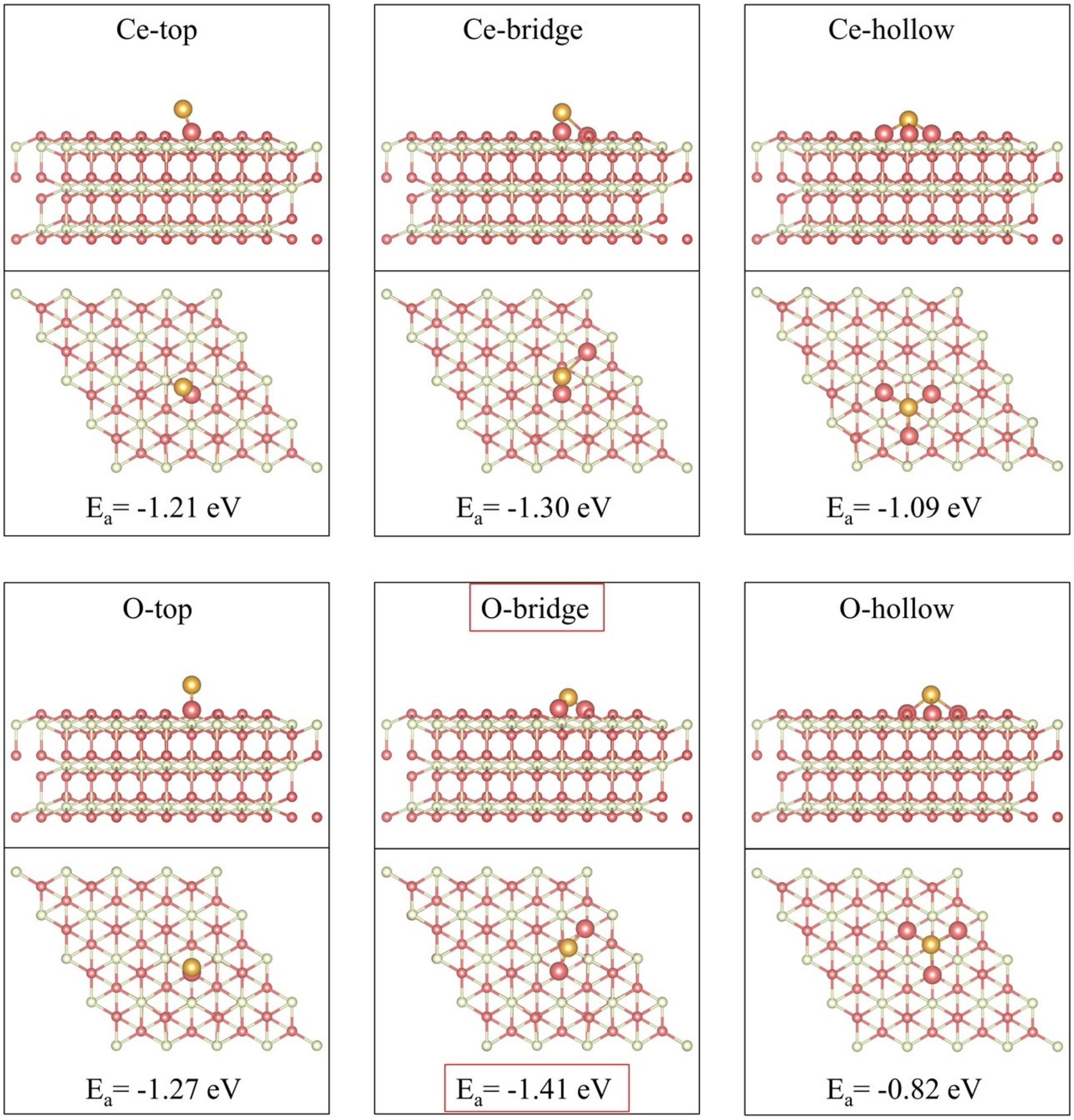

Fig. S1. The adsorption configuration of Au single atom on different high-symmetry adsorption sites CeO_2(111) surface.

