Supporting Information

Unveiling the micro-mechanism of H_2O_2 activation and the selective regulation strategy over single-atom catalysts

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S1. Computational Details

To demonstrate the stability of the catalyst, we performed binding energy calculations for the single metal atom. The following equation was used to calculate the binding energy (E_{bind}):

$$E_{bind} = E_{sur} - E_{sub} - E_M \tag{1}$$

where E_{sur}, E_{sub}, and $E_M$are the electronic energies of the catalyst, graphene substrate, and single metal atom, respectively.

Adsorption energies (E_{ads}) were computed in accordance with the following equation to examine how strongly the gas molecules adhere to the catalyst surface

$$E_{ads} = E_{absorb} - E_{sur} - E_{gas} \tag{2}$$

E_{absorb}, E_{sur}, and E_{gas} represent the total energies of the adsorption system, catalyst surface, and gas, respectively.

The reaction energy barrier (E_b) and reaction heat (ΔE) in the reaction pathways were computed based on

$$E_b = G_{TS} - G_{IS} \tag{3}$$

$$\Delta E = G_{FS} - G_{IS} \tag{4}$$

where G_{IS}, G_{TS}, and G_{FS} are the Gibbs free energy energies of the initial, transition, and final states, respectively.

The Gibbs free energies were obtained using the following equation:

$$G(T,P) = E_{ele} + ZPE + \Delta H - TS(T,P) + K_B T \ln \frac{p}{p^0} \tag{5}$$

where E_{ele} is the system energy in the ground state; ZPE is the zero-correction energy; ΔH is the enthalpy variation from 0 K to a given temperature; T is the temperature and $TS(T,P)$ is the entropy of the system acquired from vibrational frequency analyses; K_B is the Boltzmann constant, 8.6173303×10^{-5} eV·K^{-1}; and p^0

is the standing pressure.

Based on Electron Density Difference (EDD), the gain and loss of electrons of each component in the system before and after adsorption can be visualized. The calculation formula for the electron density of each point in the EDD is as follows:

$$\Delta\rho = \rho_{AB} - \rho_A - \rho_B \tag{6}$$

Where ρ_{AB} is the electron density of the adsorption system; ρ_A is the corresponding charge density of the catalyst; ρ_B is the electron density corresponding to the adsorption.

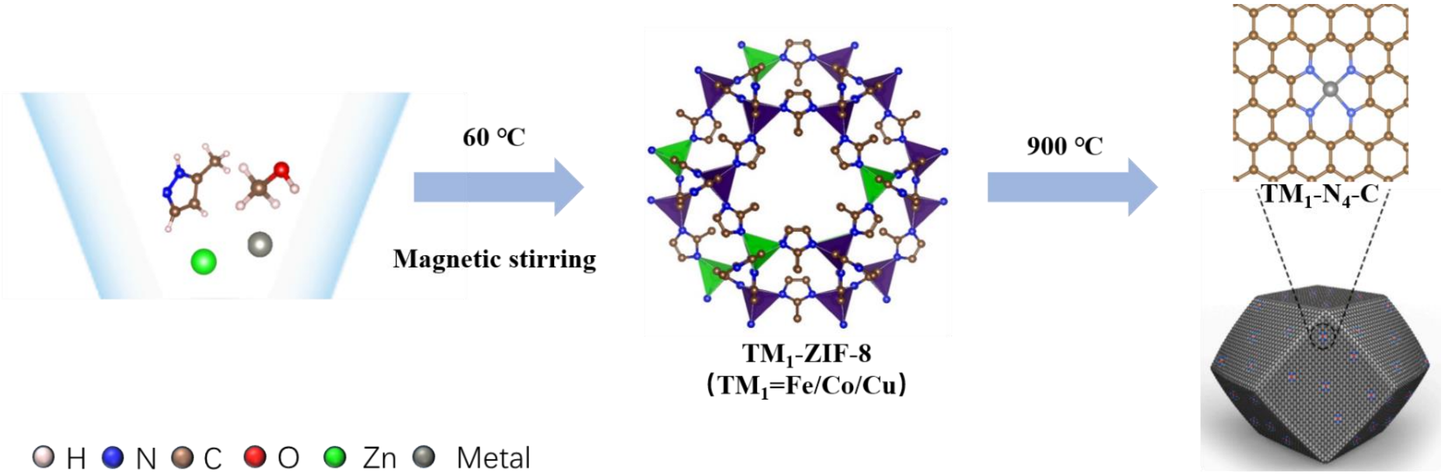


Fig. S1 Schematic diagram of SACs synthesis process

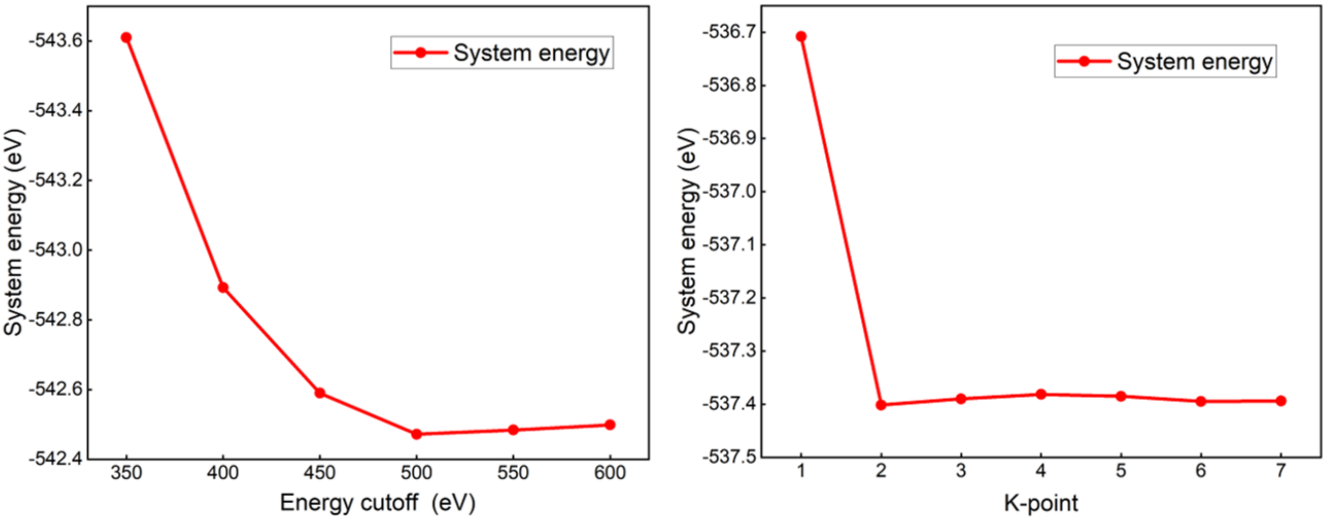


Fig. S2. (a) K point test; (b) Truncation energy test

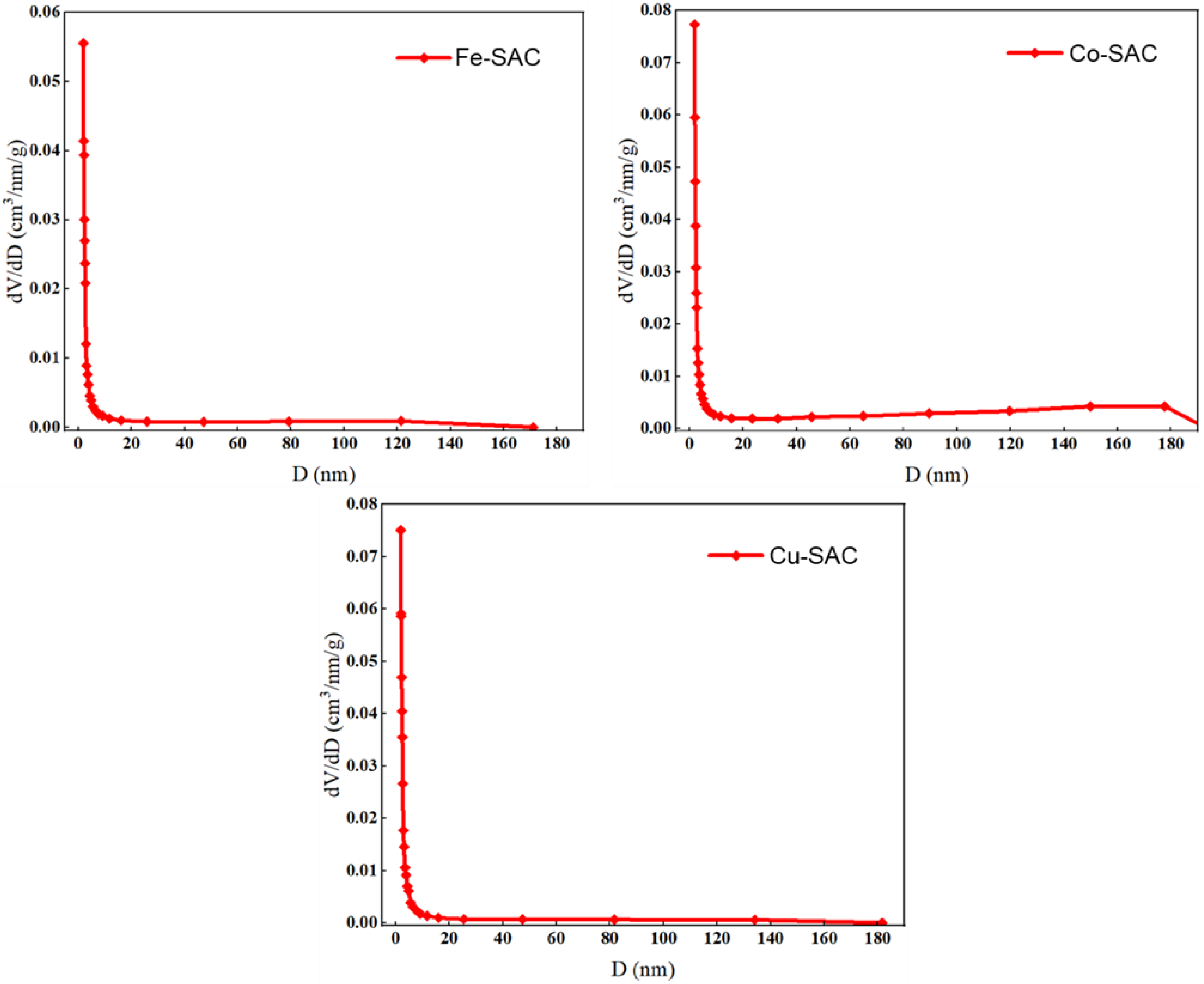
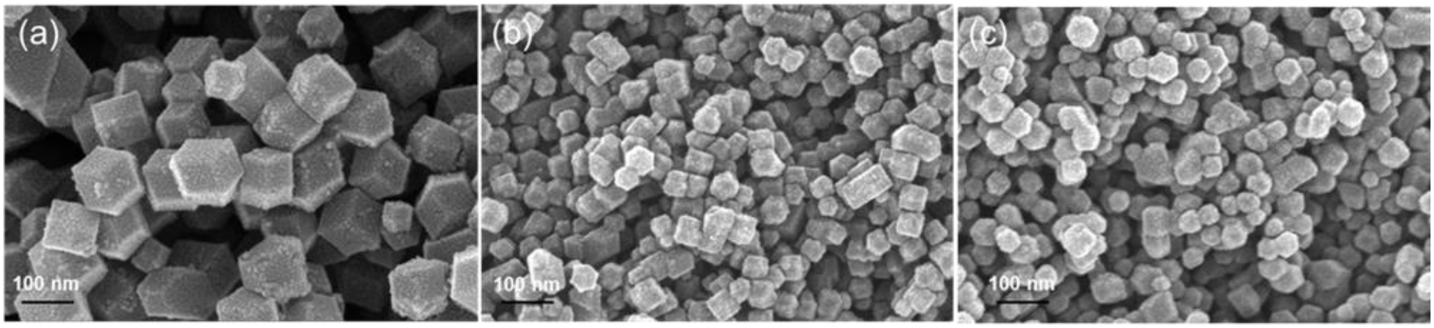


Fig. S3. Aperture distribution of three kinds of SACs (Fe, Co and Cu).



