Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Enhanced oxygen evolution reaction on 2D CoOOH via strain engineering: an insightful view from spin state transition

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1. Supplementary Methods

Calculation of Gibbs free energy. Following the Nørskov's model[1], the changes of Gibbs free energy for nucleophilic attack of hydroxide and intramolecular coupling mechanism in the water oxidation were calculated by following equations:

(a) The nucleophilic attack of hydroxide mechanism

Starting from A site:

$$\Delta G1 = G(*O) - G(*OH) - G(H_2O) + 1/2G(H_2) - eU + k_BT \ln(10)*pH \quad (s1)$$

$$\Delta G2 = G(*OOH) - G(*O) - G(H_2O) + 1/2G(H_2) - eU + k_BT \ln(10)*pH \quad (s2)$$

$$\Delta G3 = G(*OO) - G(*OOH) + 1/2G(H_2) - eU + k_BT \ln(10)*pH \quad (s3)$$

$$\Delta G4 = G(O_2) + G(*) - G(*OO) \quad (s4)$$

$$\Delta G5 = G(*OH) - G(*) - G(H_2O) + 1/2G(H_2) - eU + k_BT \ln(10)*pH \quad (s5)$$

Starting from B site:

$$\Delta G1 = G(*OOH) - G(*O) - G(H_2O) + 1/2G(H_2) - eU + k_BT \ln(10)*pH \quad (s6)$$

$$\Delta G2 = G(*OO) - G(*OOH) + 1/2G(H_2) - eU + k_BT \ln(10)*pH \quad (s7)$$

$$\Delta G3 = G(O_2) + G(*) - G(*OO) \quad (s8)$$

$$\Delta G4 = G(*OH) - G(*) - G(H_2O) + 1/2G(H_2) - eU + k_BT \ln(10)*pH \quad (s9)$$

$\Delta G5 = G(*O) - G(*OH) - G(H_2O) + 1/2G(H_2) - eU + k_BT \ln(10)*pH$ (s10)

where * denotes an active site on the catalyst surface.

(b) The intramolecular coupling mechanism

$\Delta G1 = G(*O*O) - G(*OH*O) + 1/2G(H_2) - eU + k_BT \ln(10)*pH$ (s11)

$\Delta G2 = G(**OO) - G(*O*O)$ (s12)

$\Delta G3 = G(O_2) + G(**) - G(**OO)$ (s13)

$\Delta G4 = G(*OH*) - G(**) - G(H_2O) + 1/2G(H_2) - eU + k_BT \ln(10)*pH$ (s14)

$\Delta G5 = G(*OH*OH) - G(*OH*) - G(H_2O) + 1/2G(H_2) - eU + k_BT \ln(10)*pH$ (s15)

$\Delta G6 = G(*OH*O) - G(*OH*OH) + 1/2G(H_2) - eU + k_BT \ln(10)*pH$ (s16)

where * *denotes two active sites on the catalyst surface.

Calculation on adsorption energy. The adsorption energies of each intermediates were calculated as following:

$\Delta E_{ads}(OH) = E(*OH) + 1/2E(H_2) – E(*) - E(H_2O)$ (s17)

$\Delta E_{ads}(O) = E(*O) + E(H_2) – E(*) - E(H_2O)$ (s18)

$\Delta E_{ads}(OOH) = E(*OOH) + 3/2E(H_2) – E(*) - 2E(H_2O)$ (s19)

$\Delta E_{ads}(O_2) = E(*O_2) – E(*) - E(O_2)$ (s20)

$\Delta E_{ads}(H_2O) = E(*H_2O) – E(*) - E(H_2O)$ (s21)

where E(*) is the total energy of the pristine catalyst surface and $E(H_2O)$ and $E(H_2)$ are the total energies of gas phase water and hydrogen, respectively.

