

Supplementary Information:

Oxygen Vacancy Distribution and Electron Localization on Nanocube CeO₂ (100)

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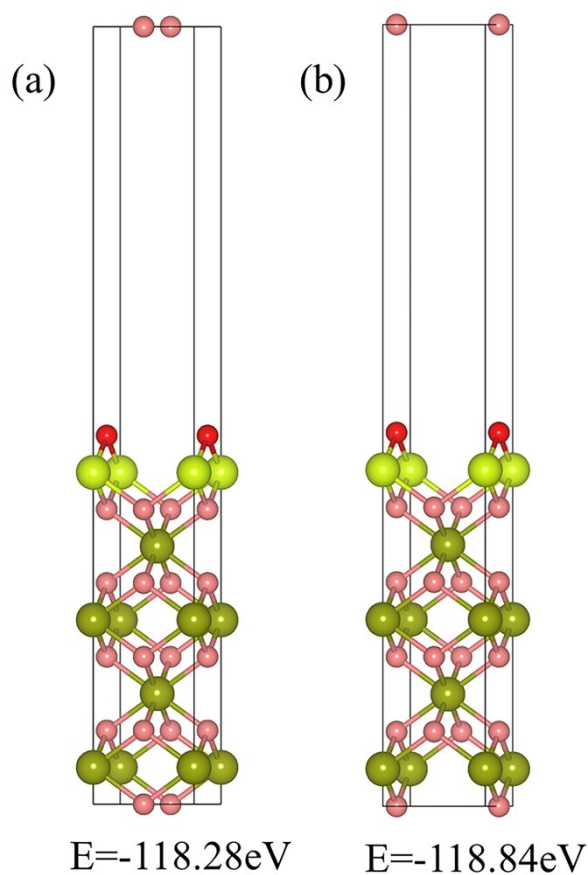


Fig. S1. Surface energy (in eV) for the CeO_2 (100) surface of (a) an asymmetrical and (b) symmetrical slab model. The color coding of atoms at different layers is depicted. Yellow and red balls respectively stand for Ce and surface O atoms.

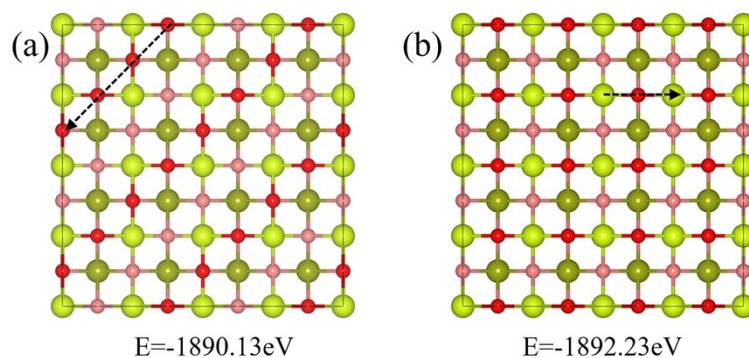


Fig. S2. Surface energy (eV) for the CeO_2 (100) surface about different oxygen vacancy orientation along the (a) $\langle 100 \rangle$ and (b) $\langle 110 \rangle$ directions.

Table S1. Surface energy (in J/m²) with different numbers of Layers (L) for CeO₂(100) surface.

CeO₂(100)			
Layers	11	15	19
E _{surf}	1.516	1.523	1.533

Table S2. Surface energy (in J/m²) for CeO₂(111), (110) and (100) surface.

CeO₂	(111)	(110)	(100)
Layers	12	7	11
E _{surf}	0.751	1.144	1.516

Table S3. Surface energy (in eV) after occupation matrix control of the unique f orbitals containing a single oxygen vacancy (O_{vac}^{sur}) on CeO₂(100) surface.

	f₃	f₂	f₁	f₀	f₁	f₂	f₃
f	fy(3x ² -y ²)	fxyz	fyz ²	fz ³	fxz ²	fz(x ² -y ²)	fx(x ² -3y ²)
E	-1885.92	-1885.98	-1885.83	-1885.91	-1885.96	-1885.86	-1885.95
ΔE	0.06	0	0.15	0.07	0.02	0.12	0.03

