Electronic Supplementary Information

for

Simultaneous Enzyme Mimicking and Chemical Reduction Mechanisms for Nanoceria as Bio-Antioxidants: A Catalytic Model Bridging Computations and Experiments for Nanozymes

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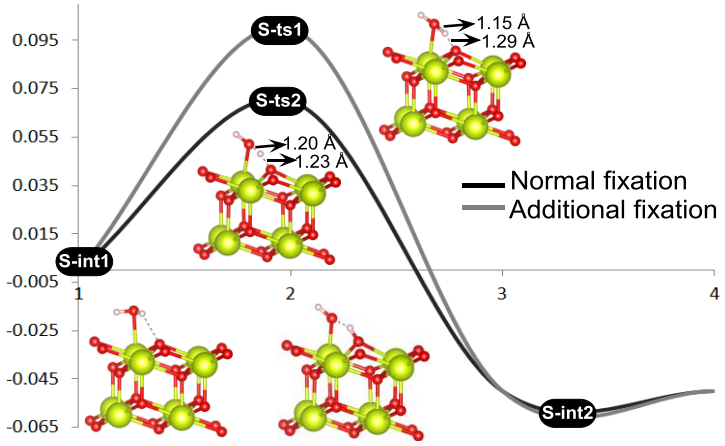

Figure S1. Energy profiles for the dissociative adsorption of H_2O on CeO_2 (111) surface with the transition states calculated by two atom fixation schemes. In the normal fixation scheme, the top six-layer atoms of ceria as well as adsorbate atoms were allowed to relax; the bottom three-layer atoms and lattice parameters of ceria were frozen. In the additional fixation scheme, only adsorbate atoms were allowed to relax. The energy unit is eV.