2. Supplementary Tables

Table S1. The Gibbs free energy are calculated by $G = E_{DFT} + ZPE + \Delta U^{0\rightarrow T} + PV – TS$. Where E_{DFT} is energy from density functional theory calculation; Zero point energy (ZPE) corrections, internal enthalpy($\Delta U^{0\rightarrow T}$) and entropy contributions (TS) to the free energies are calculated at 298.15K by vaspkit software[2]. H_2O and H_2 were calculated at 0.035 and 1 bar. The PV term was deleted for the adsorbed intermediates. The Gibbs free energy of gaseous oxygen was calculated by enforcing the total standard Gibbs free energy change during OER at room temperature to be 4.92 eV per oxygen molecule released[3,4]:$G(O_2) = 4.92\ eV + 2G(H_2O) - 2G(H_2)$;

Species	E_{DFT}(eV)	ZPE(eV)	$\Delta U^{0\rightarrow T}$ (eV)	TS(eV)	G_{corr}(eV)	G(eV)
$H_2O(l)$	-14.22	0.57	0.08	0.67	0.00	-14.22
$H_2(g)$	-6.76	0.28	0.06	0.40	-0.04	-6.80
$O_2(g)$	-	-	-	-	-	-9.92
*O	-	0.07	0.03	0.04	0.06	-
*OH	-	0.37	0.04	0.06	0.35	-
*OO	-	0.14	0.08	0.18	0.04	-
*OOH	-	0.46	0.08	0.14	0.40	-

Table S2. The calculated adsorption energies for relevant species during OER.

E_{ads}(eV)	HS	LS
*OH	0.64	-1.47
*O	2.18	0.14
*OOH	3.92	1.84
*OO	-0.13	-1.44

3. Supplementary Figures

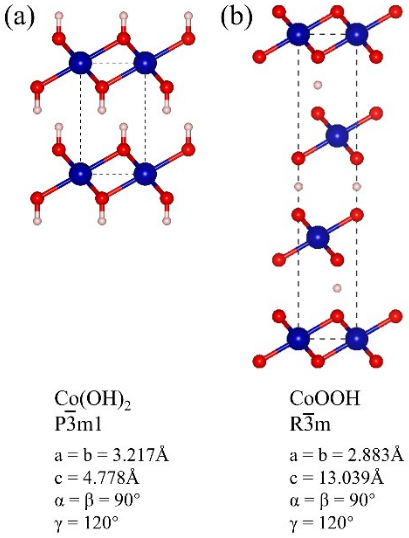


Figure S1 The structure of bulk (a) $Co(OH)_2$ and (b) CoOOH.

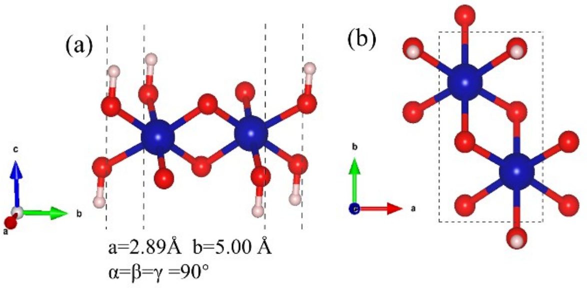


Figure S2 The top and side views of the unit cell of ground state 2D CoOOH.