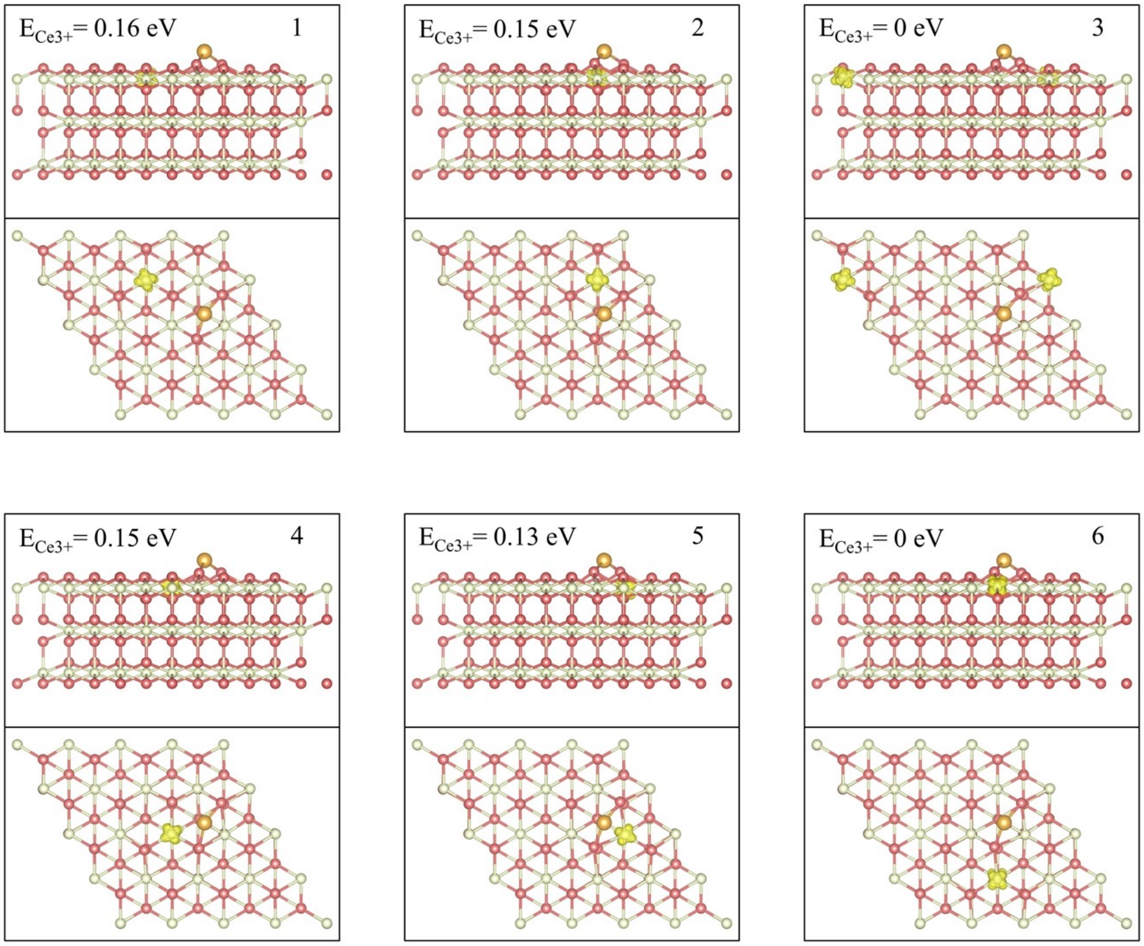

Fig. S2. Different positions of Ce^{3+} when Au atoms adsorb on O-bridge sites. Energies are relative to the most stable configuration.