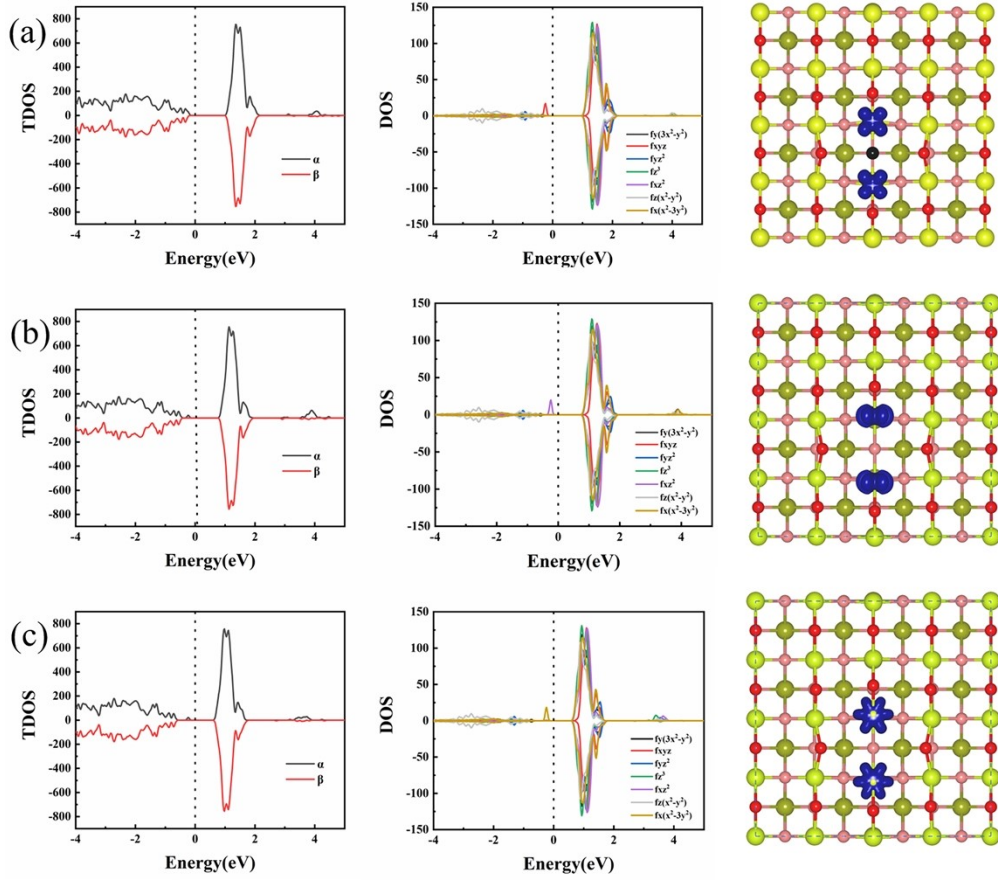


Fig. S3. Electron structures (a) f_2 , (b) f_1 and (c) f_3 orbital after occupation matrix containing a single oxygen vacancy (O_{vac}^{sur}) on $CeO_2(100)$ surface. (left: Total DOS, middle: particle DOS of 4f orbitals of Ce^{3+} ions and right: the isosurface of spin charge densities). The Fermi level is zero at in energy.

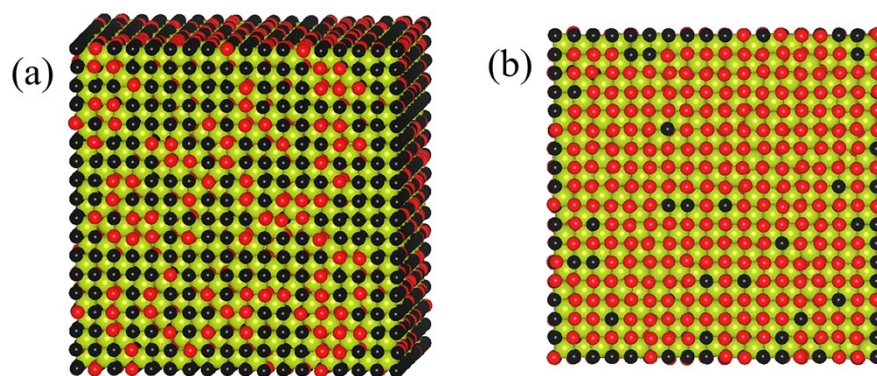


Fig. S4. Distribution of oxygen vacancies (a) the surface and (b) the interior during the Reverse Monte Carlo (RMC) simulation. Yellow and red balls respectively stand for Ce and O atoms and black balls for O vacancies.