F**ig. S4** SEM of (a)Fe-SAC, (b)Co-SAC, (c)Cu-SAC

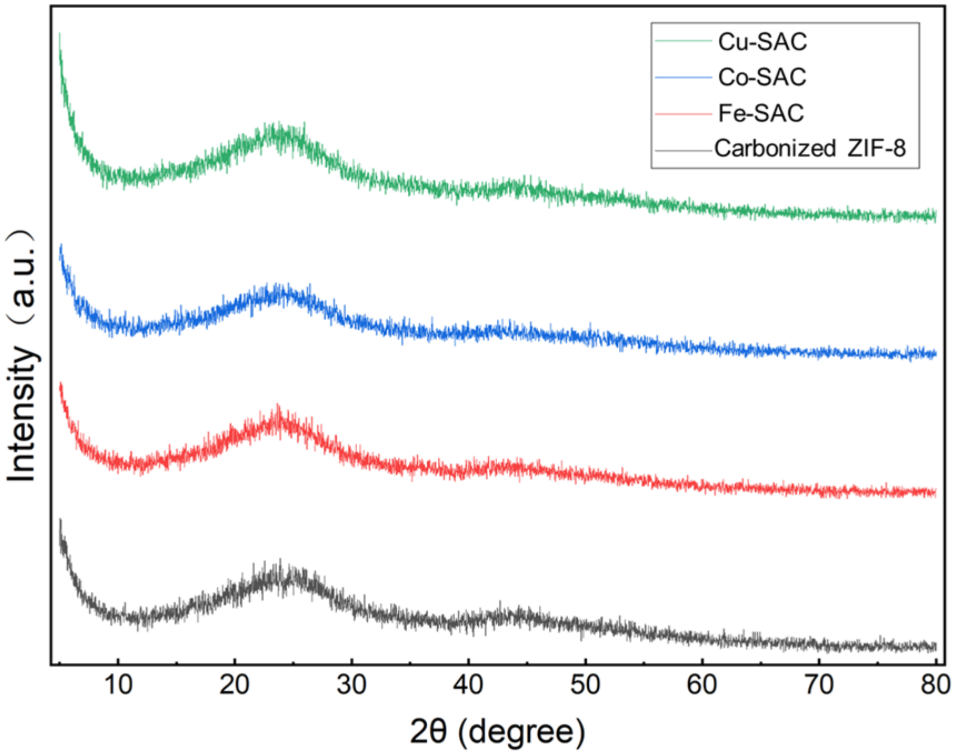


Fig. S5 XRD curves of carbonized ZIF-8, Fe-SAC, Co-SAC and Cu-SAC

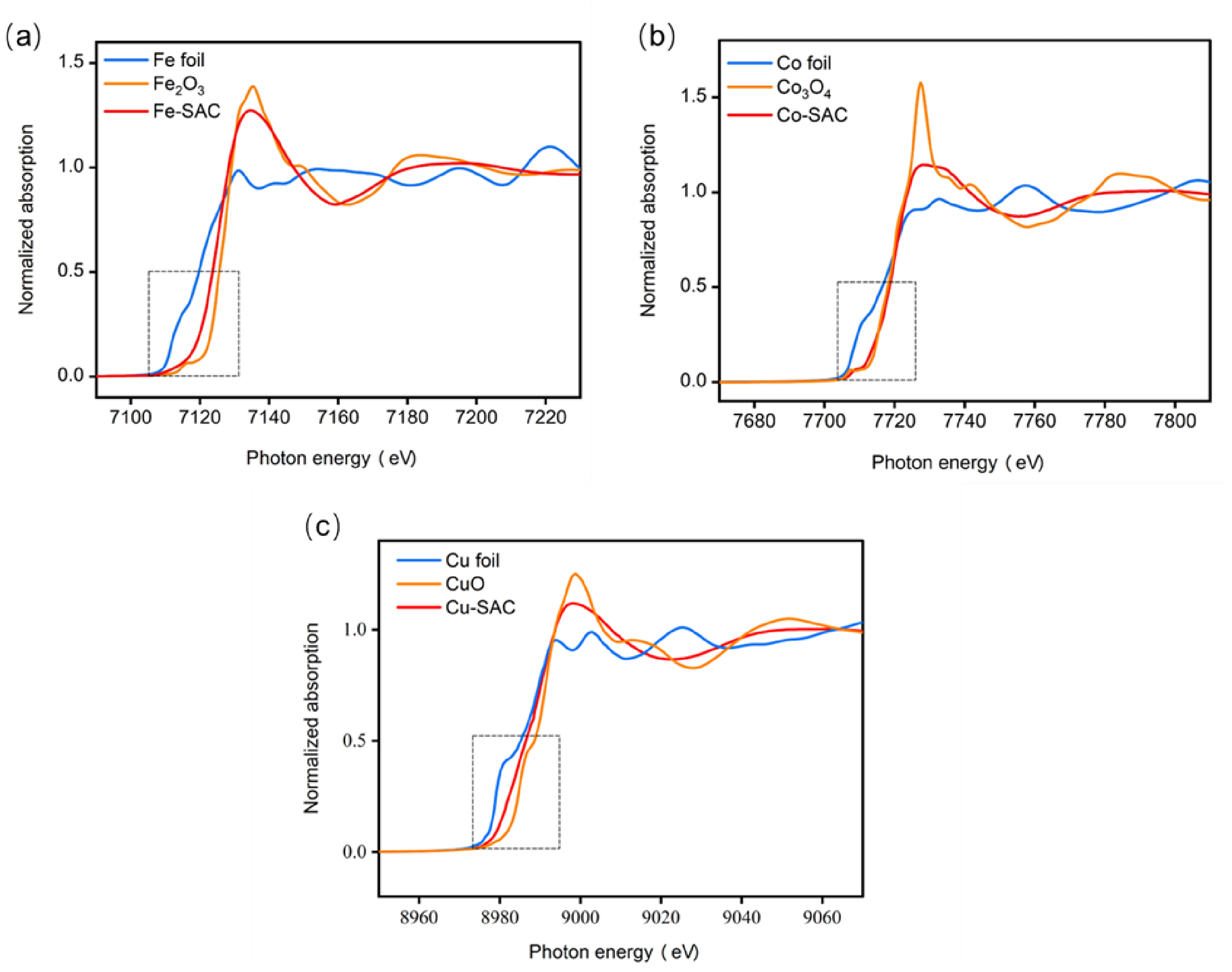


Fig. S6 XANES spectra of (a)Fe-SAC, (b)Co-SAC, (c)Cu-SAC

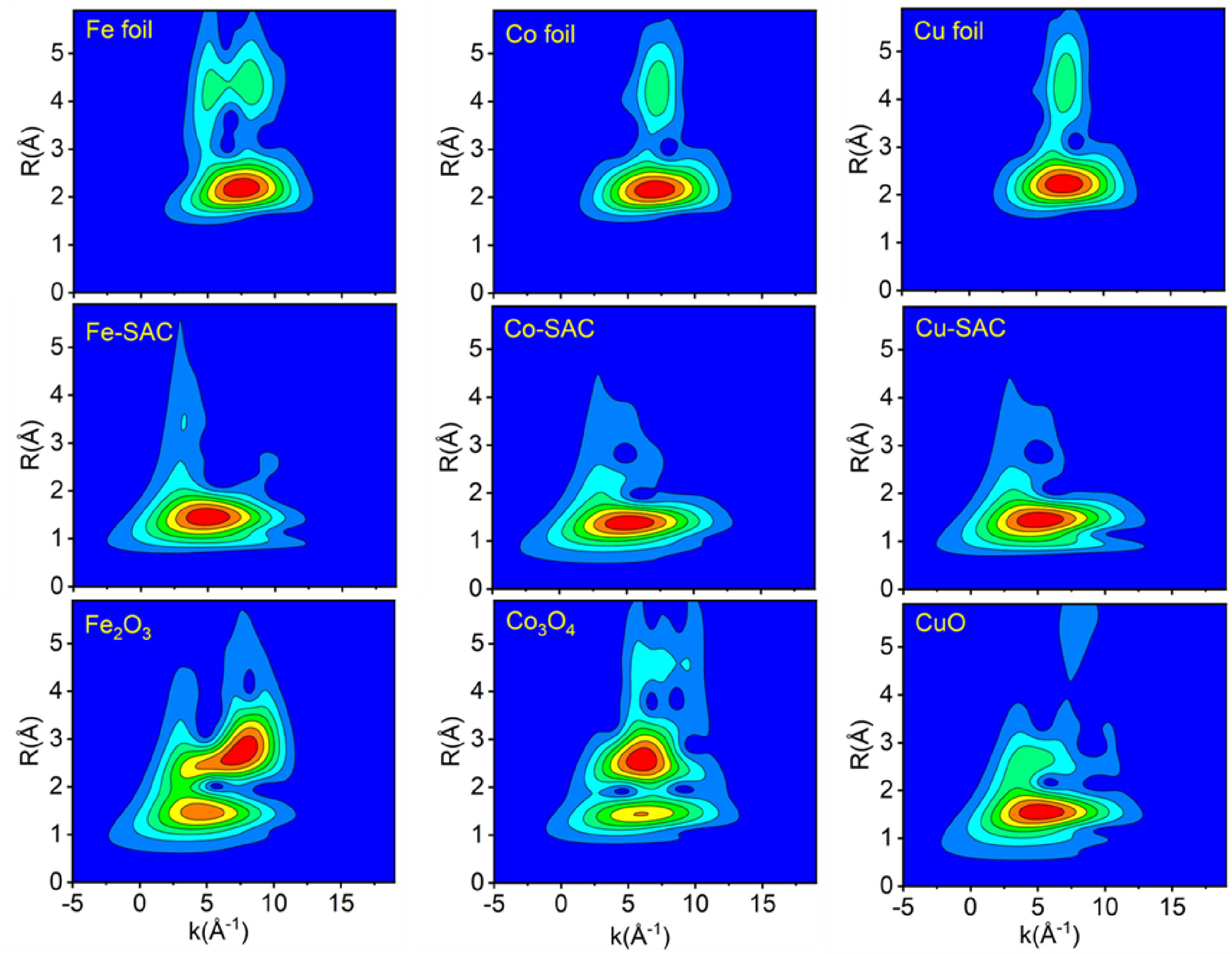