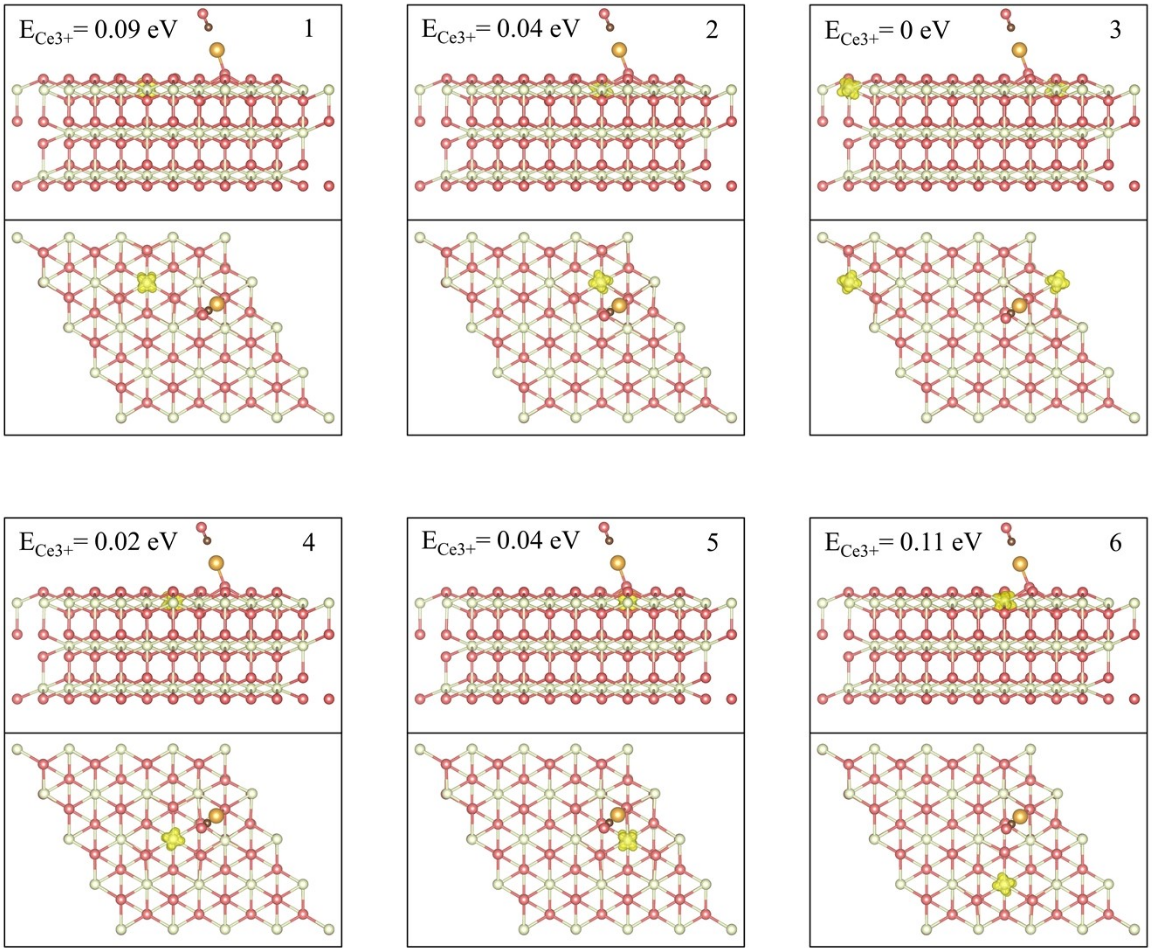

Fig. S3. Different positions of Ce^{3+} after adsorbing CO molecule. Energies are relative to the most stable configuration.

