Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information

Impact of electron transfer of atomic metals on adjacent graphyne layers on electrochemical water splitting

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Calculation method of HER and OER activity

The adsorption energies (ΔE_{ads}) are obtained through the following equation (1):

$$\Delta E_{ads} = E_{substrate + adsorbent} - E_{substrate} - E_{adsorbent} \qquad (1)$$

where the $E_{adsorbent}$, $E_{substrate}$, and $E_{substrate + adsorbent}$ are the total energies of the adsorbent, the substrate, and the substrate-adsorbent composites, respectively. The more negative ΔE_{ads} values represent the stronger binding between catalyst and intermediate as well as the better thermodynamic stability.

For HER, the H_2 generation from water splitting involves two steps: a) the atomic H adsorption on the catalysts; b) the formation and release of H_2 molecular [1]. When one H is adsorbed on the catalyst, the calculated intermediate state energy determines the HER reaction barrier (overpotential for the electron). Thus, we can assess the HER performance through ΔG_{H^*}:

$$H^+ + e^- + * \xrightarrow{\Delta G_{H^*}} H^* \qquad (2)$$

where H* and * represent the adsorbed intermediate and the active site, respectively. Under the standard conditions (pH=0, U=0, and 298.15 K), the chemical potential of $H^+ + e^-$ ($\mu_{(H+ + e-)}$) is equivalent to that of 1/2 H_2 (1/2 μ_{H2}). Namely, $\mu_{(H+ + e-)} = 1/2\ \mu_{H2}$ is obtained based on the calculation hydrogen electrode model [2]. Thus, the ΔG_{H^*} is calculated by:

$$\Delta G_{H^*} = \Delta E_{H^*} + \Delta E_{ZPE} - T\Delta S_{H^*} \qquad (3)$$

where ΔE_{H^*} means the hydrogen adsorption energy obtained from equation (1). ΔE_{ZPE} means the zero-point energy difference between gas-phase H_2 and the adsorbed H obtained by the equation $\Delta E_{ZPE} = E_{ZPE}^{H*} - E_{ZPE}^{*} - \frac{1}{2}E_{ZPE}^{H2}$, where E_{ZPE}^{*}, E_{ZPE}^{H*}, and E_{ZPE}^{H2} denote the zero-point energies of pure substrate, an adsorbed hydrogen on the substrate, and gas phase H_2, respectively. T means the temperature at 298K and ΔS_{H^*} represents the entropy difference between the gas phase and the adsorbed state. Due to the small calculated vibrational entropy of adsorbed state H*, the adsorption entropy of 1/2 H_2 is $\Delta S_H \approx -0.5\, S_{H2}^{0}$, where S_{H2}^{0} denotes the entropy of gas phase H_2 and is about 130 J·mol^{-1}·K^{-1}at the standard conditions [3]. Interestingly, it is found that the entropy and the ZPE of the adsorbed states on different catalysts show close values (Table S1 and S2). According to Nørskov's assumption [1], the overpotential of HER (η^{HER}) can be written as $|\Delta G_{H*}|/e$. The ideal ΔG_{H*} value for HER is zero. Too strong or too weak binding energy of intermediate state can lead to bad HER performance.

For OER, there are four elementary steps at pH=0 as follows:

$$H_2O(l) + * \xrightarrow{\Delta G_1} HO* + H^+ + e^- \tag{4}$$

$$HO* \xrightarrow{\Delta G_2} O* + H^+ + e^- \tag{5}$$

$$O* + H_2O(l) \xrightarrow{\Delta G_3} HOO* + H^+ + e^- \tag{6}$$

$$HOO* \xrightarrow{\Delta G_4} * + O_2(g) + H^+ + e^- \tag{7}$$

where (g) and (l) are the gas and liquid phases, respectively. HO*, O*, and HOO* are the adsorbed intermediates in OER. The change in Gibbs free energy (ΔG) for every step can be described as:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_U + \Delta G_{pH} \tag{8}$$

where ΔE, ΔS, and ΔE_{ZPE} are the energy difference of adsorption, entropy, and zero-point energy, respectively. The ΔE is calculated from DFT, and the ΔE_{ZPE} as well as TΔS are obtained by DFT and the standard thermodynamic date. $\Delta G_U = -eU$, where U (U=0) and *e* are the potential at the standard hydrogen electrode and the charge transfer, respectively. ΔG_{pH}, which equals $-k_B T\ln 10 * pH$, is the Gibbs free energy corrected by H^+ concentration, and pH=0 is employed in this work. In addition, due to the poor DFT description for the high-spin ground state of O_2, $G_{O2,g}+4G_{H2,g}-2G_{H2O,l}=4.92$ eV is used to compute the G of the gas-phase O_2 ($G_{O2,g}$). The ΔG for the above four OER steps could be described as $\Delta G_1 = \Delta G_{HO*}$, $\Delta G_2 = \Delta G_{O*} - \Delta G_{HO*}$, $\Delta G_3 = \Delta G_{HOO*} - \Delta G_{O*}$, and $\Delta G_4 = 4.92 - \Delta G_{HOO*}$. The overpotential η of OER (η^{OER}) was calculated by equation (9) [4]:

$$\eta^{OER} = \frac{\max\{\Delta G_a, \Delta G_b, \Delta G_c, \Delta G_d\}}{e} - 1.23 \tag{9}$$