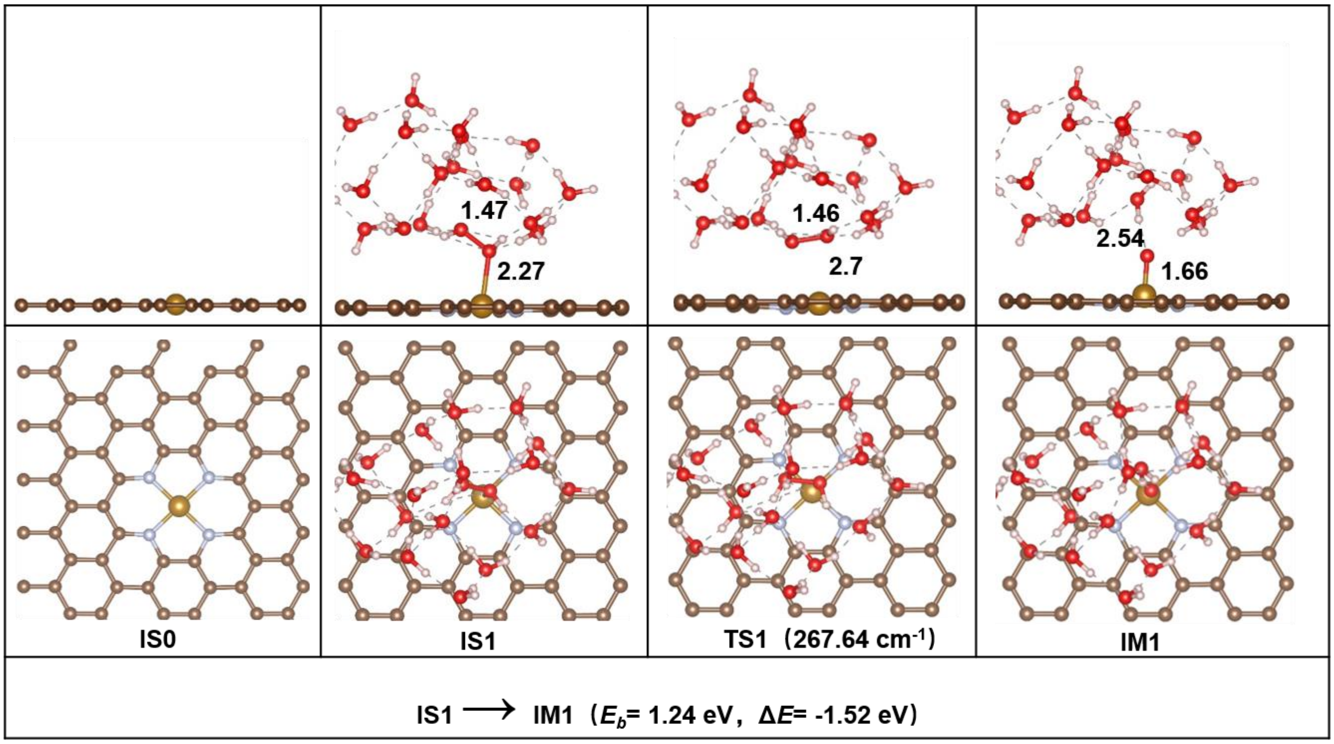
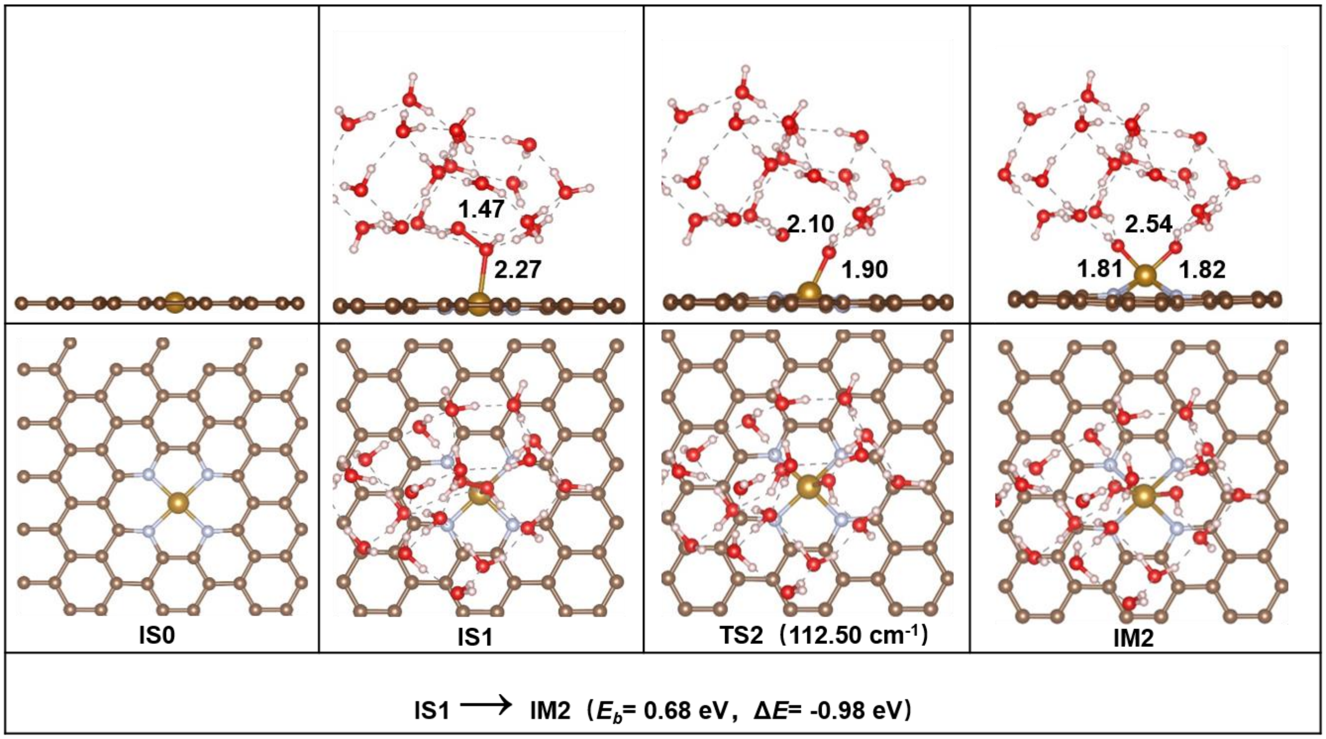


Fig. S7. Wavelet transform of EXAFS spectra at Fe K-edge, Cu K-edge, Co K-edge

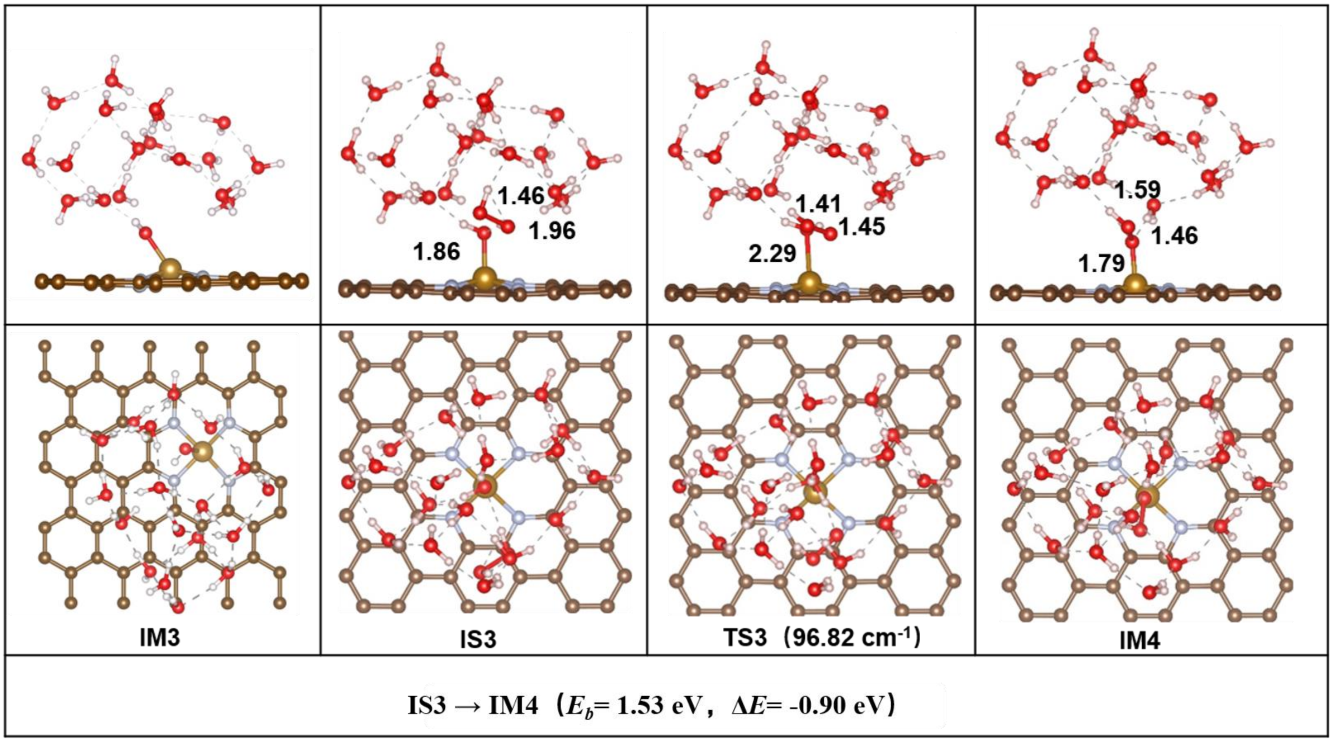
(a)


1.47
2.27
1.46
2.7
2.54
1.66
IS0
IS1
TS1（267.64 cm⁻¹）
IM1
IS1 ⟶ IM1（Eb= 1.24 eV，ΔE= -1.52 eV）