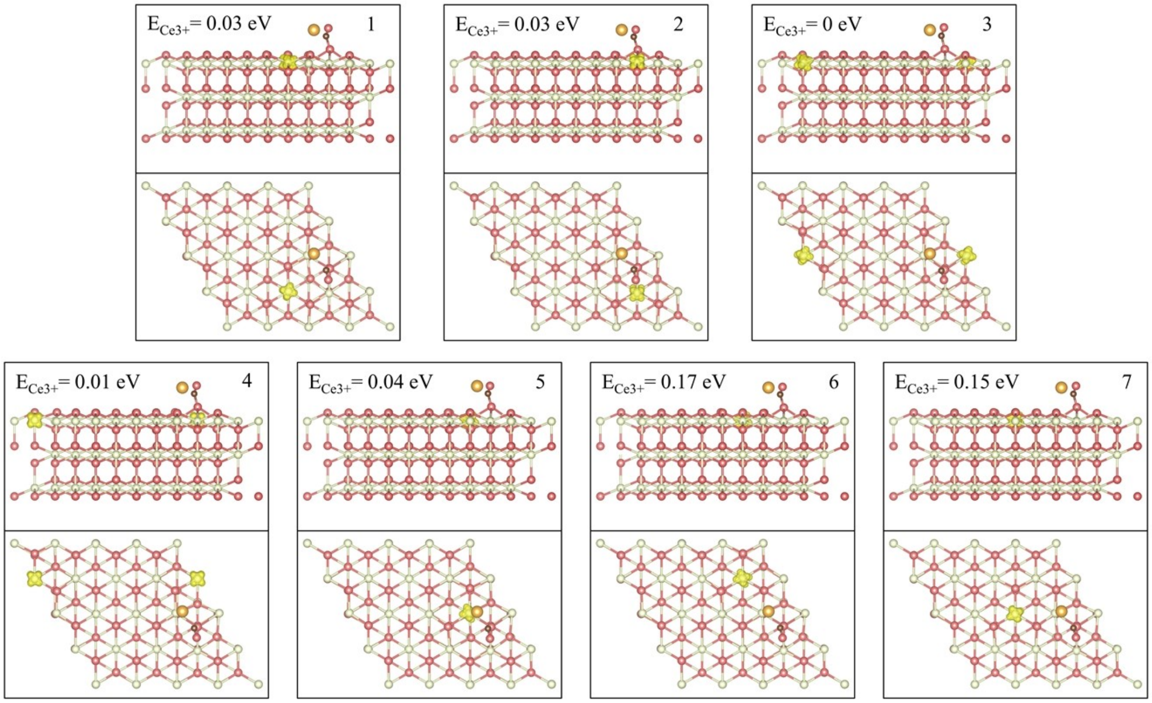

Fig. S4. Different positions of Ce^{3+} during CO adsorption on lattice oxygen. Energies are relative to the most stable configuration.

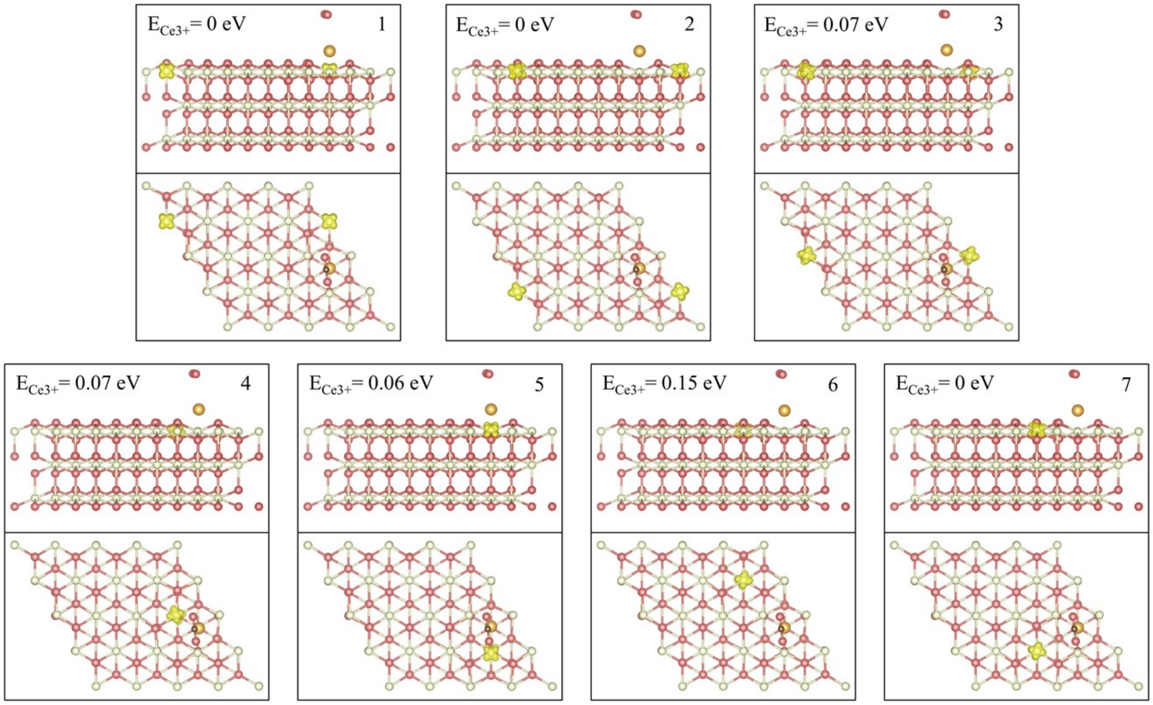

Fig. S5. Different positions of Ce^{3+} after CO is oxidized to CO_2. Energies are relative to the most stable configuration.