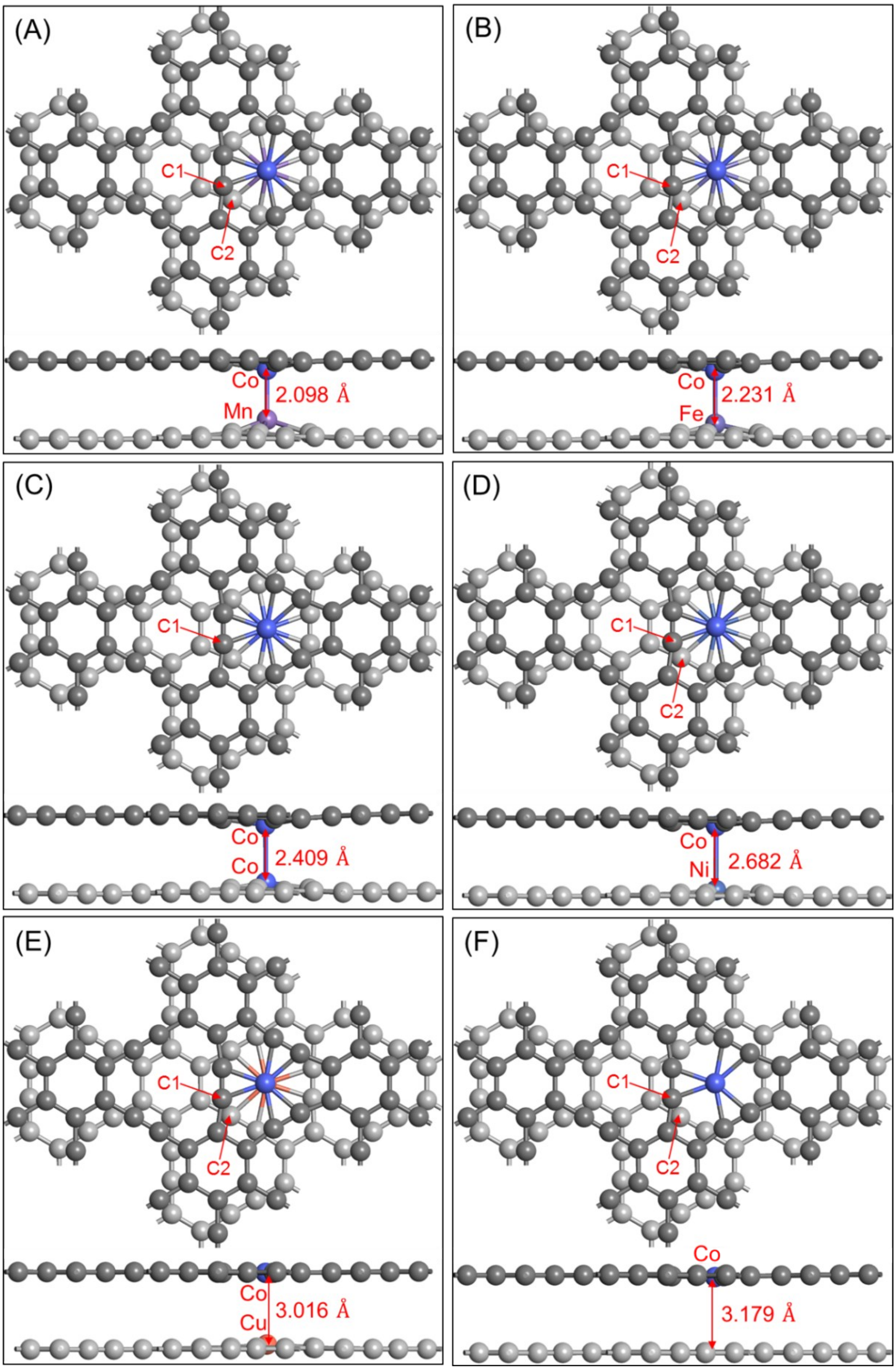

Figure S1. Top and side views of optimized structures and the active sites (Co, C1, TM, C2) of Co@GY/TM@GY (TM = Mn, Fe, Co, Ni, and Cu): (A) Co@GY/Mn@GY, (B) Co@GY/Fe@GY, (C) Co@GY/Co@GY, (D) Co@GY/Ni@GY, (E) Co@GY/Cu@GY and (F) Co@GY/GY. The gray balls are the carbon atoms of the top layer and the light gray balls are the carbon atoms of the bottom layer.