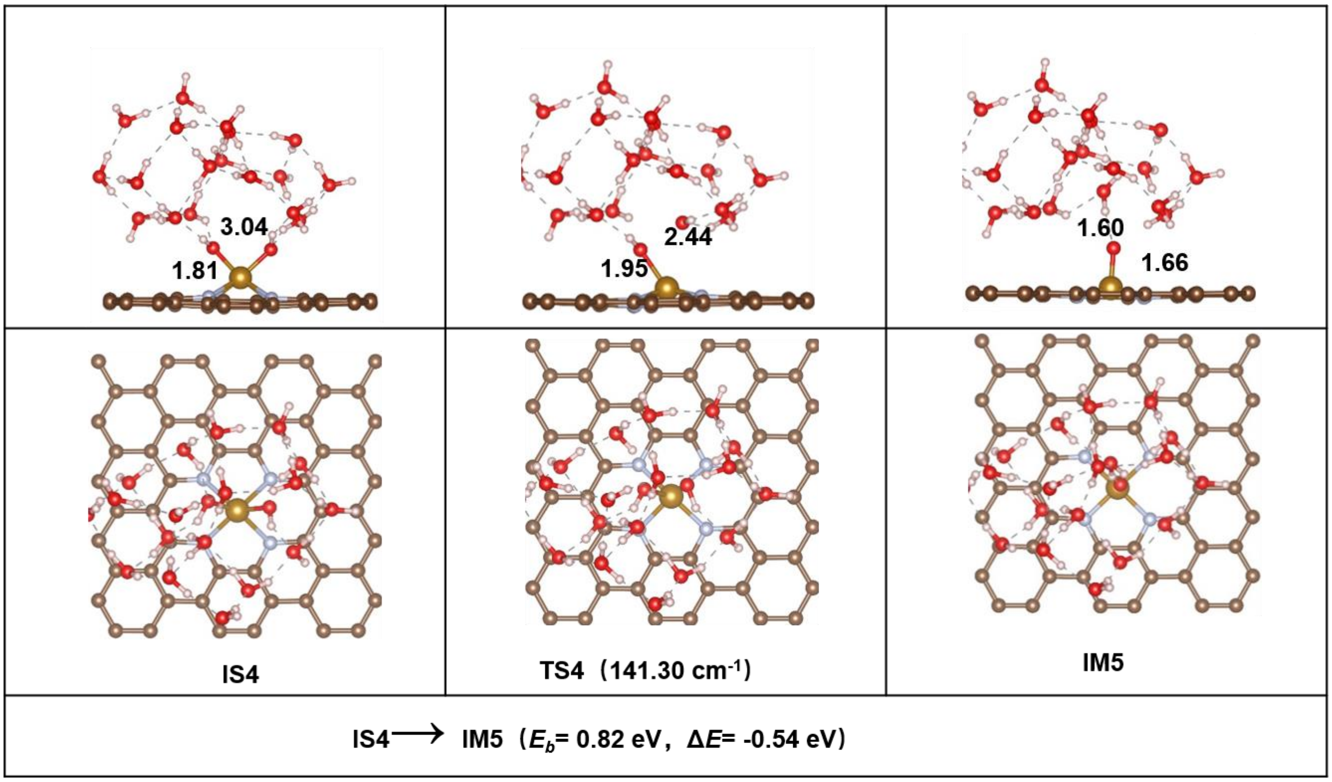
(b)

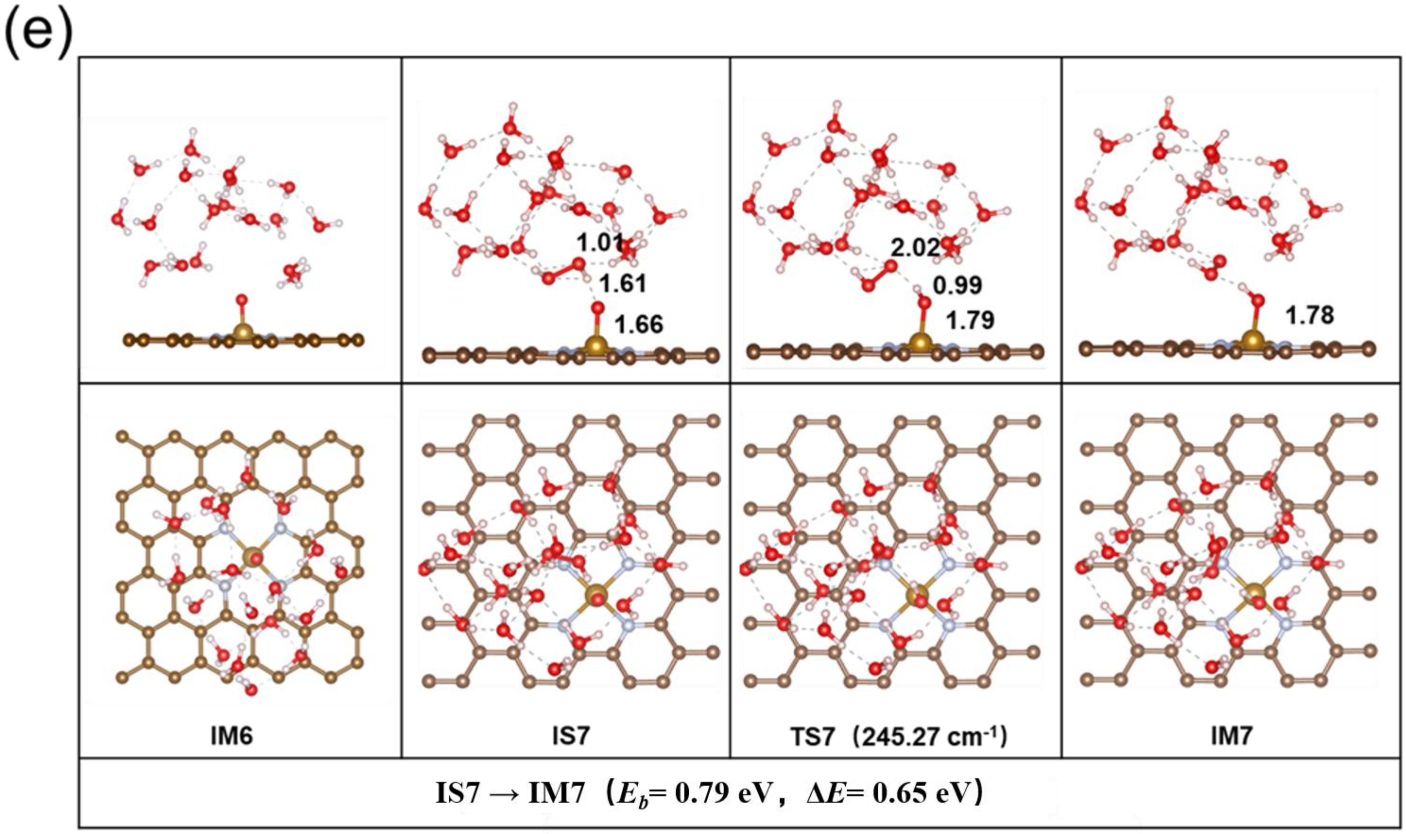

1.47
2.27
2.10
1.90
2.54
1.81
1.82
IS0
IS1
TS2（112.50 cm⁻¹）
IM2
IS1 ⟶ IM2（Eb= 0.68 eV，ΔE= -0.98 eV）

(c)


1.46
1.96
1.86
1.41
1.45
2.29
1.59
1.46
1.79
IM3
IS3
TS3（96.82 cm^{-1}）
IM4
IS3 → IM4（E_b= 1.53 eV，ΔE= -0.90 eV）

(d)


3.04
1.81
2.44
1.95
1.60
1.66
IS4
TS4（141.30 cm^{-1}）
IM5
IS4⟶ IM5（E_b= 0.82 eV，ΔE= -0.54 eV）


(e)
1.01
1.61
1.66
2.02
0.99
1.79
1.78
IM6
IS7
TS7（245.27 cm^{-1}）
IM7
IS7 → IM7（E_b= 0.79 eV，ΔE= 0.65 eV）