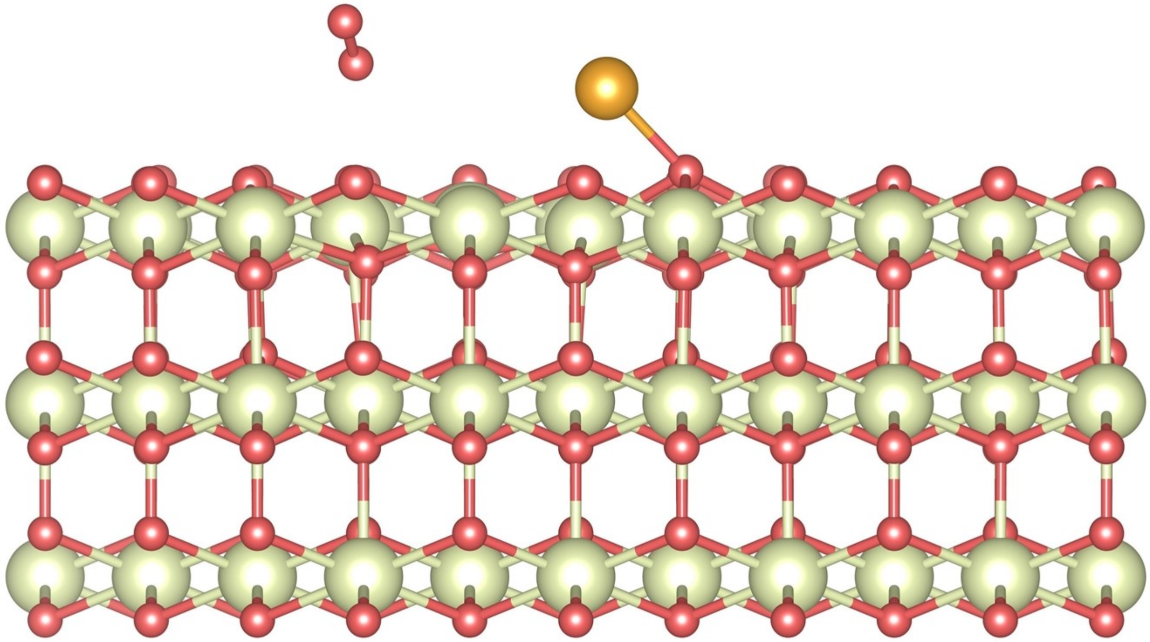

Fig. S6. Transition state configuration when the O_2 molecule filling the oxygen vacancy (O_V), and the reaction barrier is 0.34 eV.

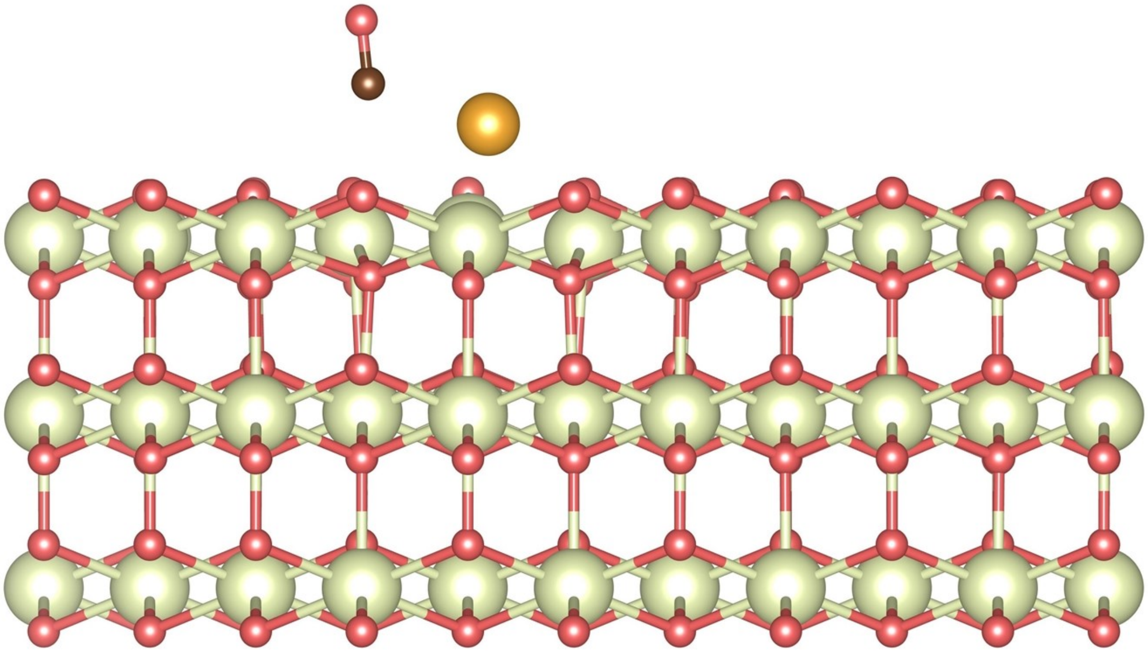

Fig. S7. Adsorption configuration of CO molecules adsorbed on oxygen vacancies under Au atom. The adsorption energy is -0.37 eV, which is substantially higher than the O_2 adsorption energy of -1.42 eV.