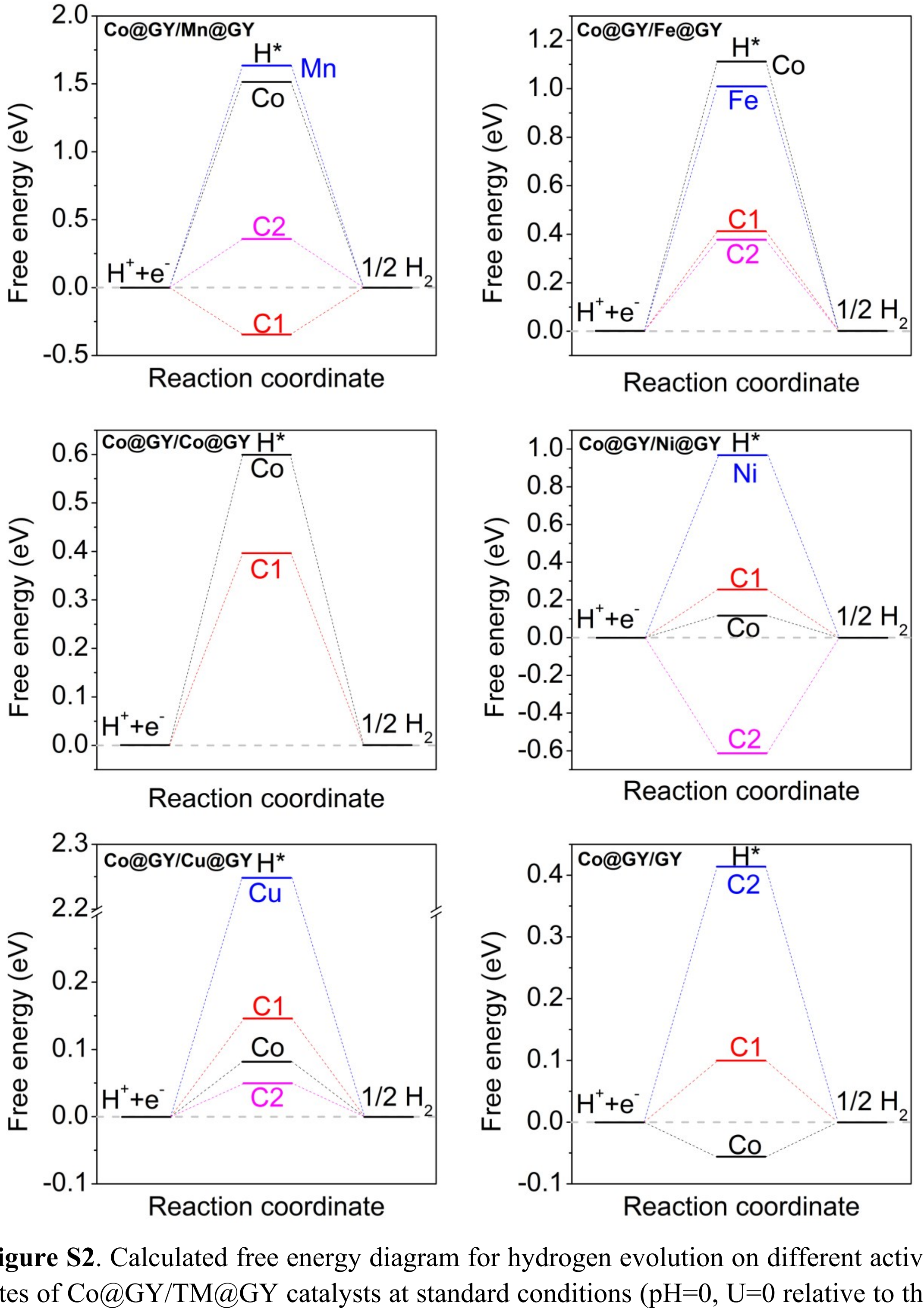

Figure S2. Calculated free energy diagram for hydrogen evolution on different active sites of Co@GY/TM@GY catalysts at standard conditions (pH=0, U=0 relative to the standard hydrogen electrode, and 298.15 K).