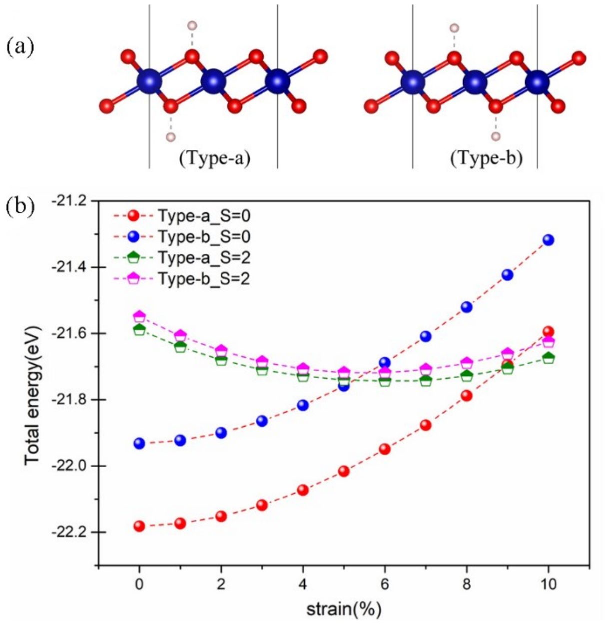


Figure S3 (a) Two possible structures of 2D CoOOH. (b) The total energies per unit cell for the two CoOOH at low spin state (S=0) and high spin state (S=2), respectively, versus strain. The type-a always has lower total energy than type-b, which is considered on our discussion.

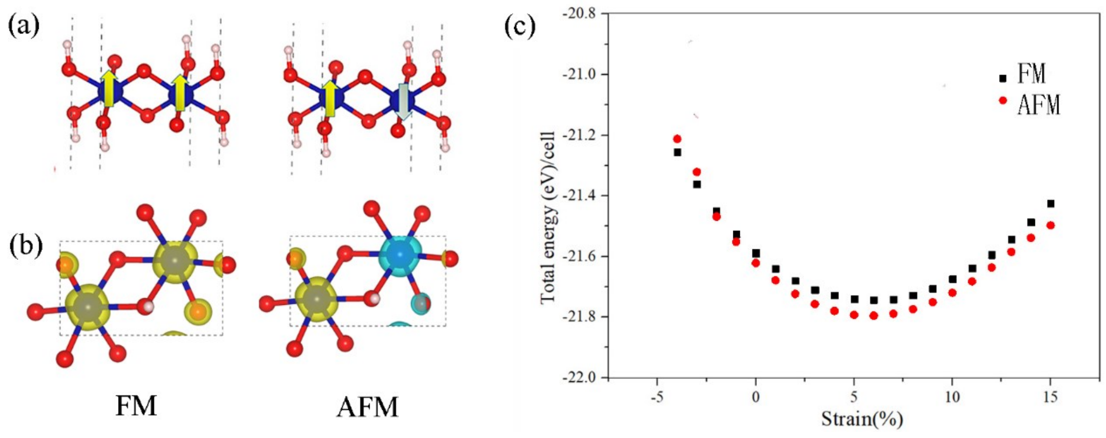
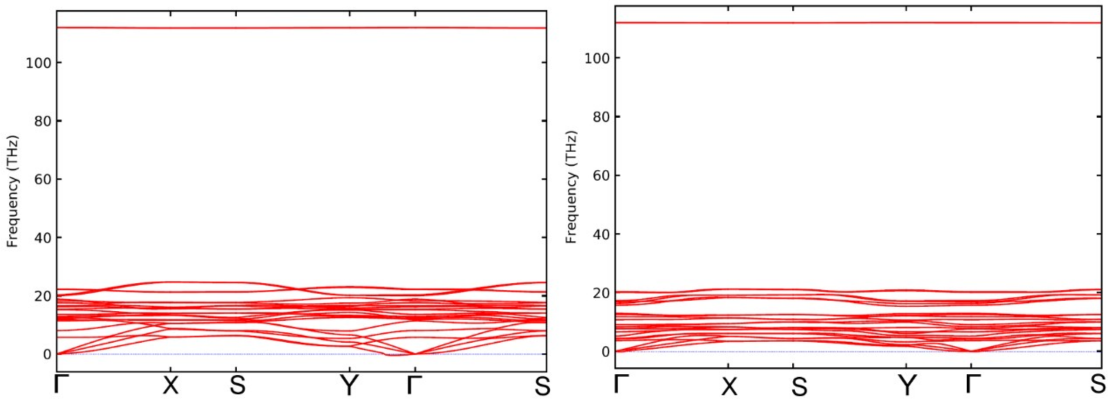


Figure S4 (a) Schematic pictures of two magnetic orderings: FM and AFM. (b)Top view of the spin density isosurfaces at the value of 0.05 e/Å^3 for AM and AFM magnetic orderings. (c) The total energies of FM and AFM states versus strain. The AFM magnetic ordering has the lower total energy as ε increases from 0 to 15%. Therefore, we set to the AFM magnetic ordering in our calculation.