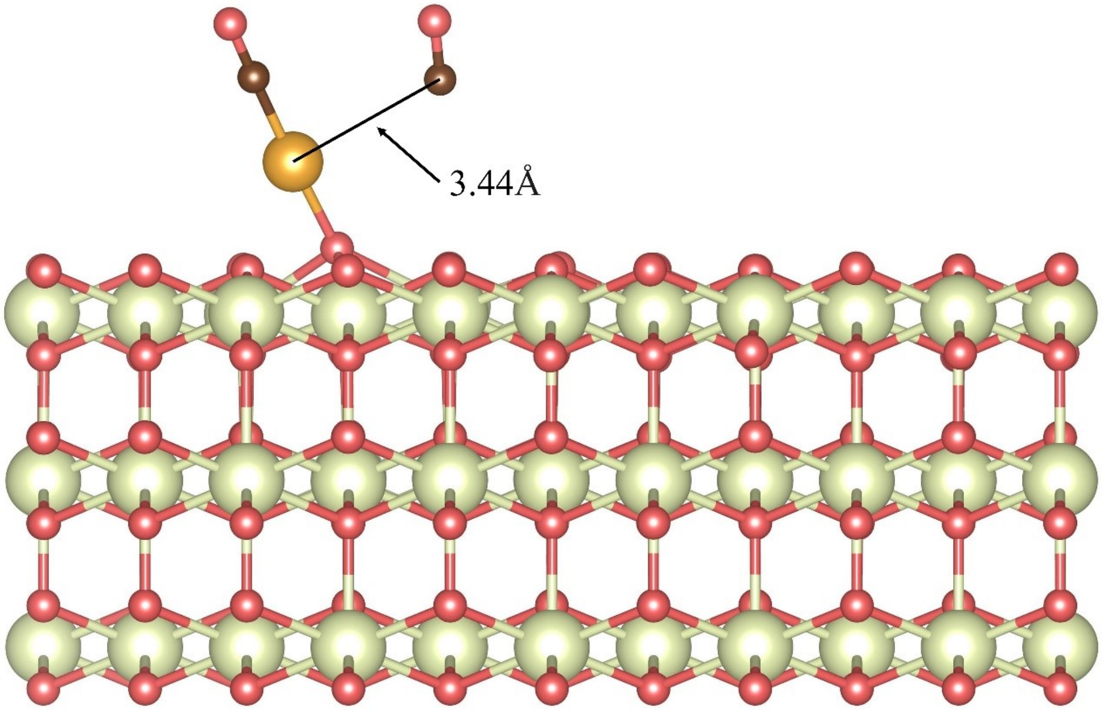

Fig. S8. Adsorption configuration of two CO molecules adsorbed by Au atoms above O_V.

The distance between the second CO molecule and the Au atom increased to 3.44 Å.