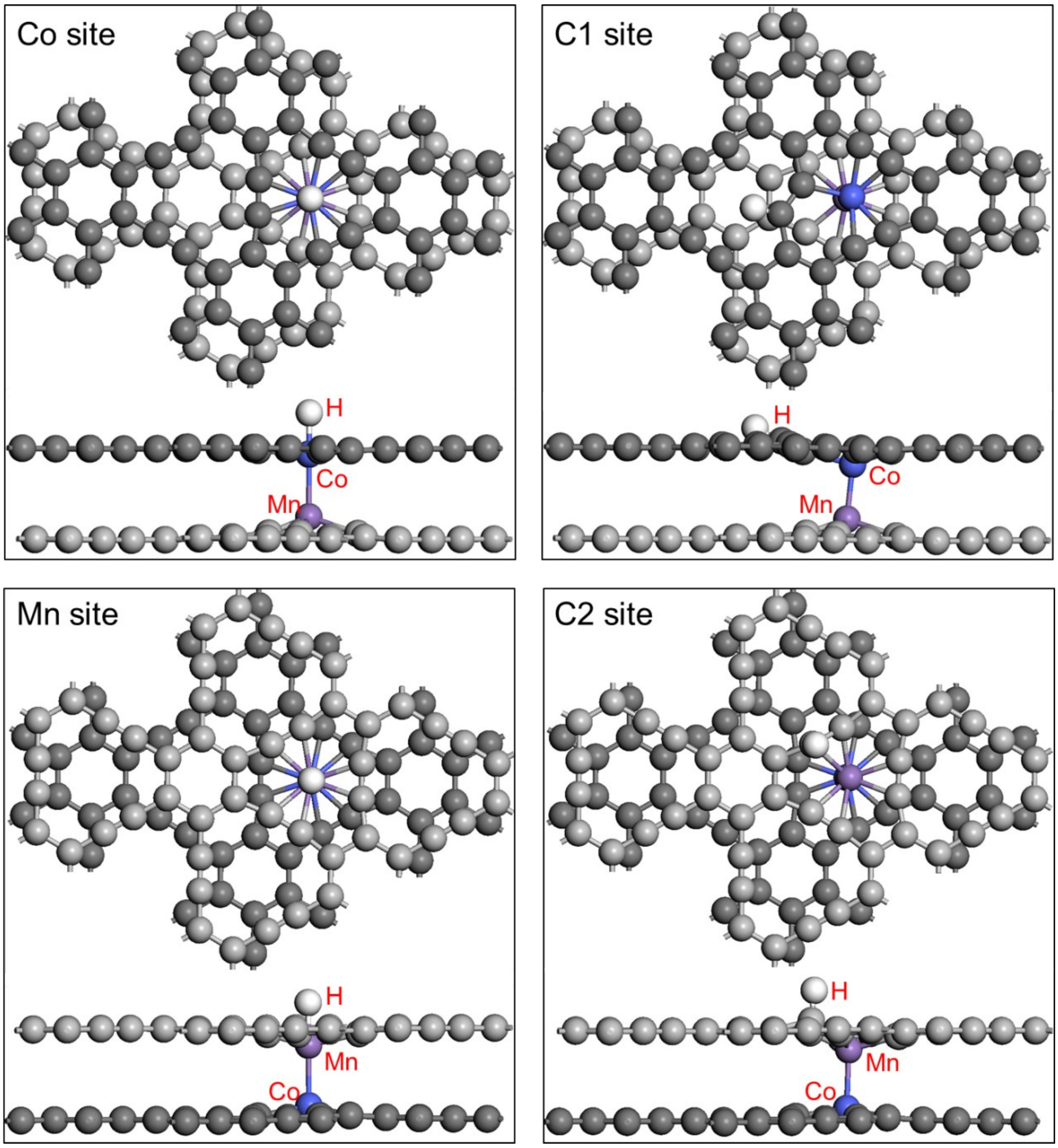

Figure S3. Adsorption configurations of H on different sites of the Co@GY/Mn@GY catalyst for HER. White, light grey, grey, blue, and violet balls represent H, C, C, Co, and Mn atoms, respectively.

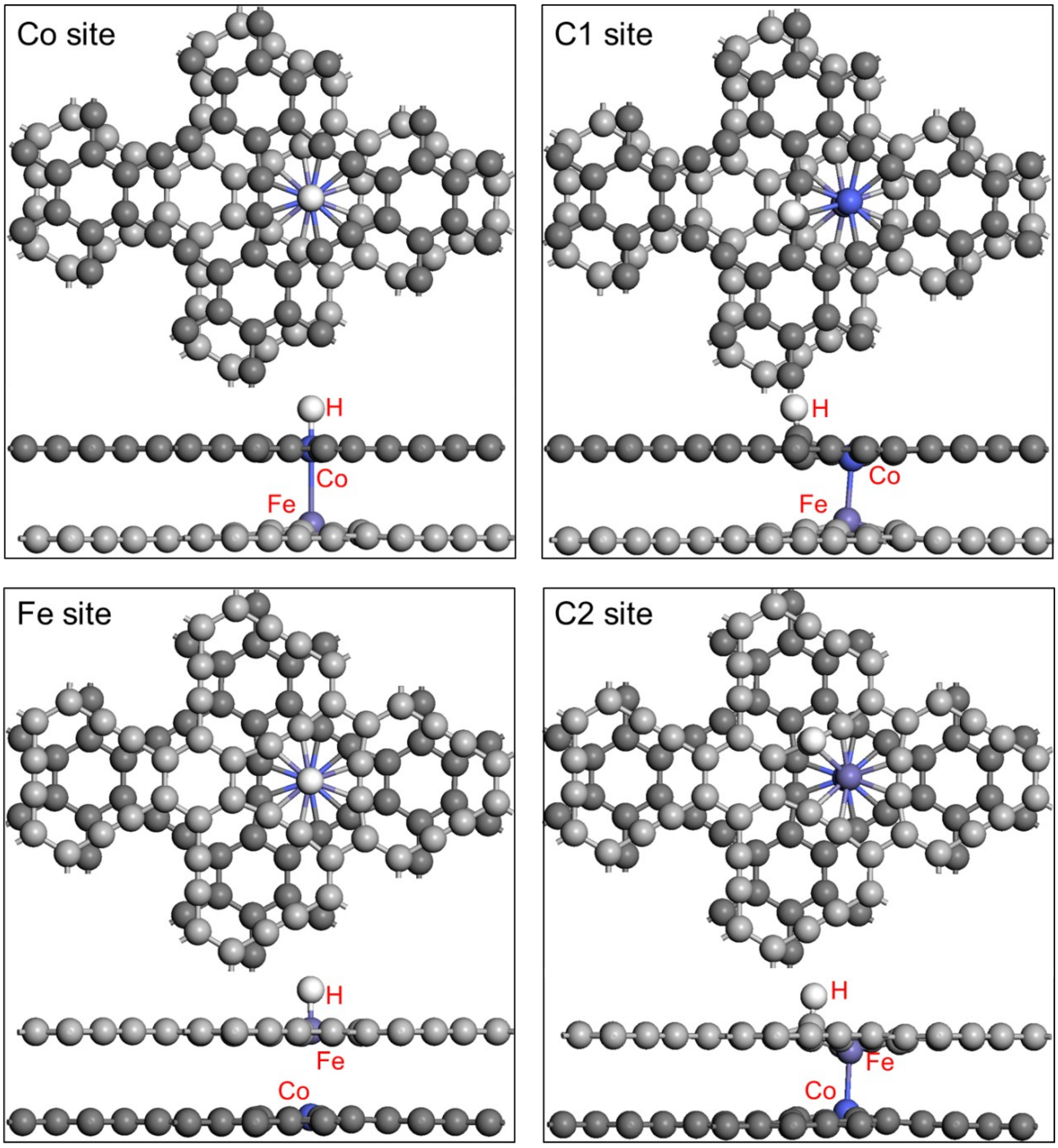

Figure S4. Adsorption configurations of H on different sites of the Co@GY/Fe@GY catalyst for HER. White, light grey, grey, blue, and light violet balls represent H, C, C, Co, and Fe atoms, respectivelyss.