(a)Strain=0 (b)Strain=9%

Figure S5 The phonon spectra of CoOOH at (a) ε = 0 and (b) ε = 9%.

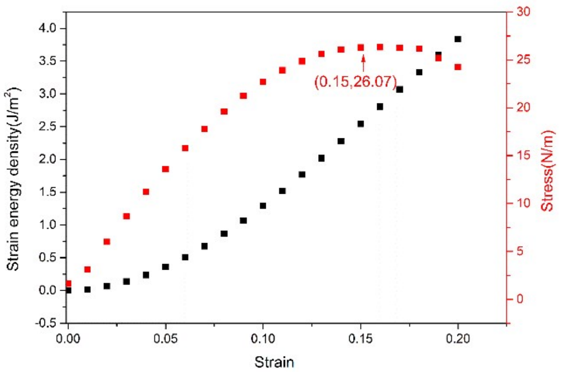


Figure S6 Strain energy density (black) under biaxial strain and the stress–strain response(red).

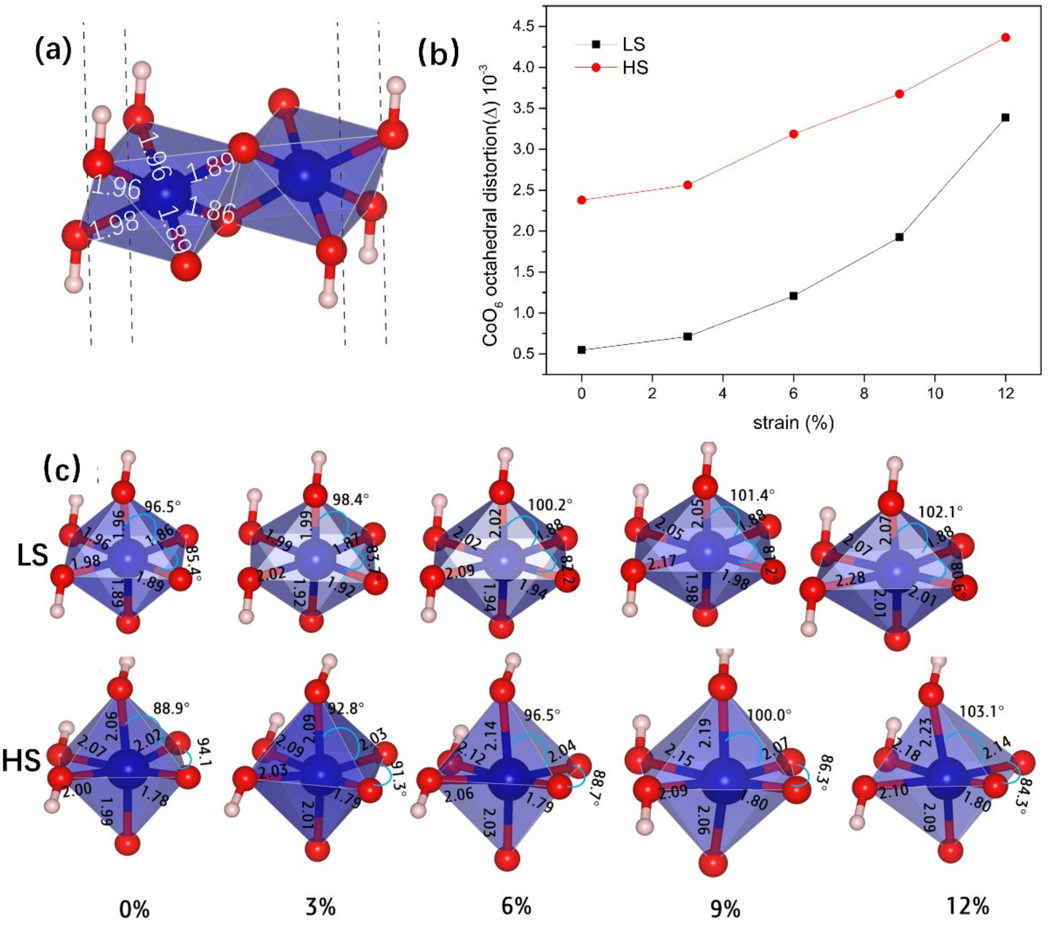