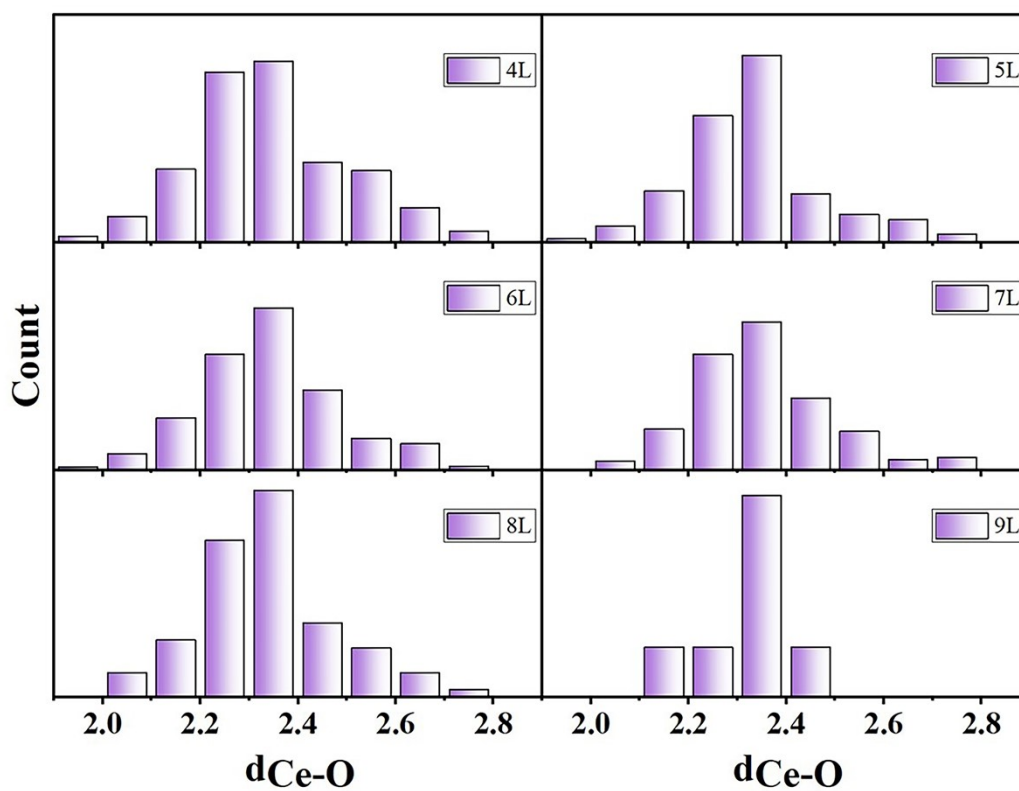


Fig. S5. Pair-distance statistics of Ce-O pairs from the fourth layer surface to the interior.