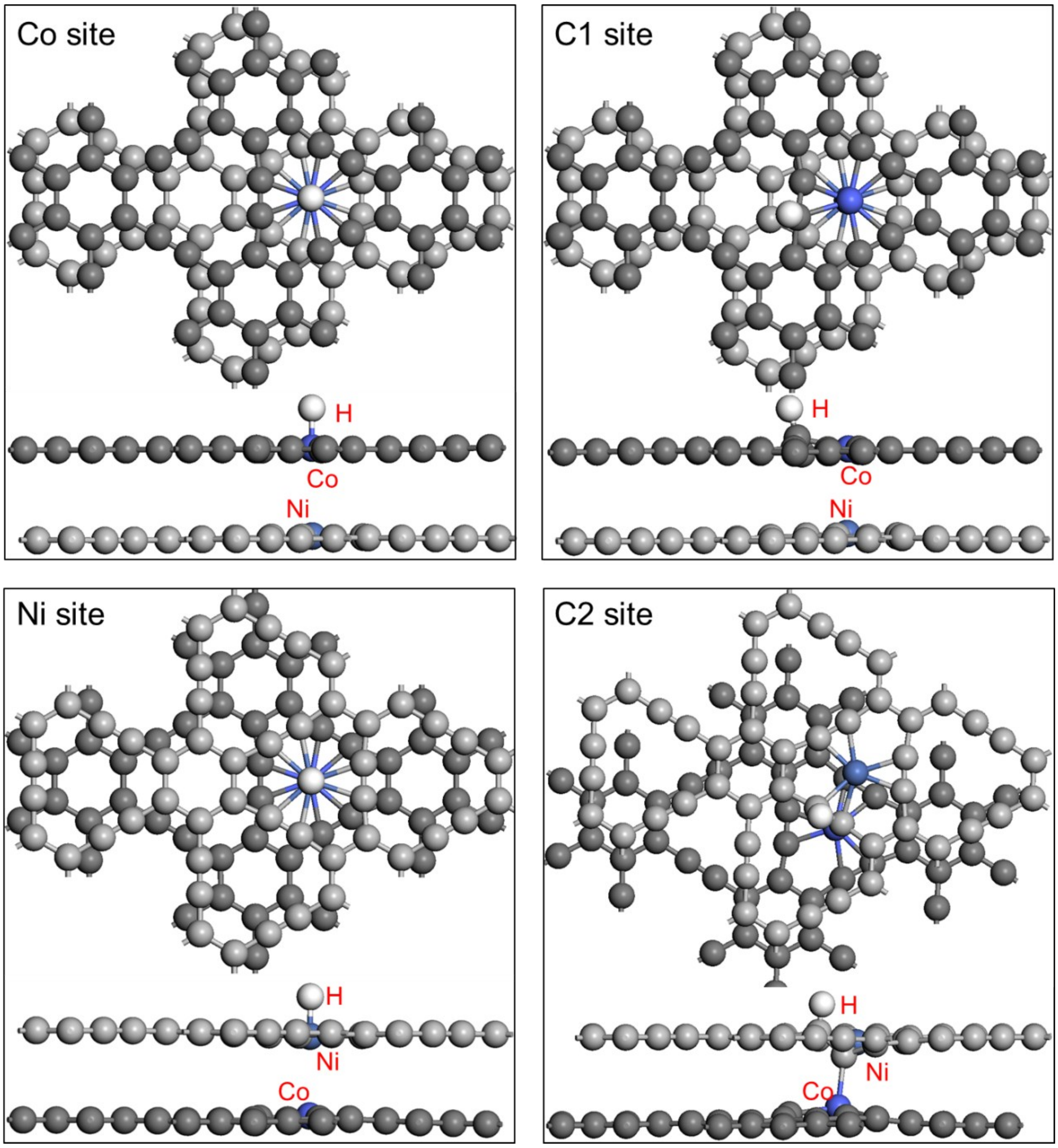

Figure S5. Adsorption configurations of H on different sites of the Co@GY/Ni@GY catalyst for HER. White, light grey, grey, blue, and light blue balls represent H, C, C, Co, and Ni atoms, respectively.