Figure S7 (a) The structure of ground state CoOOH, (b) the CoO_6 distortion (Δ) in octahedral, and (c) the Co-O bond structure in CoO_6 octahedral with different strains for LS and HS CoOOH.

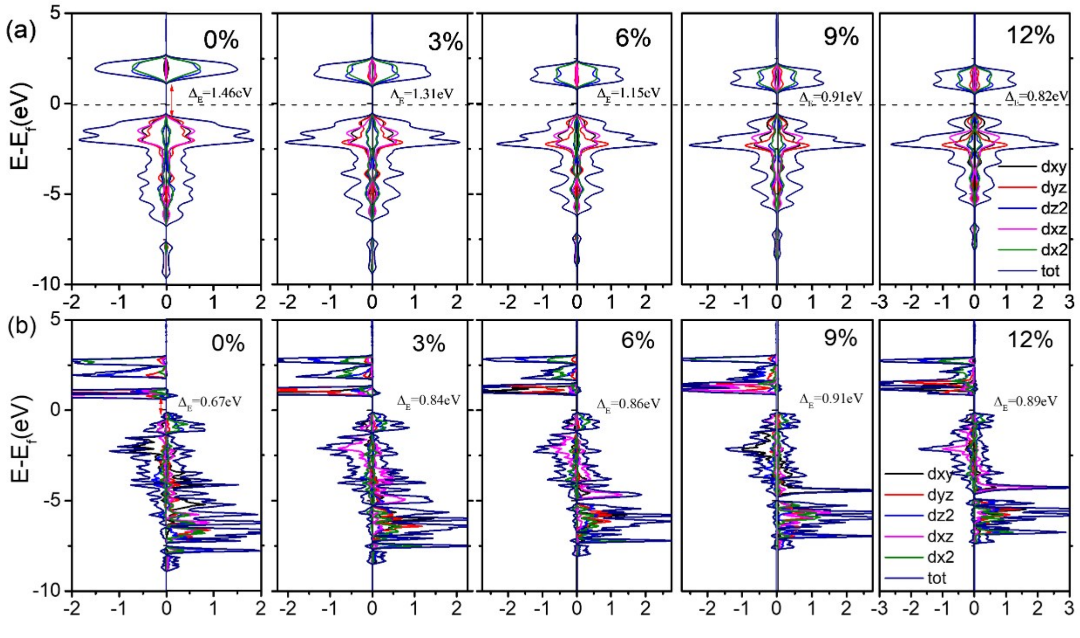


Figure S8 The PDOSs of Co_3d orbitals under strain of 0 ~ 12 % for (a) LS and (b)HS CoOOH.