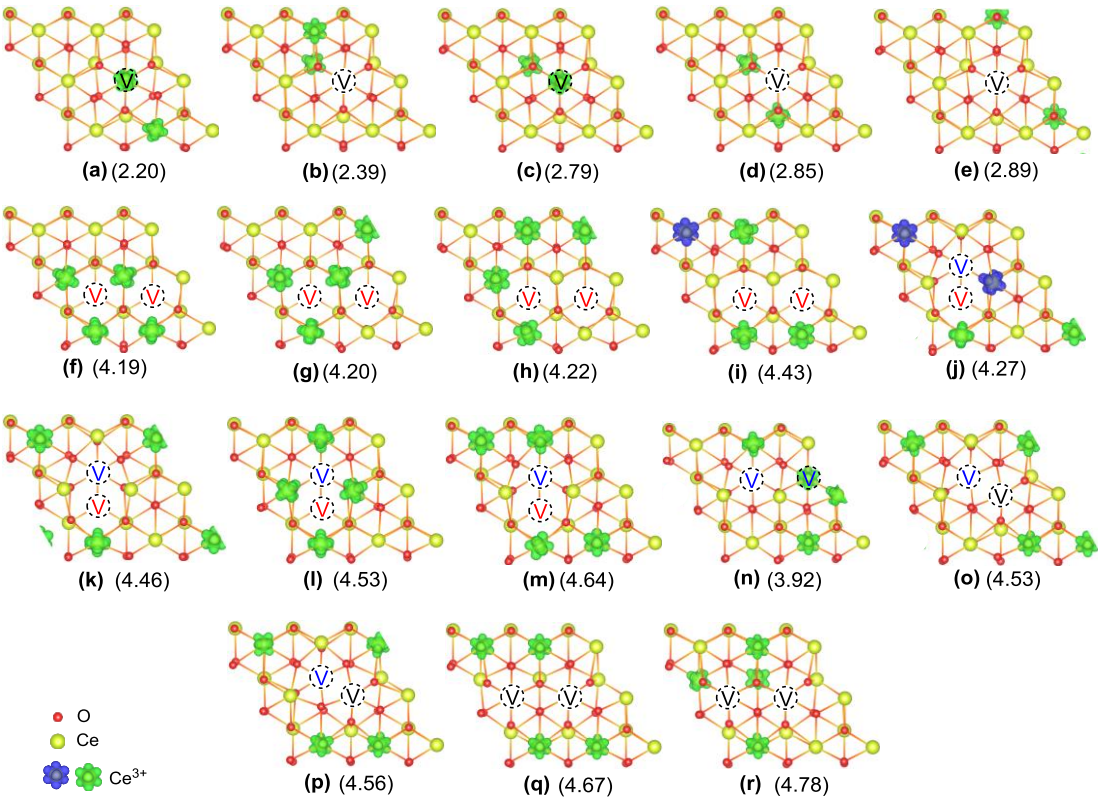

Figure S2. Spin density distribution CeO_2 (111) containing single or double O_v: (a-e) O_{3c}, (f-i) $O_{1a,1f}$, (j-m) $O_{1a,2b}$, (n) $O_{2b,2d}$, (o, p) $O_{2b,3c}$, (q, r) $O_{3c,3e}$. The corresponding O_v formation energies (in eV) are marked in the parentheses. The isosurfaces (0.2 e/Å^3) of spin-up and spin-down charge densities are in green and purple, respectively. The dotted circles represent O_v.

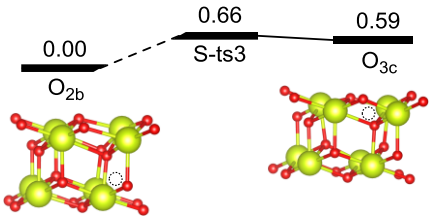

Figure S3. The energy profile of transformation between O_{2b} and O_{3c}. The energy unit is eV.

Table S1. Redox potentials for ceria structures with or without oxygen vacancies, derived from their calculated electronic band structures.

structures[a]	φ_1 [b]	φ_2 [c]
CeO_2	1.72	−0.50
$O_{1a,1f}$	0.25	−0.80
$O_{1a,2b}$	0.34	−0.77
$O_{2b,2d}$	0.39	−0.69
$O_{3c,3e}$	0.42	−0.51
$O_{2b,3c}$	0.50	−0.59
O_{1a}	0.66	−0.63
O_{2b}	0.68	−0.67
O_{3c}	0.75	−0.46

[a] For structures, see Figure 2 and Figure 3; [b] ceria as the electron donors, for which φ_1 correspond to the energies of the HOMOs; [c] ceria as electron acceptors, for which φ_2 correspond to the energies of the LUMOs.

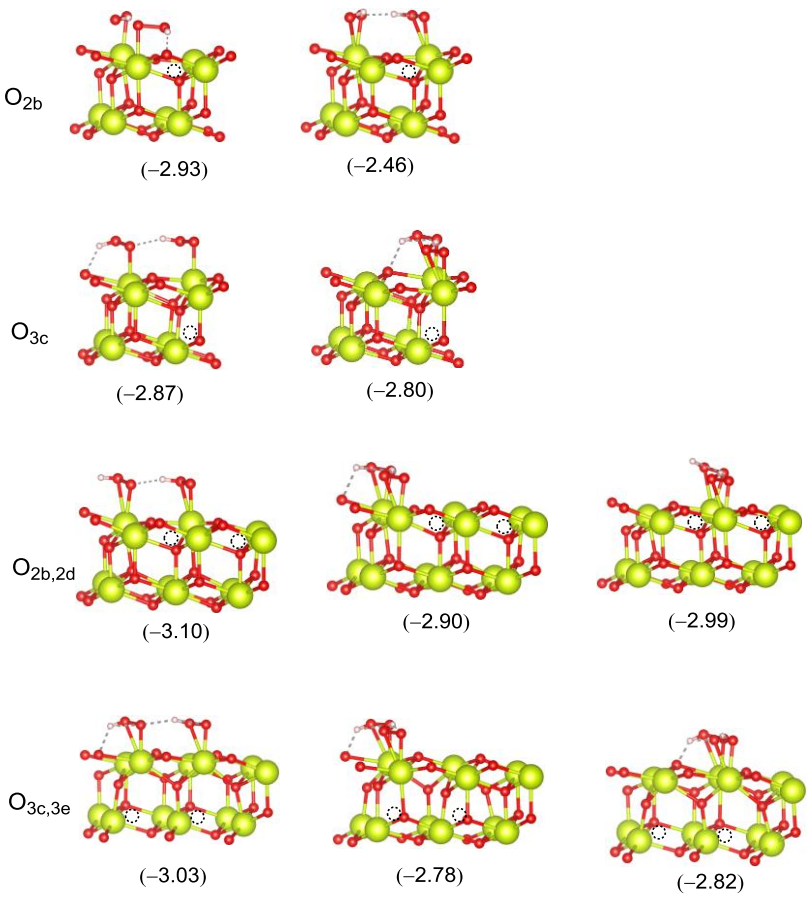

Figure S4. The optimized structures for ceria with two adsorbed $HO_2^{\bullet}$ radicals with different adsorption positions; the adsorption energies are given in the parentheses. The energy unit is eV.