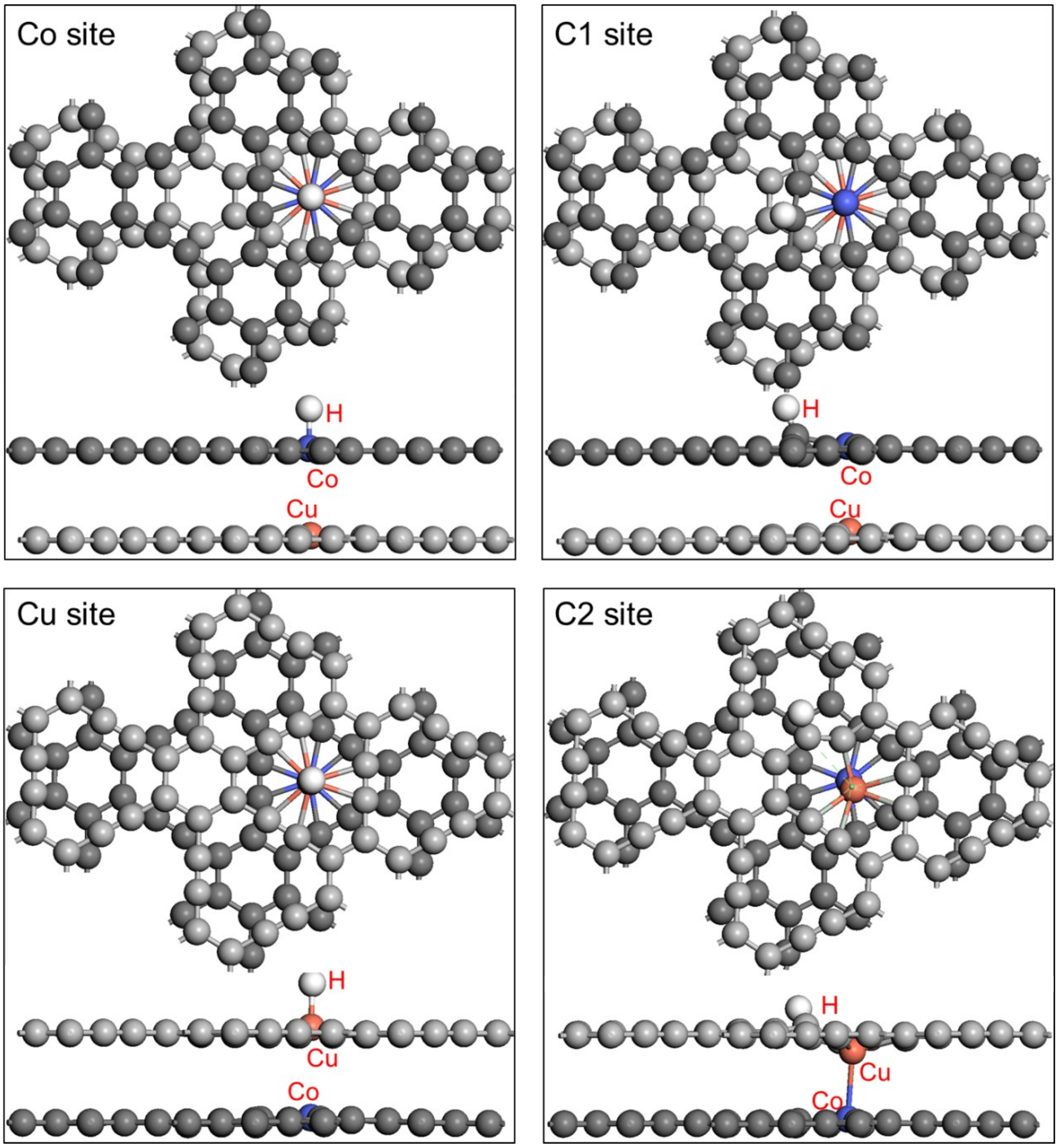

Figure S6. Adsorption configurations of H on different sites of the Co@GY/Cu@GY catalyst for HER. White, light grey, grey, blue, and orange balls represent H, C, C, Co, and Cu atoms, respectively.

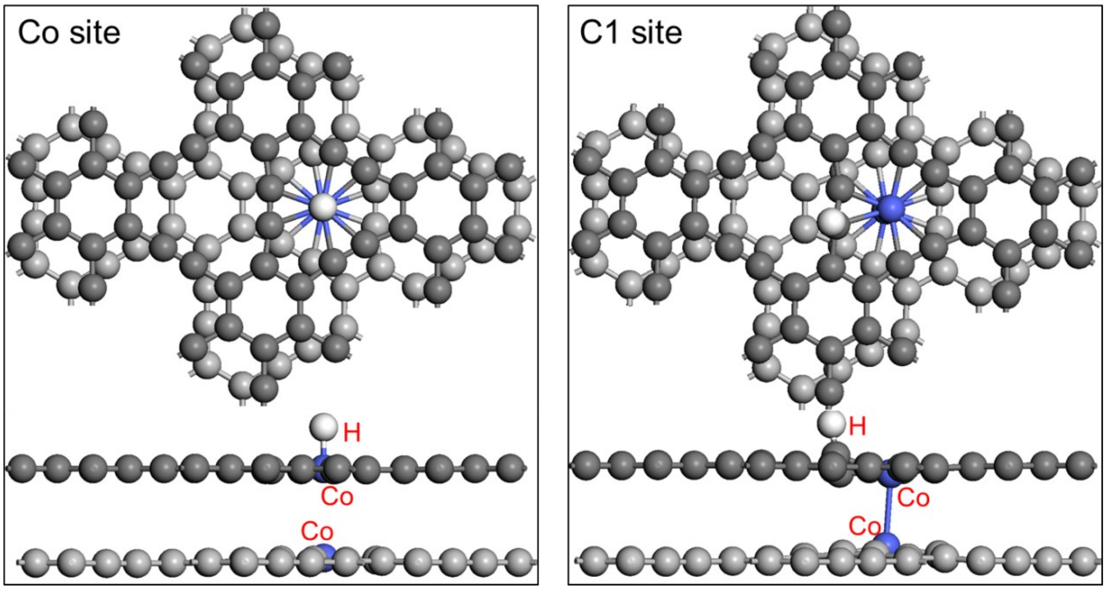

Figure S7. Adsorption configurations of H on different sites of the Co@GY/Co@GY catalyst for HER. White, light grey, grey, and blue balls represent H, C, C, and Co atoms, respectively.