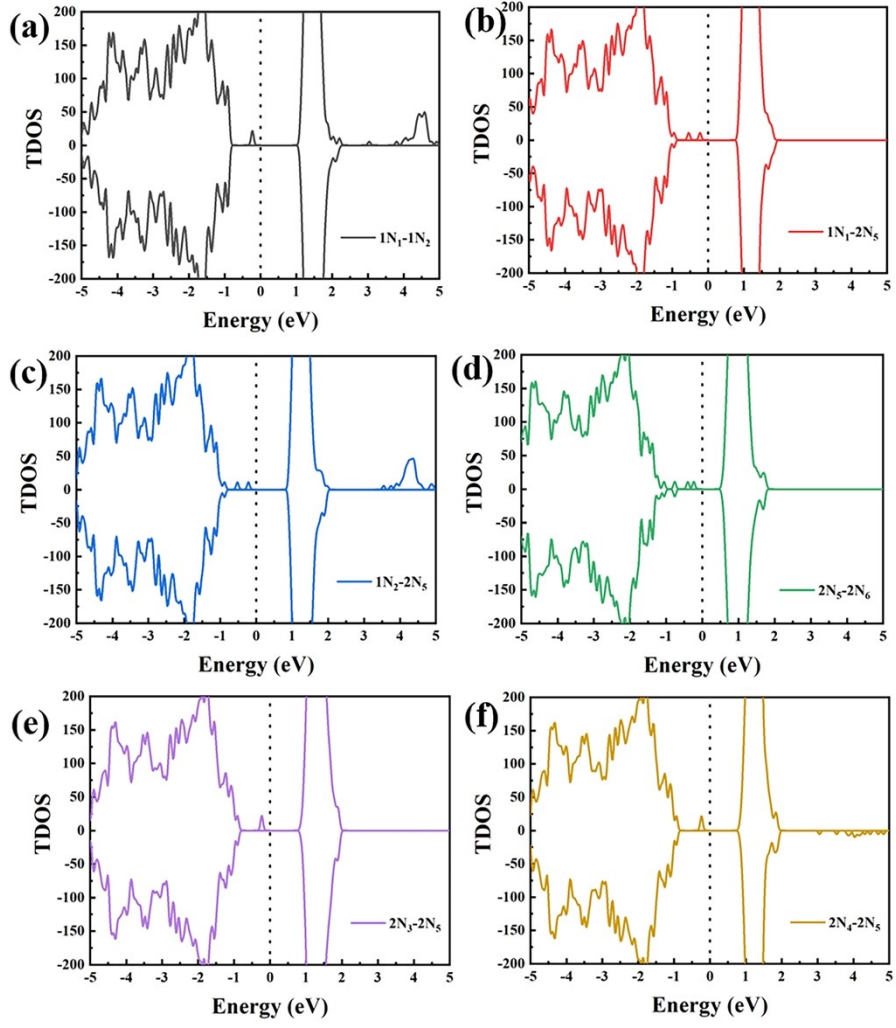


Fig. S6. Total DOS of O_{vac}^{sur} which are localized on the two Ce^{3+} ions neighboring the oxygen vacancy on (a) $1N_1-1N_2$, (b) $1N_1-2N_5$, (c) $1N_2-2N_5$, (d) $2N_5-2N_6$, (e) $2N_3-2N_5$ and (f) $2N_4-2N_5$ on $CeO_2(100)$ surface respectively.