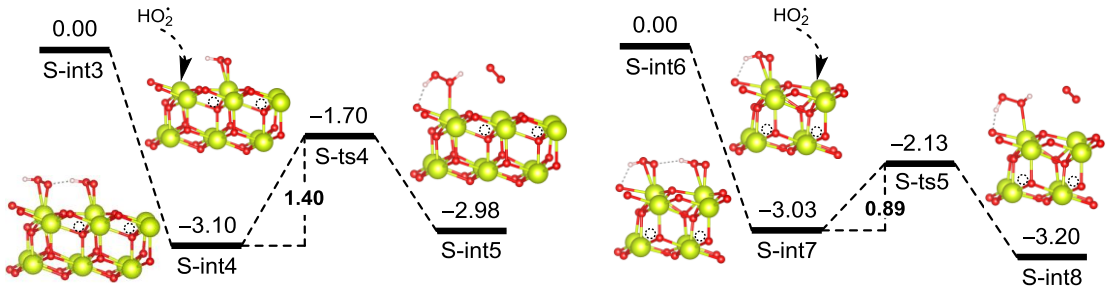

Figure S5. The energy profiles for the SOD mimetic mechanisms of $O_{2b,2d}$ and $O_{3c,3e}$. The energy unit is eV.

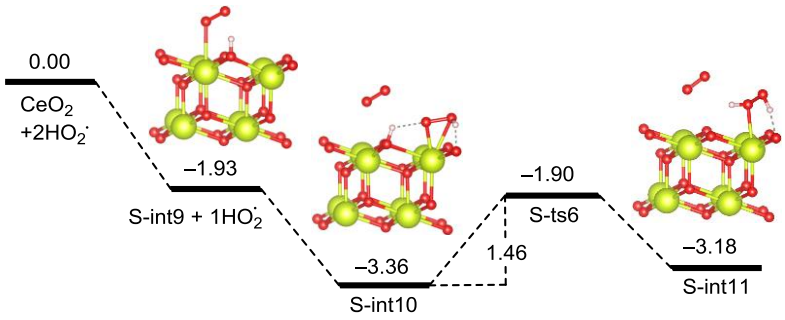

Figure S6. The energy profiles for the SOD mimetic mechanism of CeO_2 (111). The energy unit is eV.

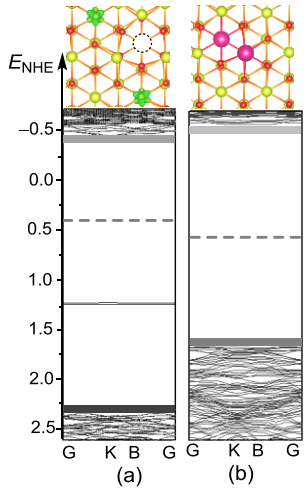

Figure S7. Electronic structures for O_{2b} (a) and O_{2b} with two Ce atoms substituted by Sm (b). In (b), the two SDSs disappear after the Sm substitutions.

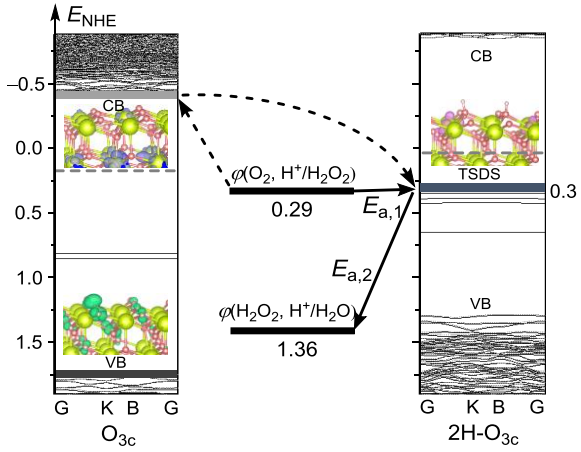

Figure S8. Electronic band structures for O_{3c} and intermediate 2H-O_{3c}. E_{TSDS} of 2H-O_{3c} is not located in between $\varphi(O_2, H^+/H_2O_2)$ and $\varphi(H_2O_2, H^+/H_2O)$, in agreement with that reduced nanoceria has poor CAT mimetic activity.