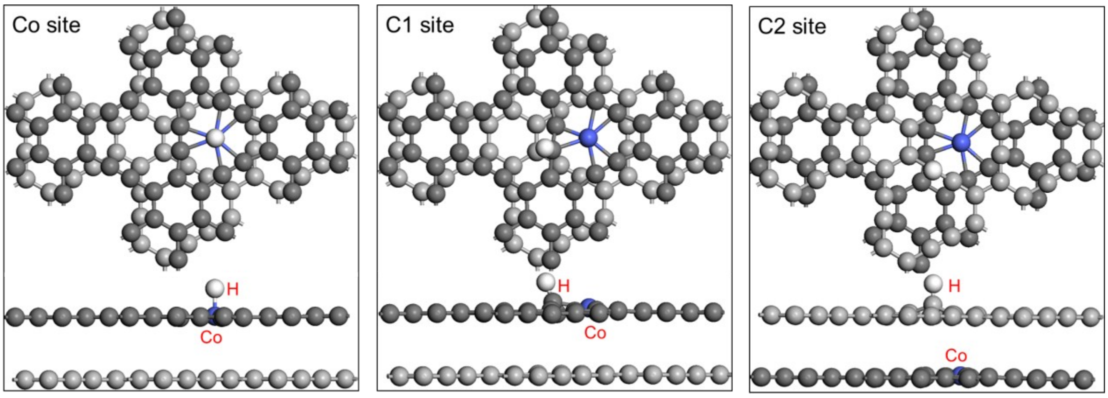

Figure S8. Adsorption configurations of H on different sites of the Co@GY/GY catalyst for HER. White, light grey, grey, and blue balls represent H, C, C, and Co atoms, respectively.

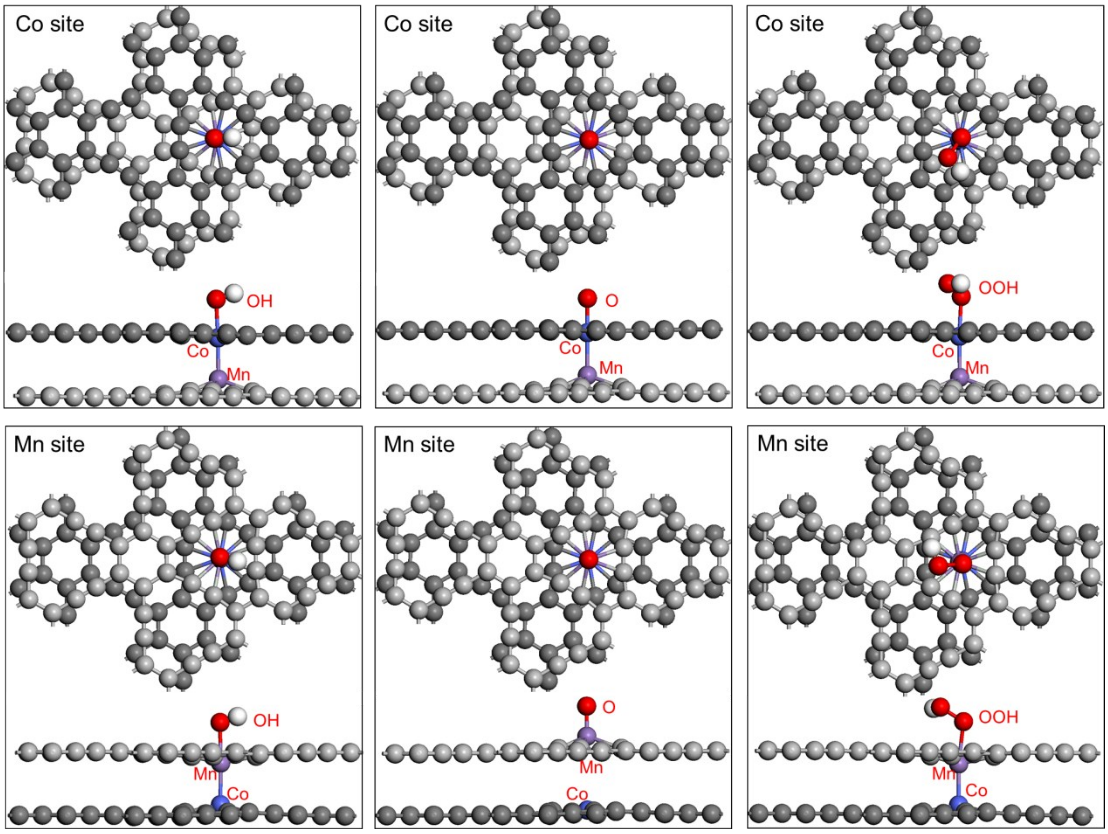

Figure S9. Adsorption configurations of OH, O, and OOH intermediates on the Co and Mn sites of the Co@GY/Mn@GY catalyst for OER. White, red, light grey, grey, blue, and violet balls represent H, O, C, C, Co, and Mn atoms, respectively.