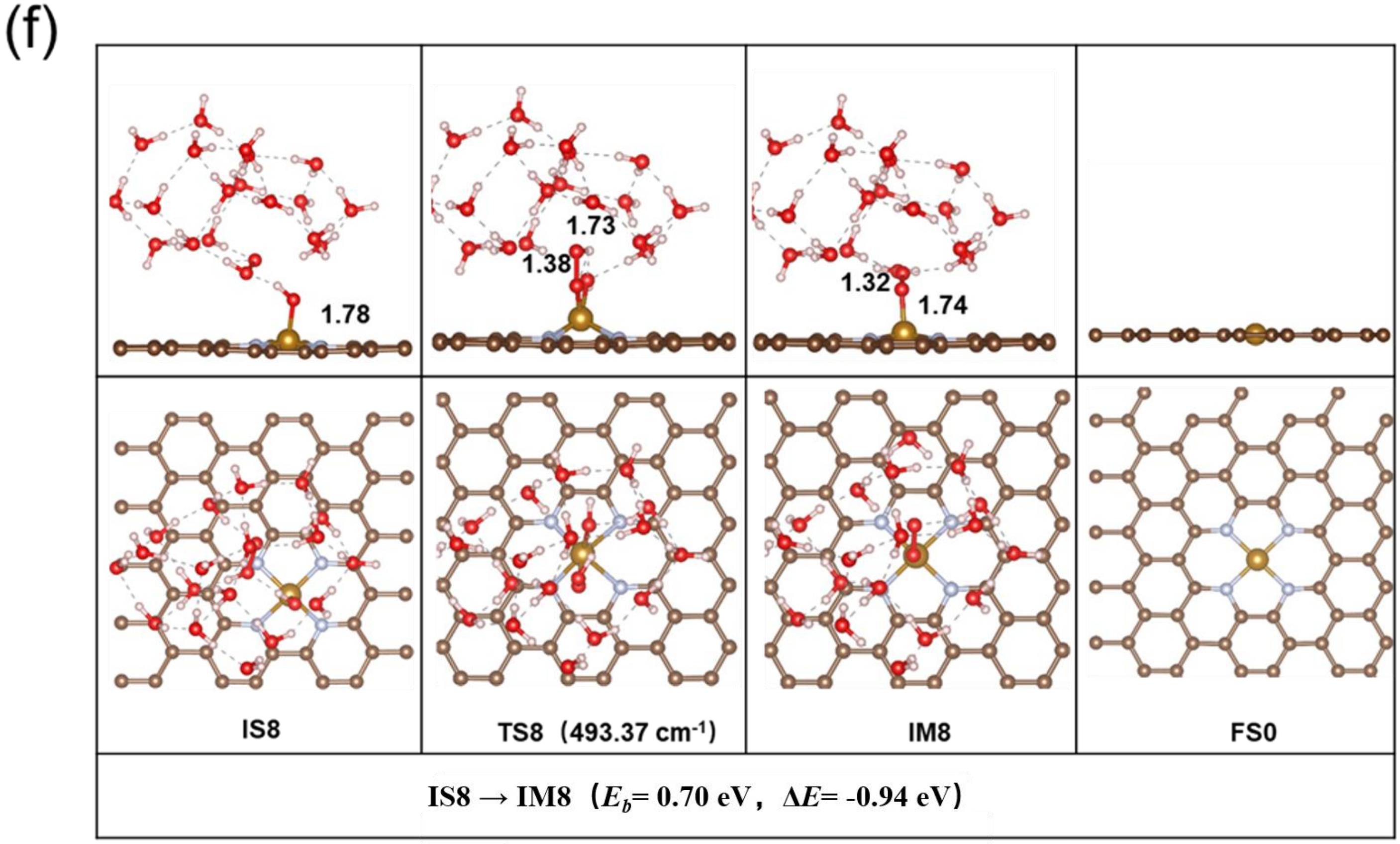
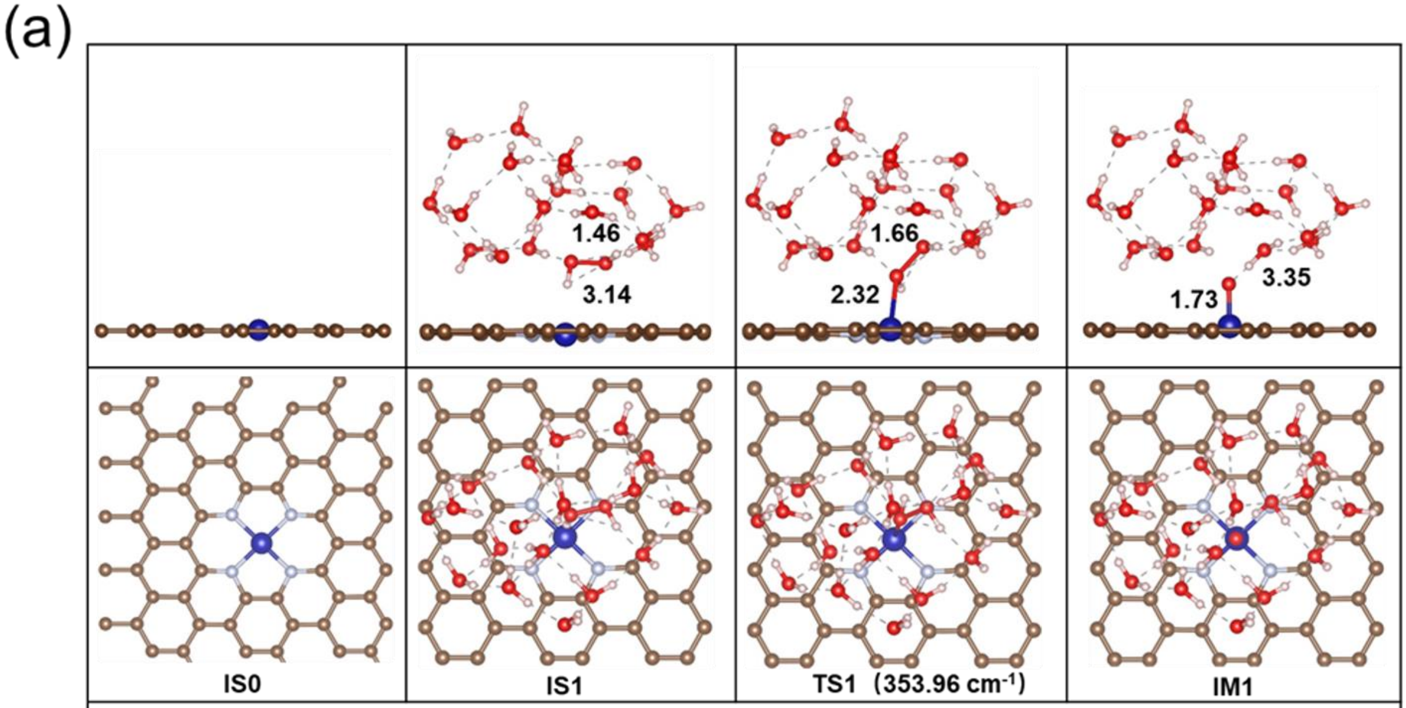
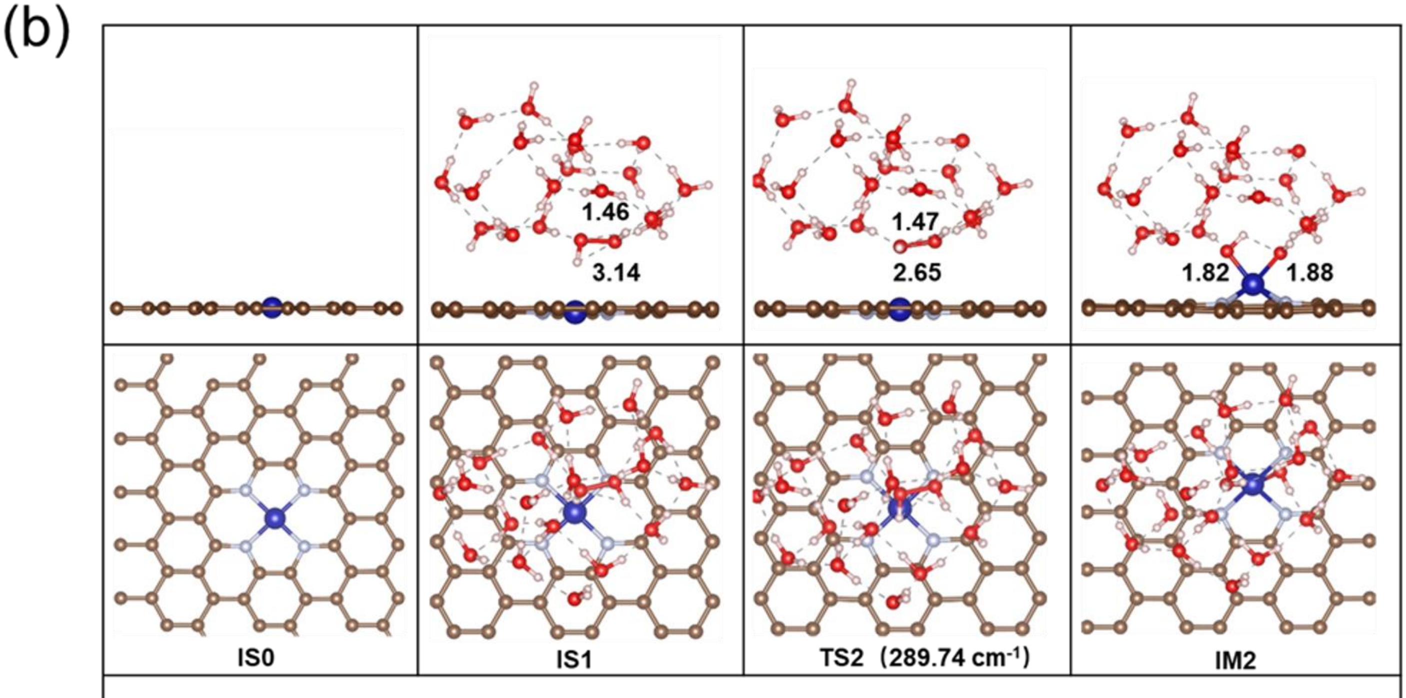


Fig. S8. Fe-SAC catalyzes the H_2O_2 activation of the reaction 4. (a) H_2O_2→$^*O$+H_2O (b) H_2O_2→$^*OH$+$^*OH$ (c) $^*OH$+H_2O_2→$^*OOH$+H_2O (d) $^*OH$+$^*OH$→$^*O$+H_2O (e) and (f) $^*O$+H_2O_2→$^*OOH$+$^*OH$→$^1O_2$+H_2O The brown, red, white, pink, yellow, spheres represent C, O, N, H, Fe, respectively.