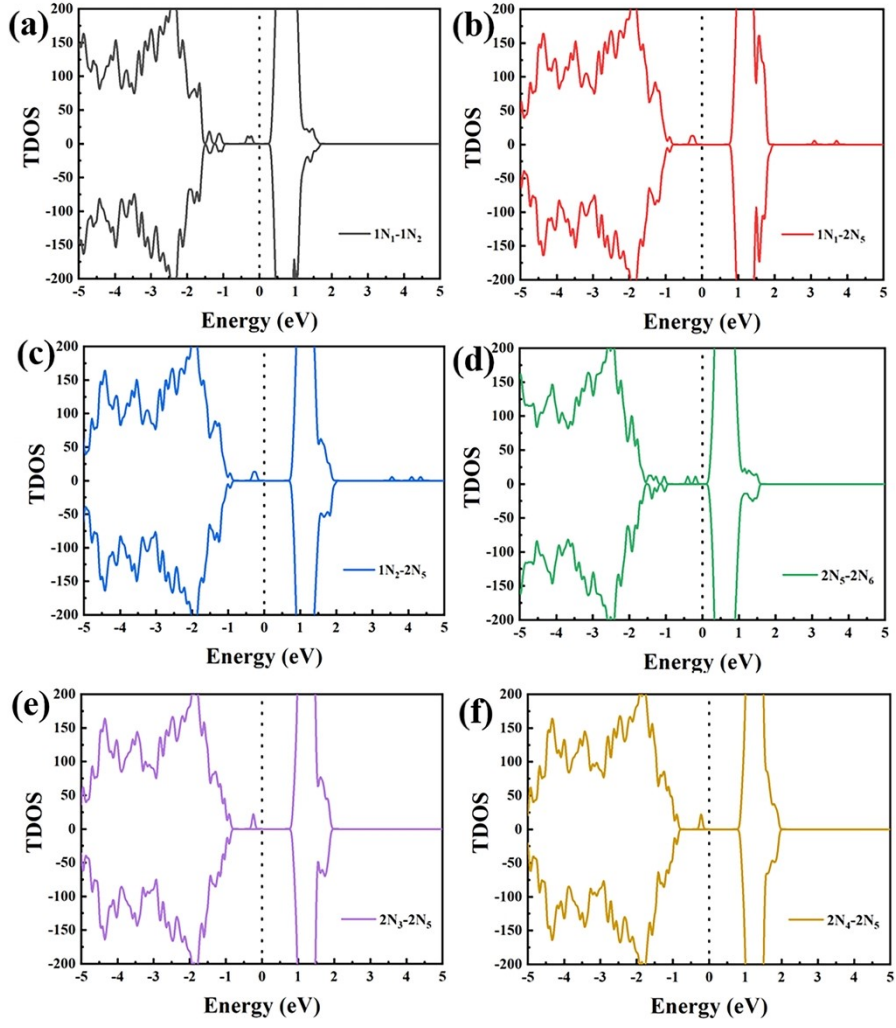


Fig. S7. Total DOS of O_{vac}^{sub1} which are localized on the two Ce^{3+} ions neighboring the oxygen vacancy on (a) $1N_1-1N_2$, (b) $1N_1-2N_5$, (c) $1N_2-2N_5$, (d) N_5-2N_6 , (e) $2N_3-2N_5$ and (f) $2N_4-2N_5$ on $CeO_2(100)$ surface respectively.

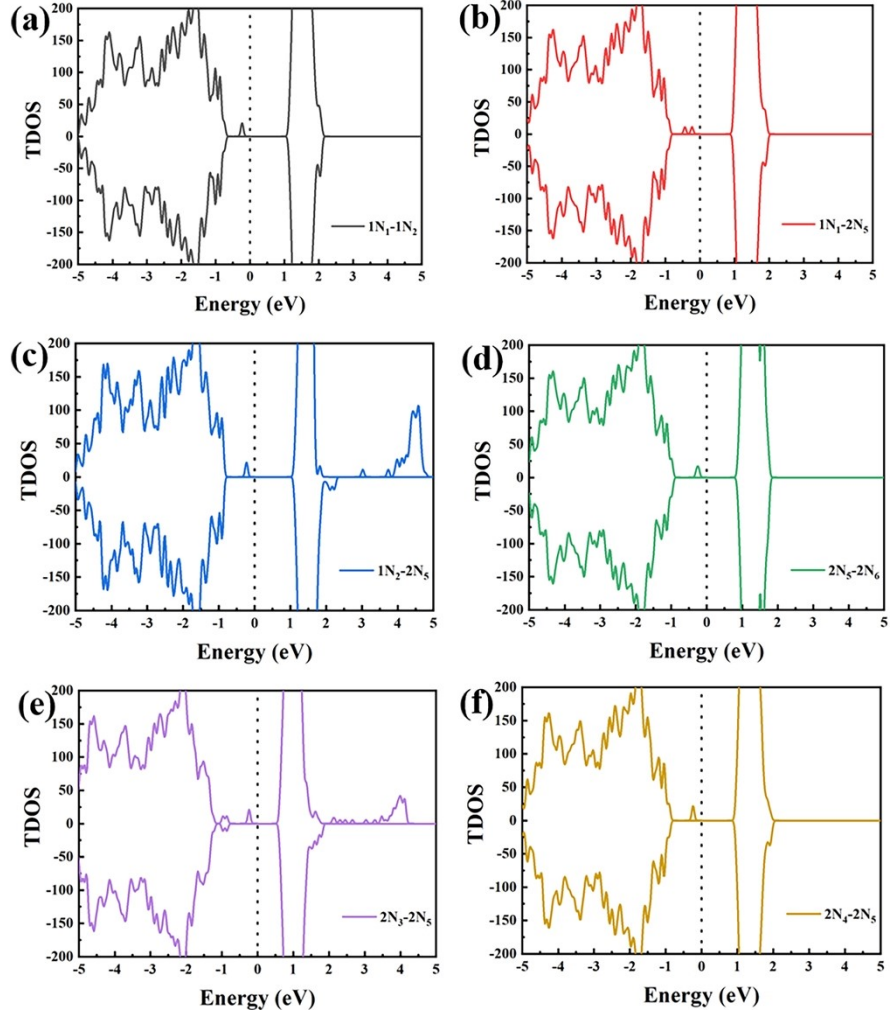


Fig. S8. Total DOS of O_{vac}^{sub2} which are localized on the two Ce^{3+} ions neighboring the oxygen vacancy on (a) $1N_1-1N_2$, (b) $1N_1-2N_5$, (c) $1N_2-2N_5$, (d) N_5-2N_6 , (e) $2N_3-2N_5$ and (f) $2N_4-2N_5$ on $CeO_2(100)$ surface respectively.