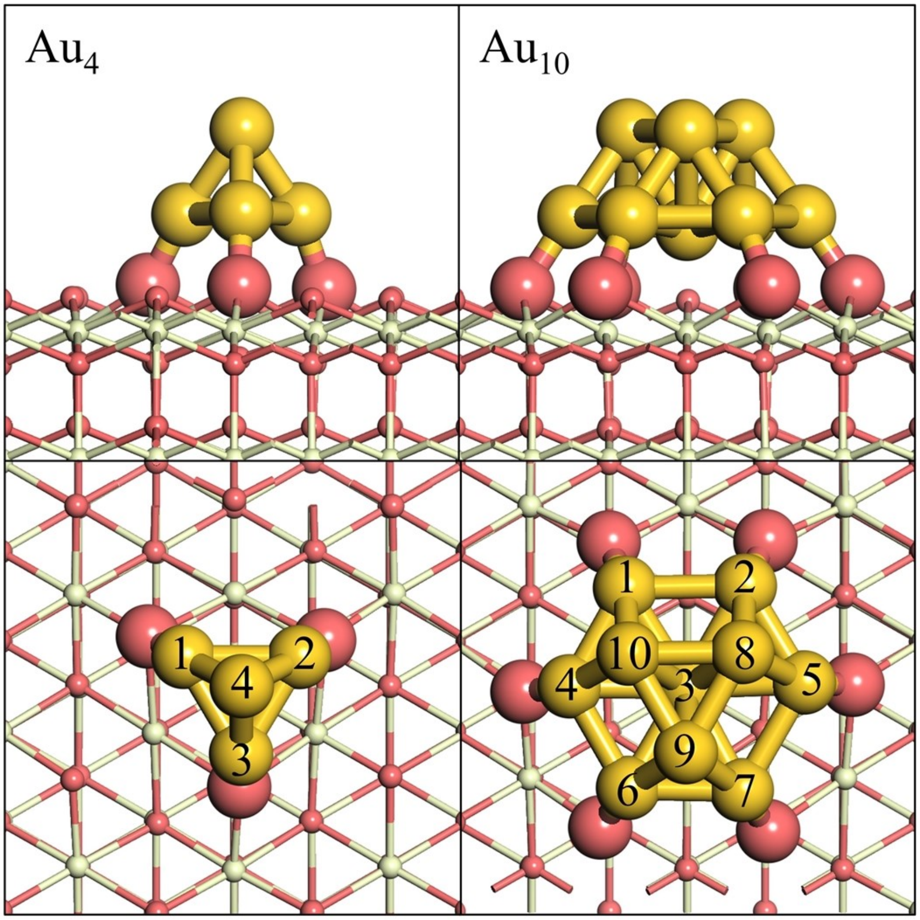

Fig. S9. Configurations of Au$_4$ and Au$_{10}$ cluster.

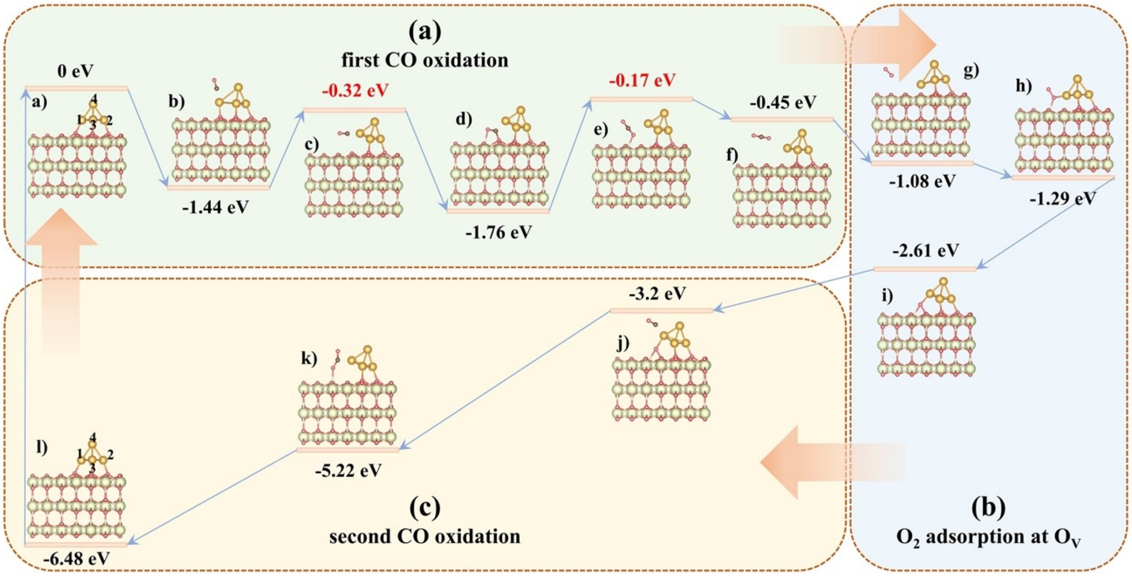

Fig. S10. CO oxidation reaction pathway of $Au_4@CeO_2(111)$ catalyst.