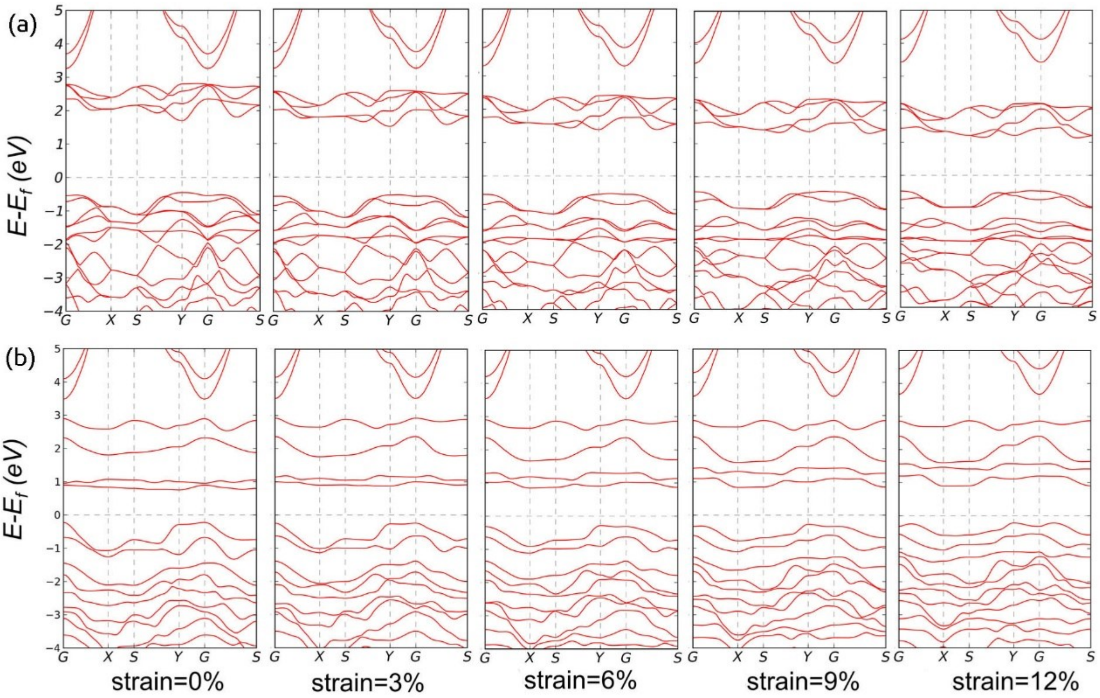


Figure S9 The band structure of CoOOH under strain at: (a) LS and (b) HS.