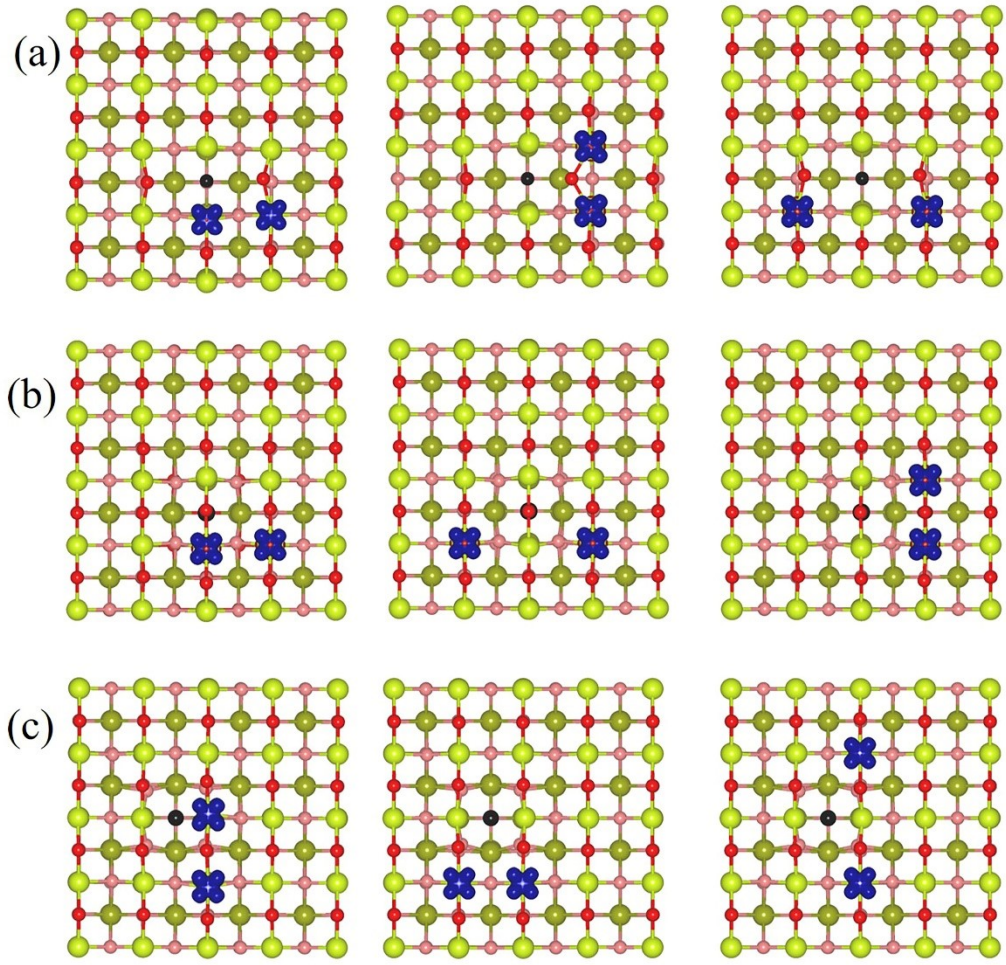


Fig. S9. Calculated structures of the CeO_2 (100) surface (top view) containing single (a) surface (O_{vac}^{sur}) (b) subsurface1 (O_{vac}^{sub1}) and (c) subsurface2 (O_{vac}^{sub2}) oxygen vacancy. The isosurface of spin charge densities are blue, which are localized on the two Ce ions neighboring the oxygen vacancy on $1N_1$ - $2N_5$ (left panel), $2N_5$ - $2N_6$ (middle panel) and $2N_3$ - $2N_5$ (right panel) respectively.