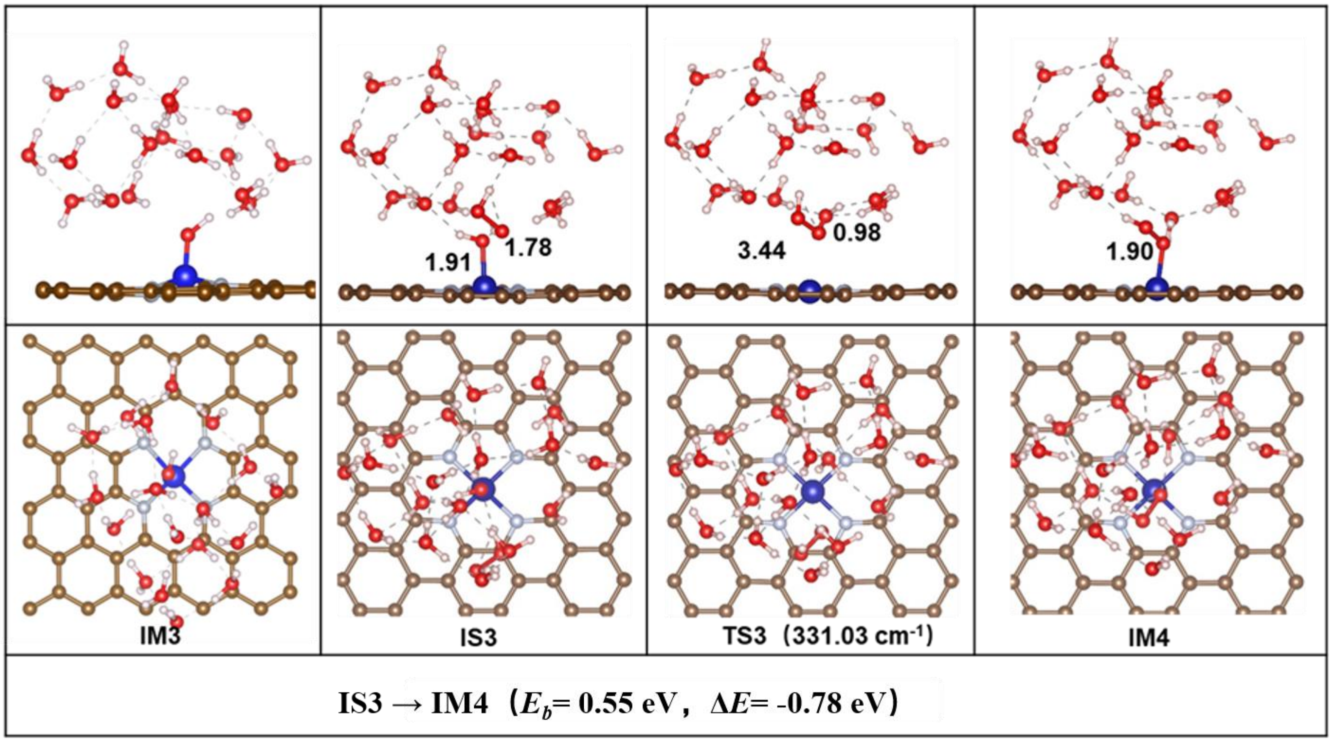


IS1 → IM1（E_b= 1.41 eV，ΔE= -0.89 eV）

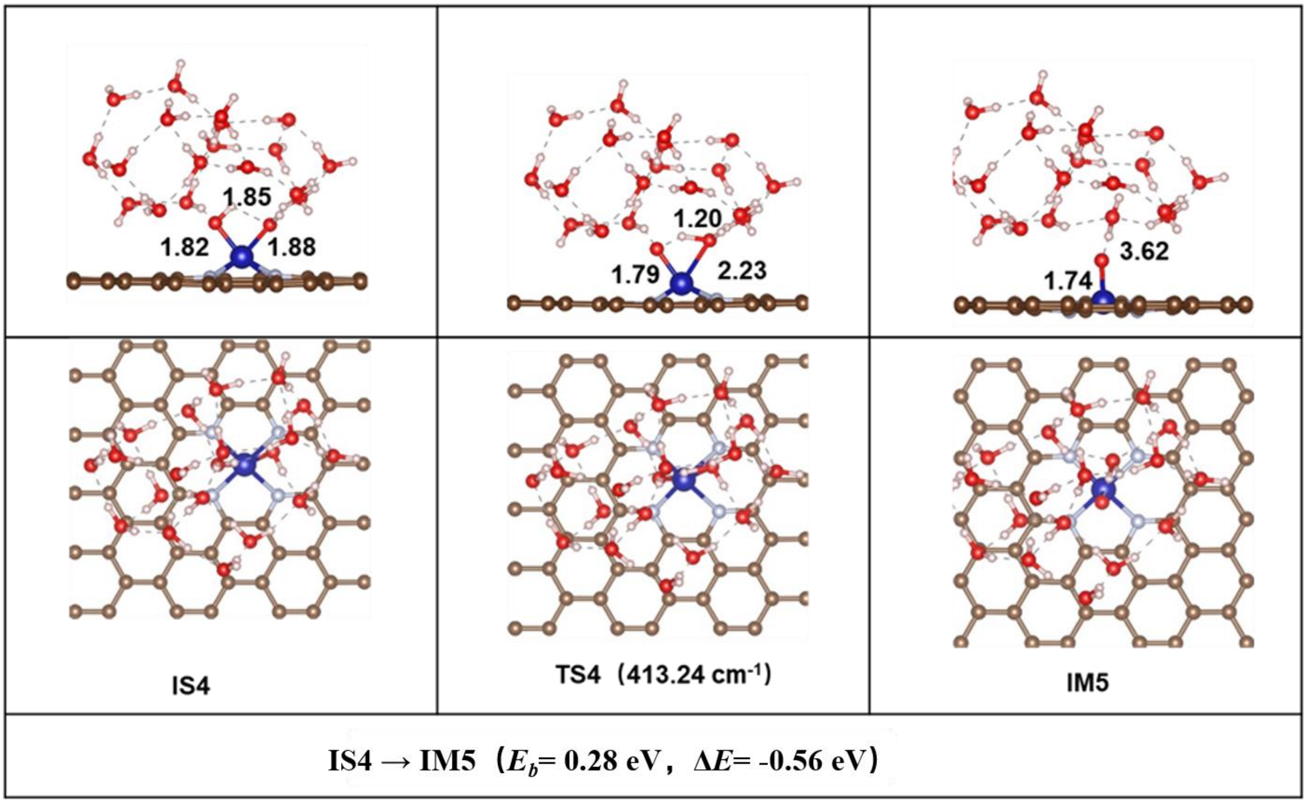


IS1 → IM2（E_b= 0.54 eV，ΔE= -0.15 eV）

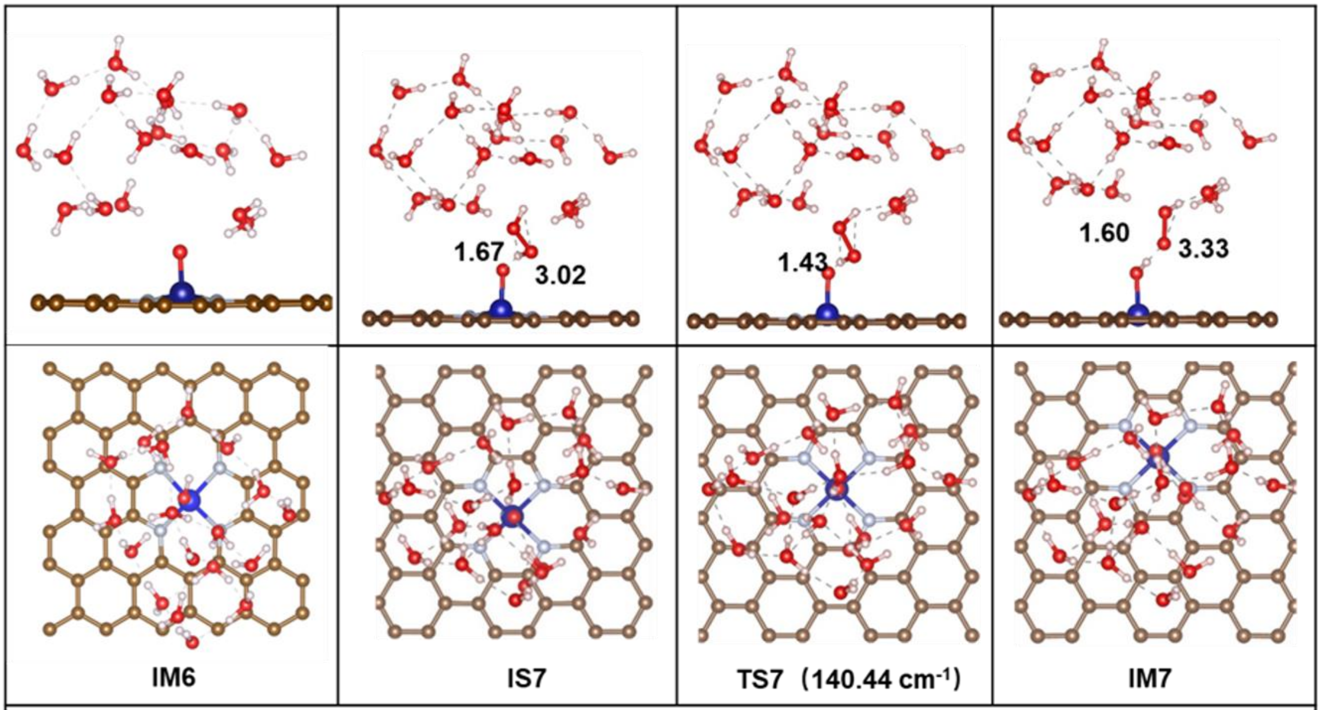
(c)


1.91
1.78
3.44
0.98
1.90
IM3
IS3
TS3（331.03 cm-1）
IM4
IS3 → IM4（E_b= 0.55 eV， ΔE= -0.78 eV）

(d)


1.85
1.82
1.88
1.20
1.79
2.23
3.62
1.74
IS4
TS4（413.24 cm-1）
IM5
IS4 → IM5（E_b= 0.28 eV， ΔE= -0.56 eV）

(e)



IS7 → IM7（E_b= 0.26 eV， ΔE= -0.63 eV）

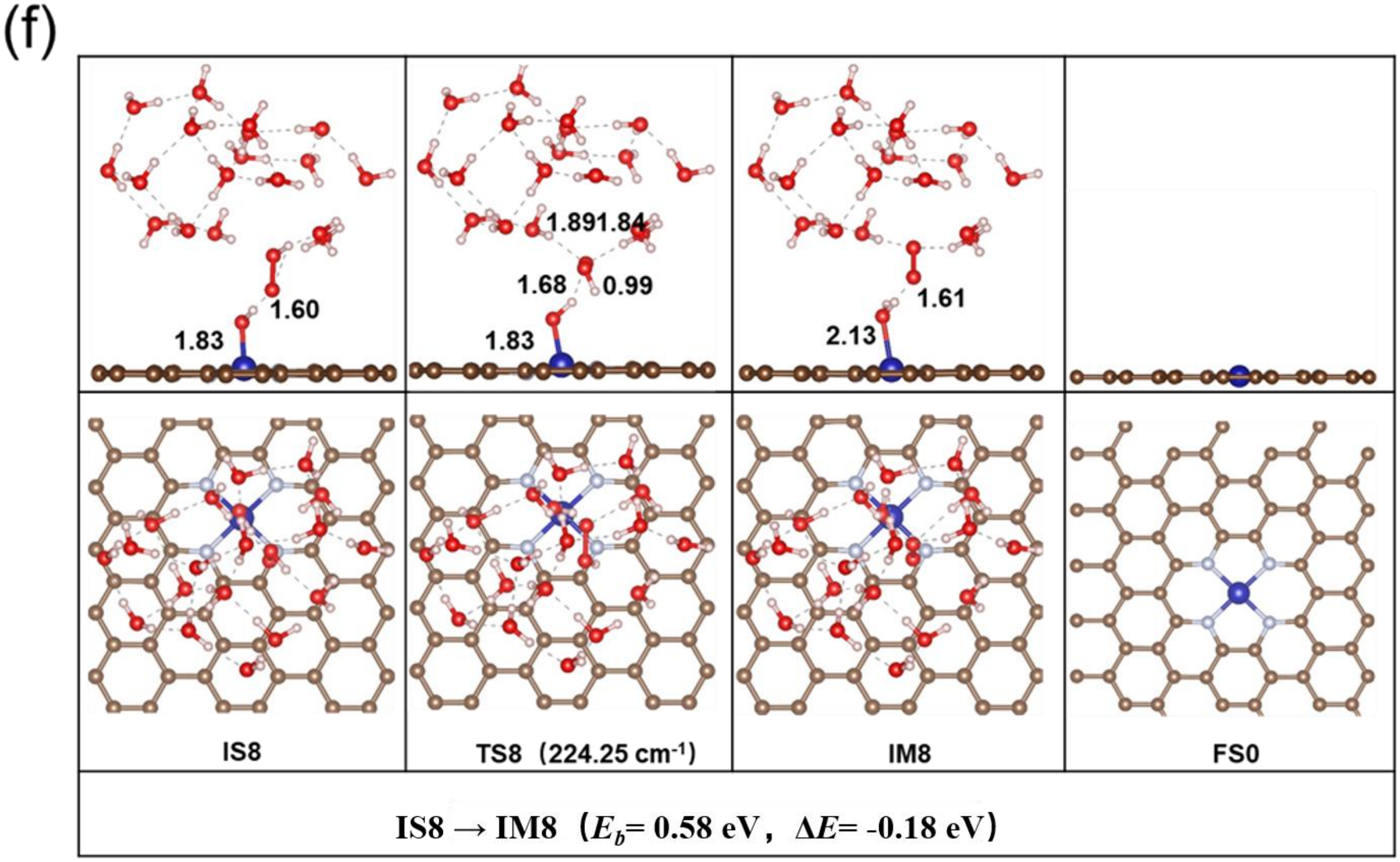


Fig. S9. Co-SAC catalyzes the H_2O_2 activation of the reaction (a) $H_2O_2 \rightarrow {}^{*}O + H_2O$ (b) $H_2O_2 \rightarrow {}^{*}OH + {}^{*}OH$ (c) ${}^{*}OH + H_2O_2 \rightarrow {}^{*}OOH + H_2O$ (d) ${}^{*}OH + {}^{*}OH \rightarrow {}^{*}O + H_2O$ (e) and (f) ${}^{*}O + H_2O_2 \rightarrow {}^{*}OOH + {}^{*}OH \rightarrow {}^{1}O_2 + H_2O$. The brown, red, white, pink, dark blue, spheres represent C, O, N, H, Co, respectively.