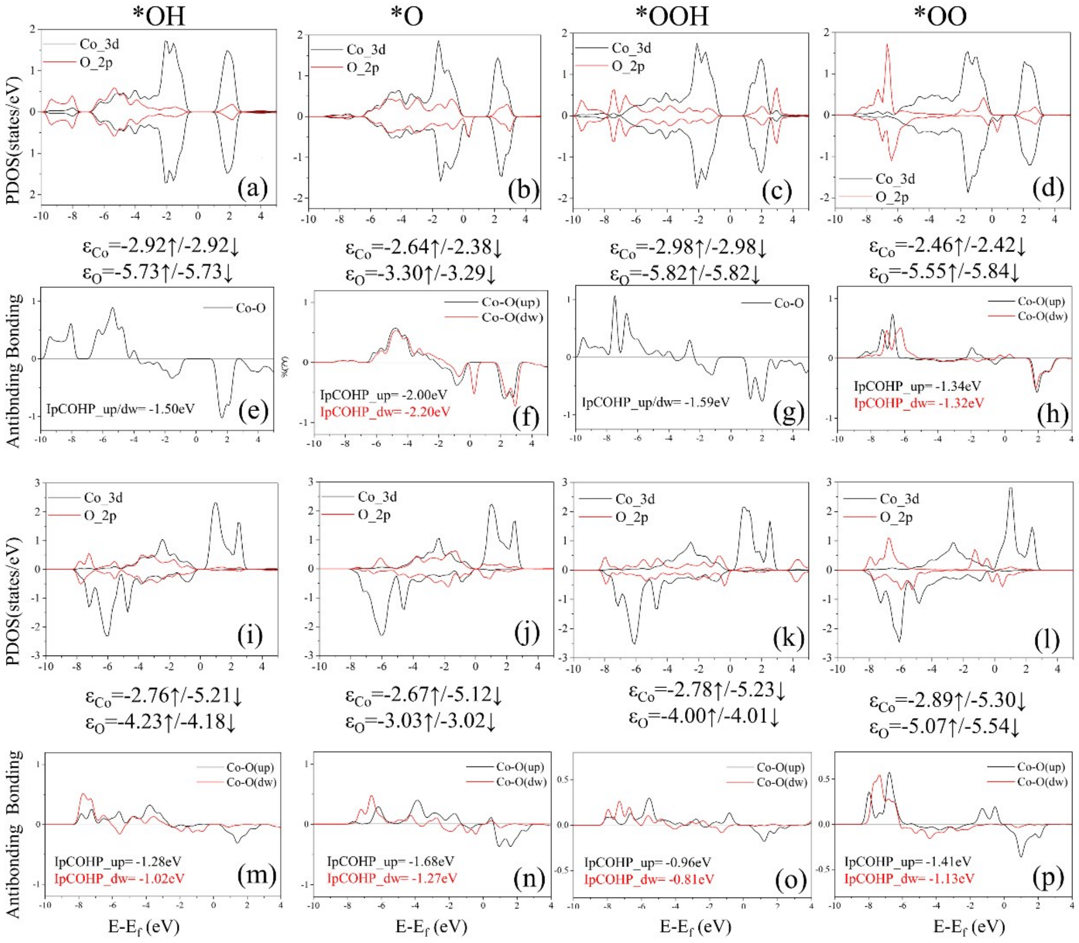


Figure S10 (a)-(d) The PDOSs of Co-d and O-p orbitals for LS CoOOH adsorbed with *OH, *O, *OO and *OOH intermediates. (e)-(h) IpCOHP of Co-O bond for LS CoOOH adsorbed with different intermediates. (i)-(l) The PDOSs of Co-d and O-p orbitals for HS CoOOH with different intermediates. (m)-(p) IpCOHP of Co-O bond for HS CoOOH with different intermediates.

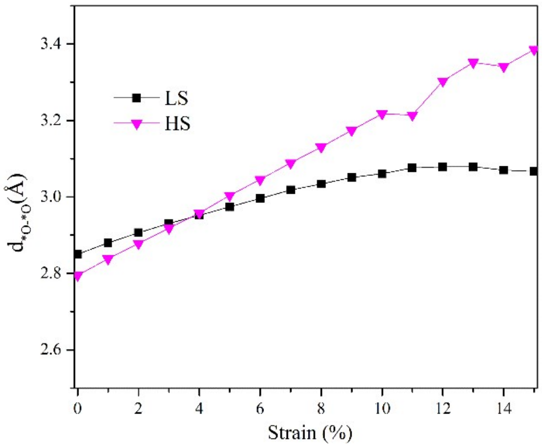


Figure S11 The distance between the neighboring O ions on LS and HS CoOOH.