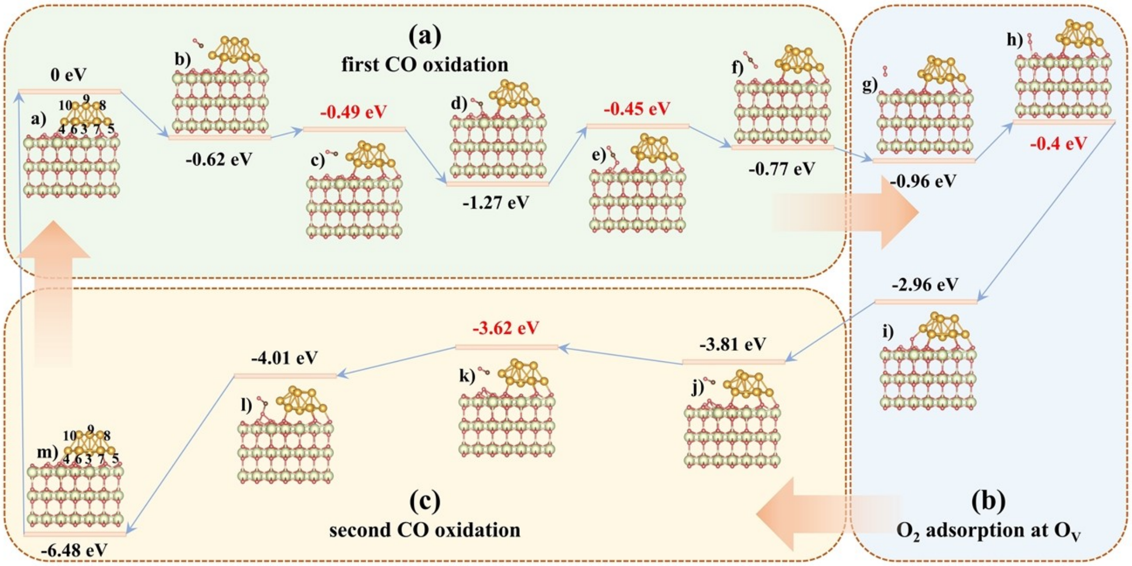

Fig. S11. CO oxidation reaction pathway of $Au_{10}@CeO_2(111)$ catalyst.

3. Supporting Tables (Table S1-S2)

Table S1. Bader charge statistics of Au atoms in each configuration of the Au_4@CeO_2(111) catalyst during CO oxidation reactions.

Au4	a	b	c	d	e	f	g	h	i	j	k	l
1	0.12	0.63	0.2	0.27	-0.02	-0.09	-0.17	0.41	0.63	0.66	-0.15	0.16
2	0.62	0.33	0.75	0.52	0.58	0.09	0.49	0.44	0.53	0.18	0.2	0.66
3	0.13	0.23	0.22	-0.01	-0.02	0.21	0.09	0.4	0.25	0.69	0.37	-0.17
4	0.29	0.01	-0.02	0.03	-0.15	0.11	0	0.03	0	-0.46	0.13	0.37

Table S2. Bader charge statistics of Au atoms in each configuration of the $Au_{10}@CeO_2(111)$ catalyst during CO oxidation reactions.

Au10	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**h**	**i**	**j**	**k**	**l**	**m**
1	**-0.2**	**0.53**	**0.47**	**0.32**	**1.04**	**0.69**	**0.58**	**0.35**	**0.5**	**0.44**	**0.5**	**0.45**	**0.53**
2	**0.05**	**0.39**	**0.02**	**0.25**	**0.03**	**0.13**	**-0.23**	**-0.04**	**0.01**	**0.27**	**0.43**	**0.24**	**0.1**
3	**-0.06**	**-0.41**	**-0.1**	**-0.81**	**-0.38**	**-0.2**	**-0.29**	**0.02**	**-0.08**	**-0.31**	**-0.14**	**-0.2**	**-0.16**
4	**0.7**	**-0.05**	**-0.09**	**0.23**	**-0.09**	**0.2**	**0.3**	**0.37**	**0.24**	**-0.26**	**-0.49**	**-0.39**	**0.1**
5	**0.49**	**0.23**	**0.24**	**0.2**	**0.13**	**0.18**	**0.47**	**0.31**	**0.23**	**0.16**	**0.19**	**0.07**	**0.19**
6	**0.36**	**0.16**	**0.14**	**0.38**	**0.51**	**0.42**	**0.17**	**0.17**	**0.41**	**0.3**	**0.13**	**0.22**	**0.25**
7	**0.27**	**0.16**	**0.3**	**0.14**	**0.31**	**0.1**	**0.49**	**0.51**	**0.41**	**0.33**	**0.31**	**0.26**	**0.18**
8	**0**	**-0.23**	**-0.21**	**0.11**	**0.07**	**-0.05**	**0.19**	**0.2**	**0.07**	**0**	**-0.15**	**-0.08**	**-0.08**
9	**-0.24**	**0.06**	**0.01**	**0.1**	**0.1**	**0.05**	**-0.52**	**-0.67**	**-0.12**	**0.04**	**-0.01**	**0.04**	**0.09**
10	**0.38**	**0.14**	**0.04**	**-0.06**	**-0.17**	**-0.41**	**0.09**	**0.08**	**0.19**	**-0.01**	**0.14**	**-0.04**	**-0.07**