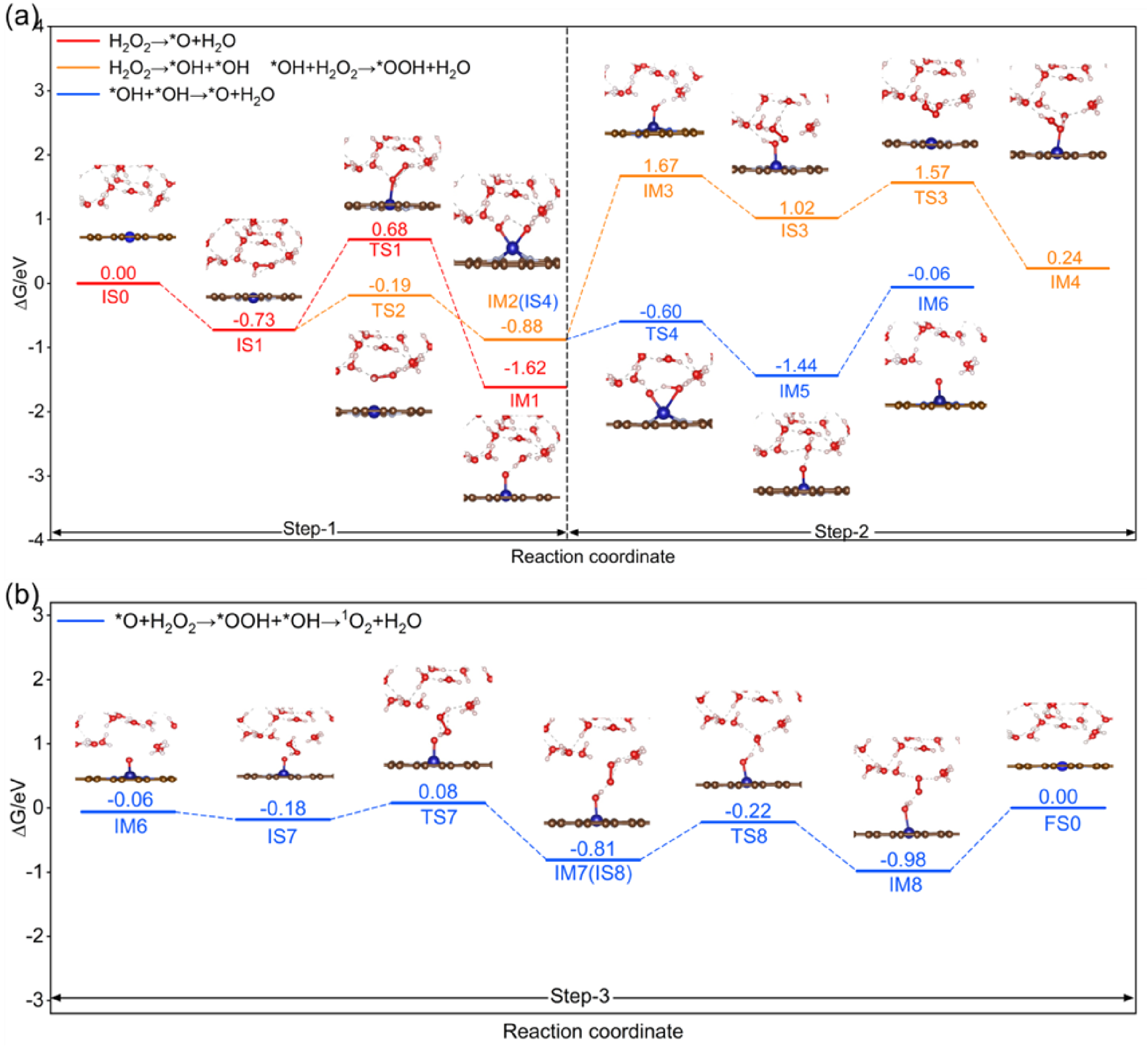
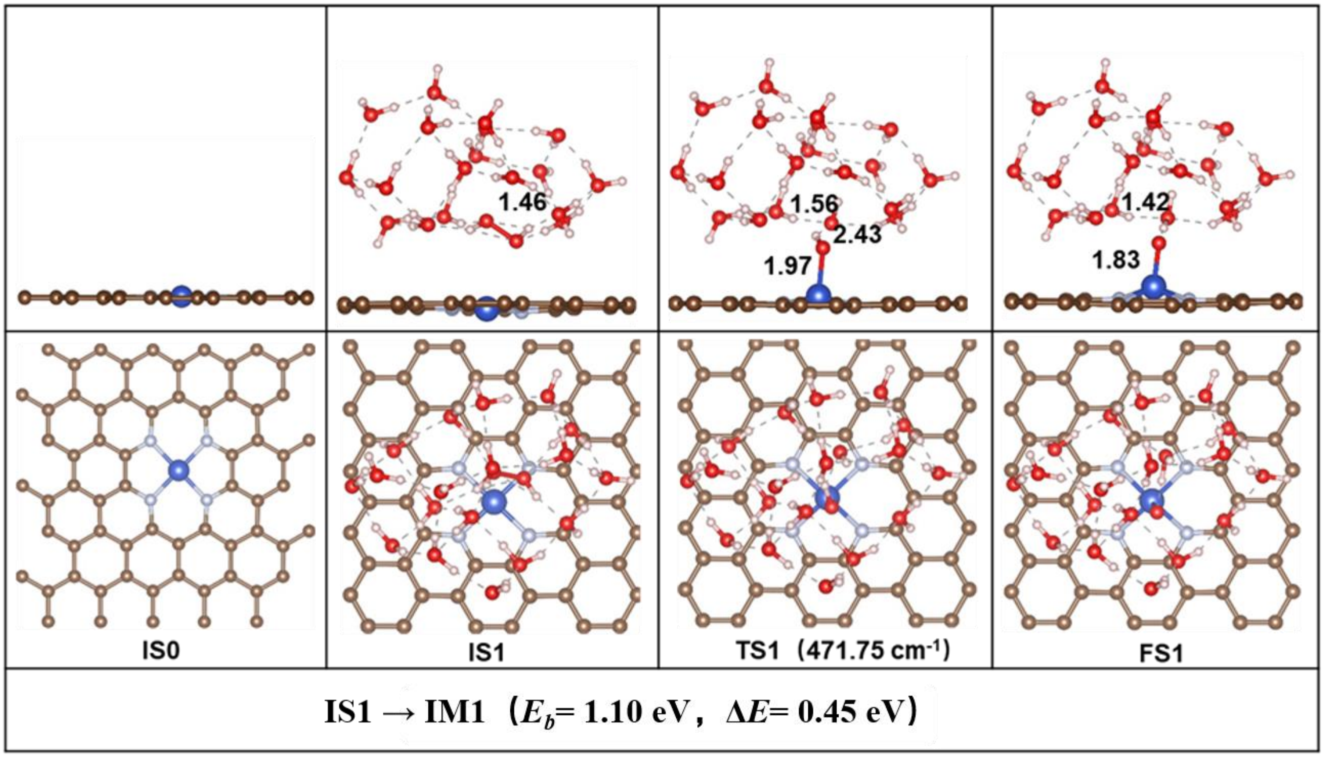


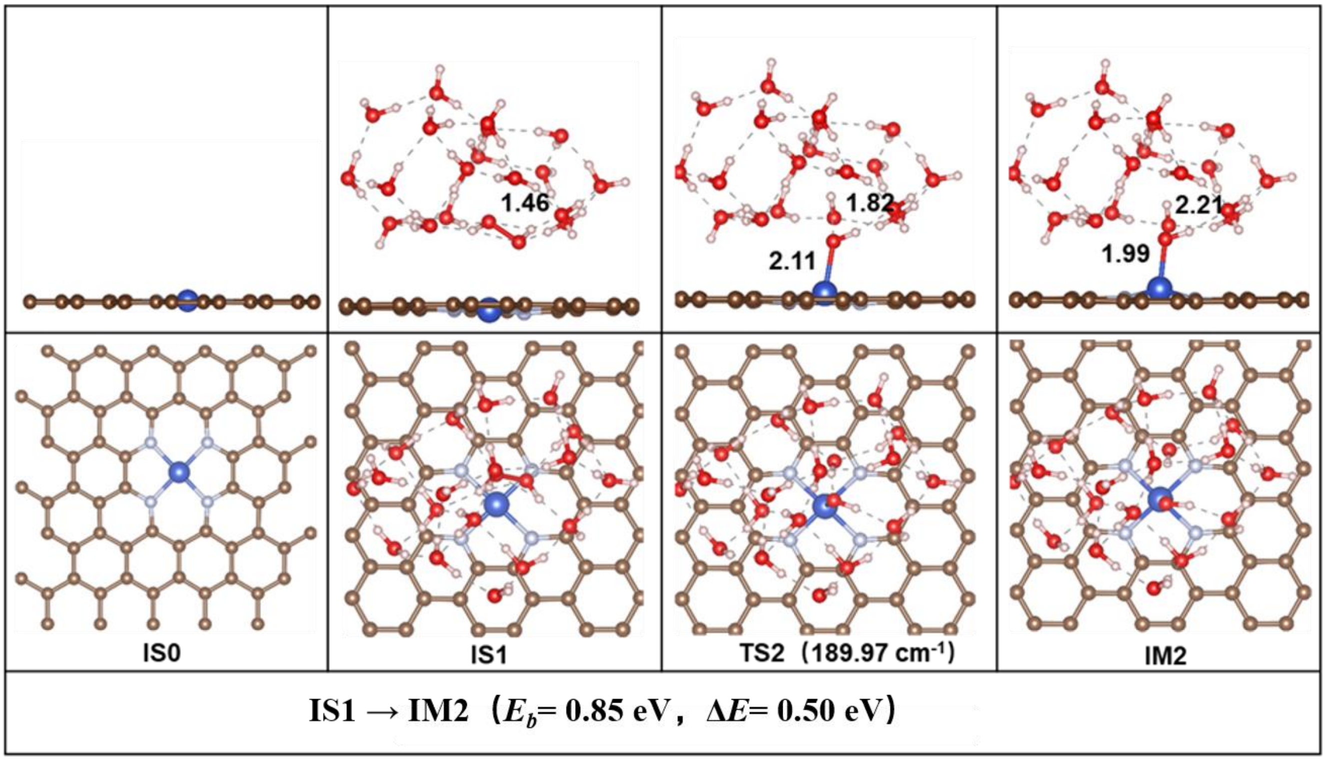
Fig. S10 Activation reaction network of H_2O_2 on Co-SAC. (a) Step-1 and Step-2. (b) Step-3. The brown, red, white, pink, dark blue, spheres represent C, O, N, H, Co, respectively.

(a)



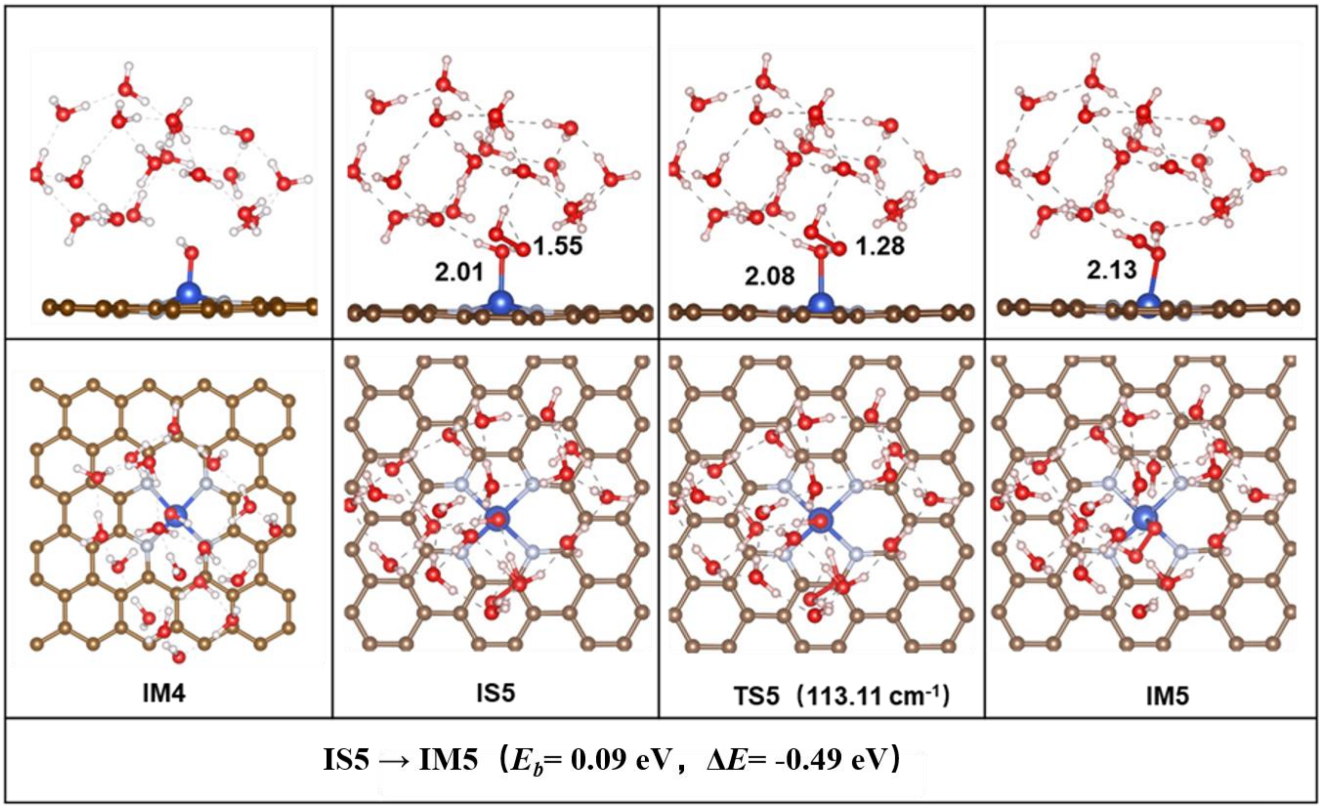
IS1 → IM1（E_b= 1.10 eV，ΔE= 0.45 eV）

(b)