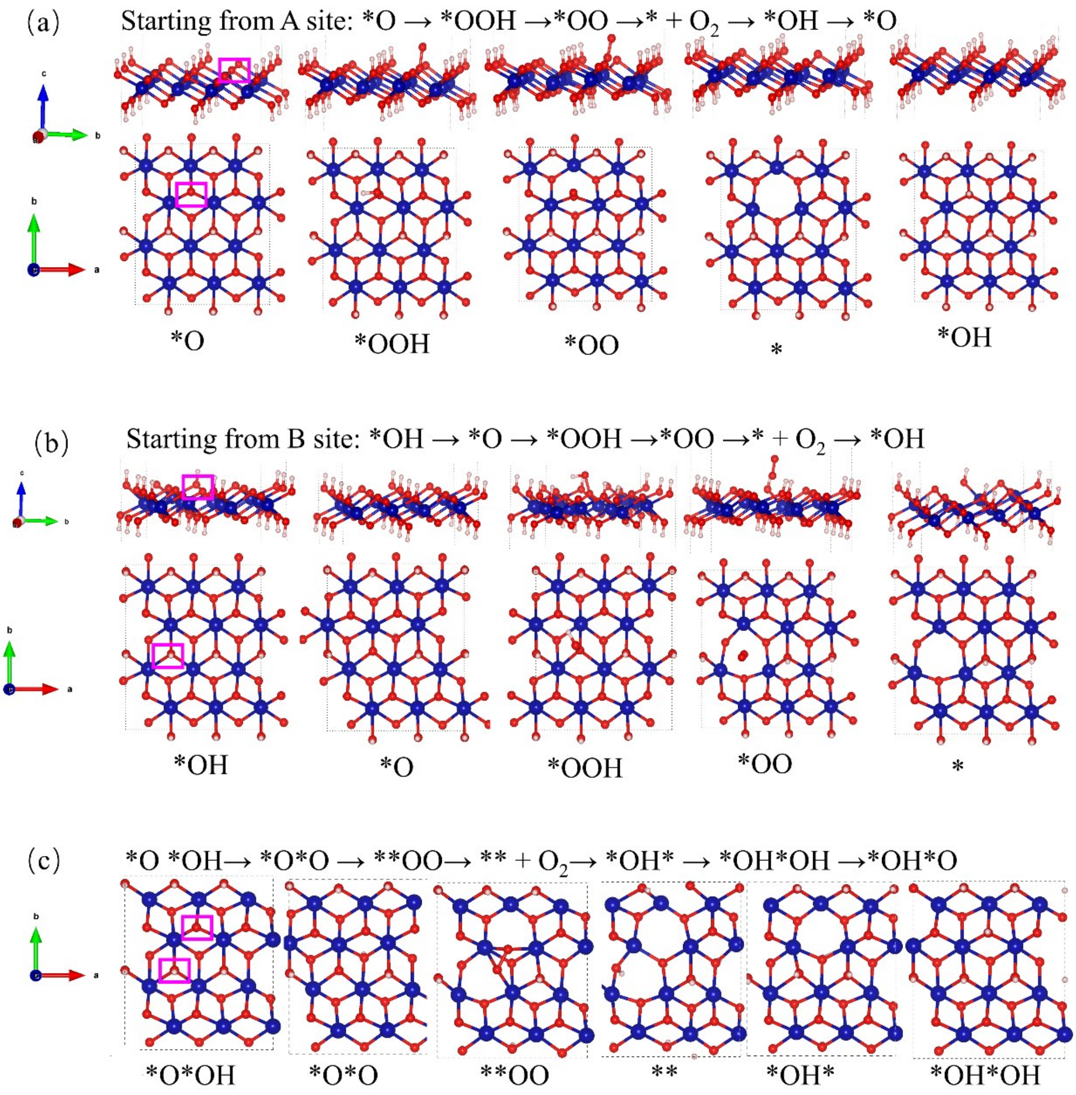


Figure S12 Adsorption models of intermediates in each OER step. (a)&(b) nucleophilic attack of hydroxide mechanism, and (c) intramolecular coupling mechanism.

Supplementary References

[1] Jens Kehlet Nørskov, Jan Rossmeisl, Ashildur Logadottir, LRKJ Lindqvist, John R Kitchin, Thomas Bligaard, and Hannes Jonsson, J. Phys. Chem. B **108** (46), 17886 (2004).

[2] Vei Wang, Nan Xu, Jin Cheng Liu, Gang Tang, and Wen-Tong Geng, arXiv preprint arXiv:1908.08269 (2019).

[3] Hieu H Pham, Mu-Jeng Cheng, Heinz Frei, and Lin-Wang Wang, ACS Catal. **6** (8), 5610 (2016).

[4] Ananth Govind Rajan, John Mark P Martirez, and Emily A Carter, J. Am. Chem. Soc. **142** (7), 3600 (2020).