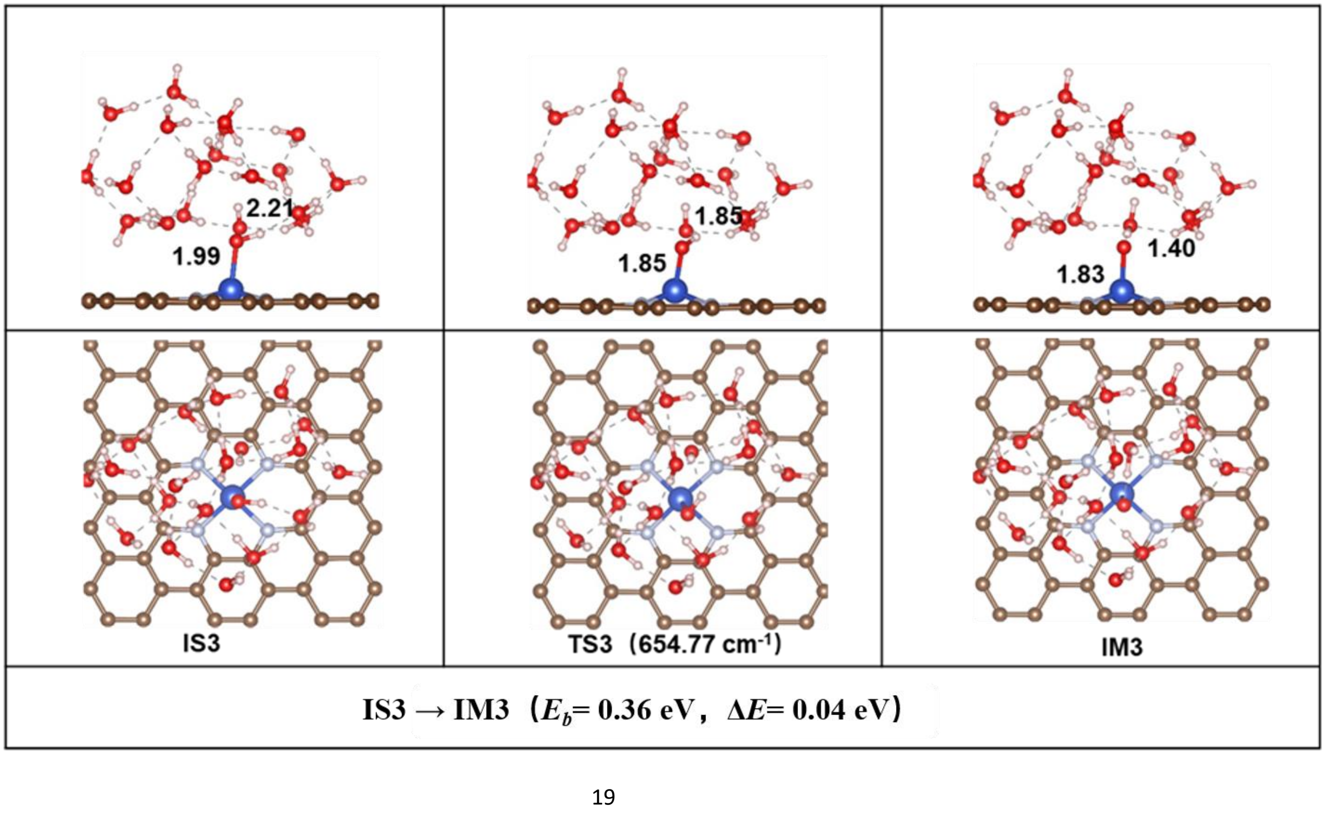
IS1 → IM2（E_b= 0.85 eV，ΔE= 0.50 eV）

(c)



IS5 → IM5（E_b= 0.09 eV，ΔE= -0.49 eV）

(d)



IS3 → IM3（E_b= 0.36 eV，ΔE= 0.04 eV）

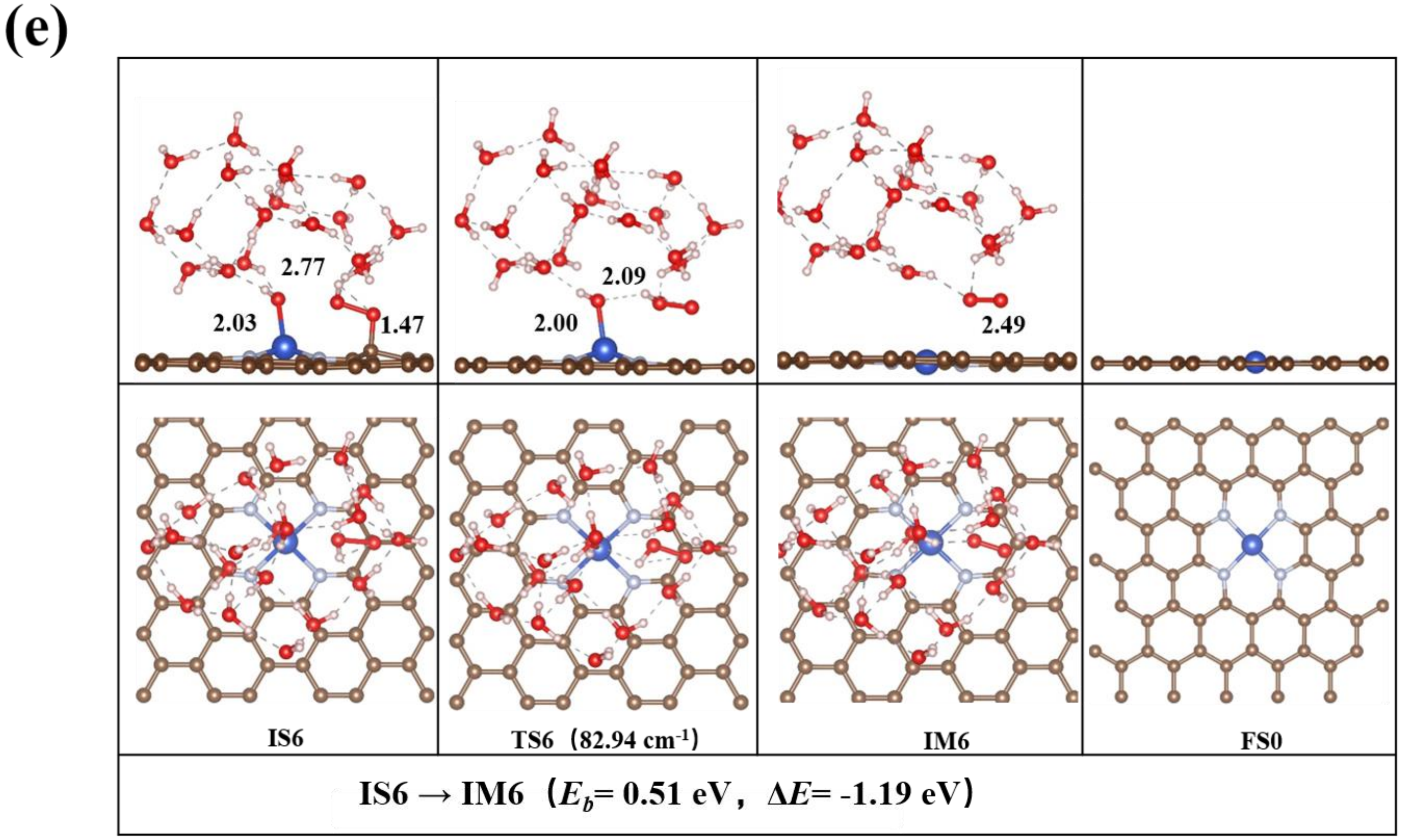


Fig. S11. Cu-SAC catalyzes the H_2O_2 activation of the reaction (a) $H_2O_2 \rightarrow {}^*O + H_2O$ (b) $H_2O_2 \rightarrow {}^*OH + {}^*OH$ (c) ${}^*OH + H_2O_2 \rightarrow {}^*OOH + H_2O$ (d) ${}^*OH + {}^*OH \rightarrow {}^*O + H_2O$ (e) ${}^*OOH + {}^*OH \rightarrow {}^1O_2 + H_2O$. The brown, red, white, pink, blue spheres represent C, O, N, H, Cu, respectively.

Table S1. Pore size and metal content of catalyst

Catalyst	Mean pore size of adsorption，nm	Metal element content %wt
Fe-N_4-C	8.744	1.33
Co-N_4-C	16.290	1.07
Cu-N_4-C	5.684	0.98

Table S2. BET specific surface area of catalyst

Catalyst	BET specific surface area，m^2/g	Catalyst	BET specific surface area，m^2/g
Fe-N_4-C	432.6	TiO_2 based MnO_x	122.1
Co-N_4-C	537.9	$Fe_{2.5}M_{0.5}O_4$	20~50
Cu-N_4-C	349.0	SiO_2 based CuO_x	481.9

Table S3. EXAFS fitting of fresh SACs

Sample	Scattering path	Distance (Å)	C.N.	σ^2 (Å^2)	ΔE_0 (eV)	R-factor
Co sample	Co-N	1.89	3.9	0.006	-9.7	0.001
Fe sample	Fe-N	1.98	4.2	0.007	-6.7	0.011
Cu sample	Cu-N	1.93	3.6	0.005	-4.3	0.004

Table S4. Statistics of adsorption energy and transfer charge of different free radicals adsorbed by Fe-SACs

Fe-SAC	E_{ads}(eV)	Q(e)
OH	-3.09	-1.076
OOH	-1.27	-1.028
$^1O_2$	-0.18	-0.982

Table S5. Statistics of adsorption energy and transfer charge of different free radicals adsorbed by Co-SACs

Co-SAC	E_{ads}(eV)	Q(e)
OH	-3.47	-1.299
OOH	-1.87	-1.074
$^1O_2$	-0.83	-1.076

Table S6. Statistics of adsorption energy and transfer charge of different free radicals adsorbed by Cu-SACs

Cu-SAC	E_{ads}(eV)	Q(e)
OH	-2.67	-1.032
OOH	-2.30	-1.201
$^1O_2$	-1.34	-1.202