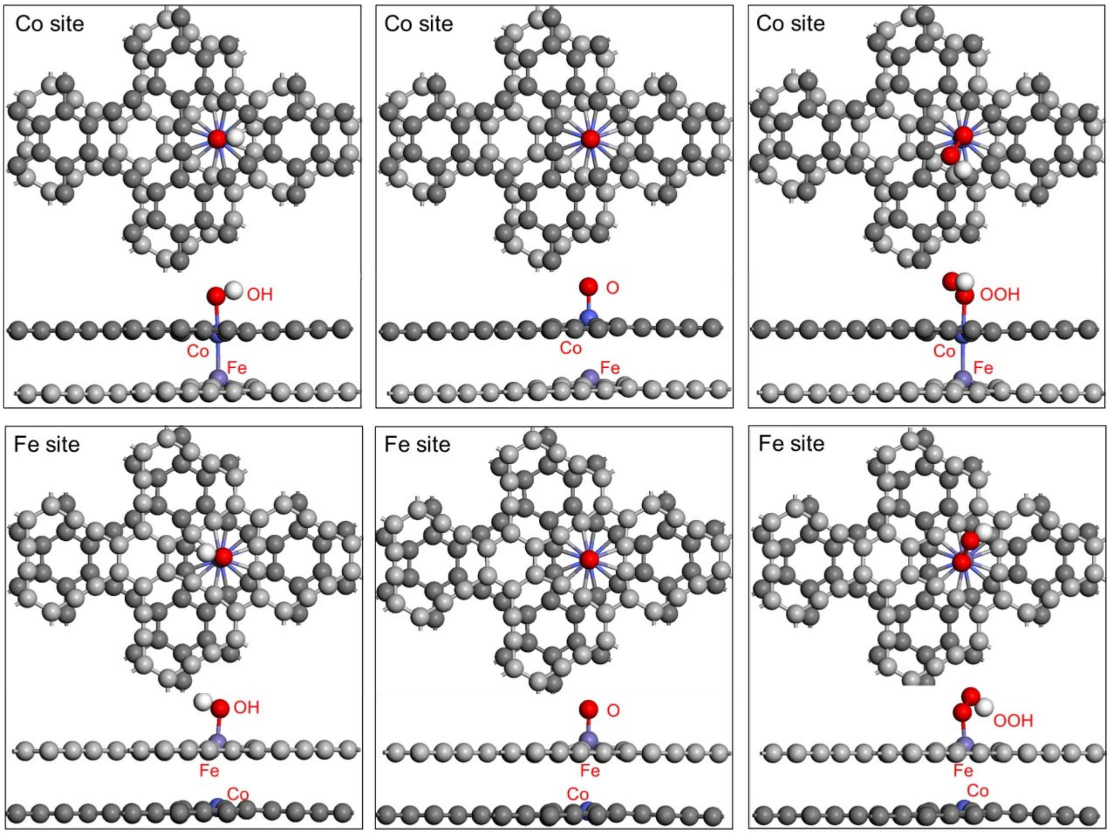

Figure S10. Adsorption configurations of OH, O, and OOH intermediates on the Co and Fe sites of the Co@GY/Fe@GY catalyst for OER. White, red, light grey, grey, blue, and light violet balls represent H, O, C, C, Co, and Fe atoms, respectively.

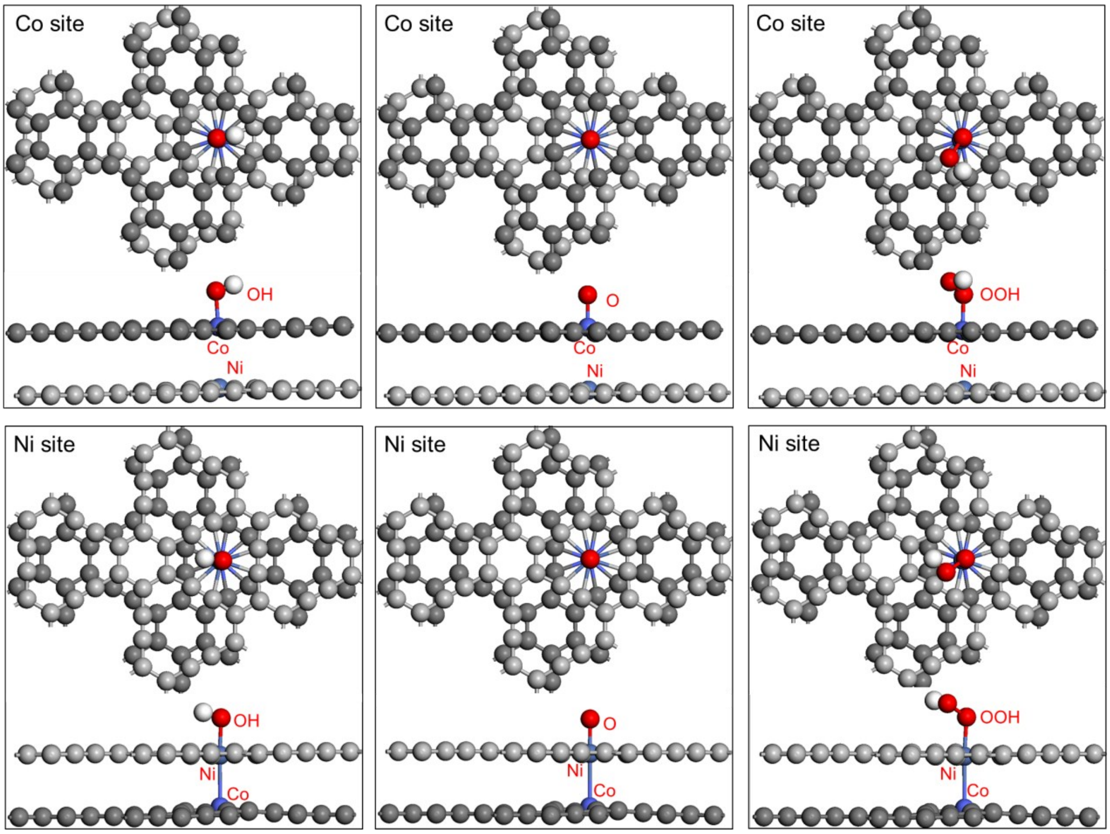

Figure S11. Adsorption configurations of OH, O, and OOH intermediates on the Co and Ni sites of the Co@GY/Ni@GY catalyst for OER. White, red, light grey, grey, blue, and light blue balls represent H, O, C, C, Co, and Ni atoms, respectively.

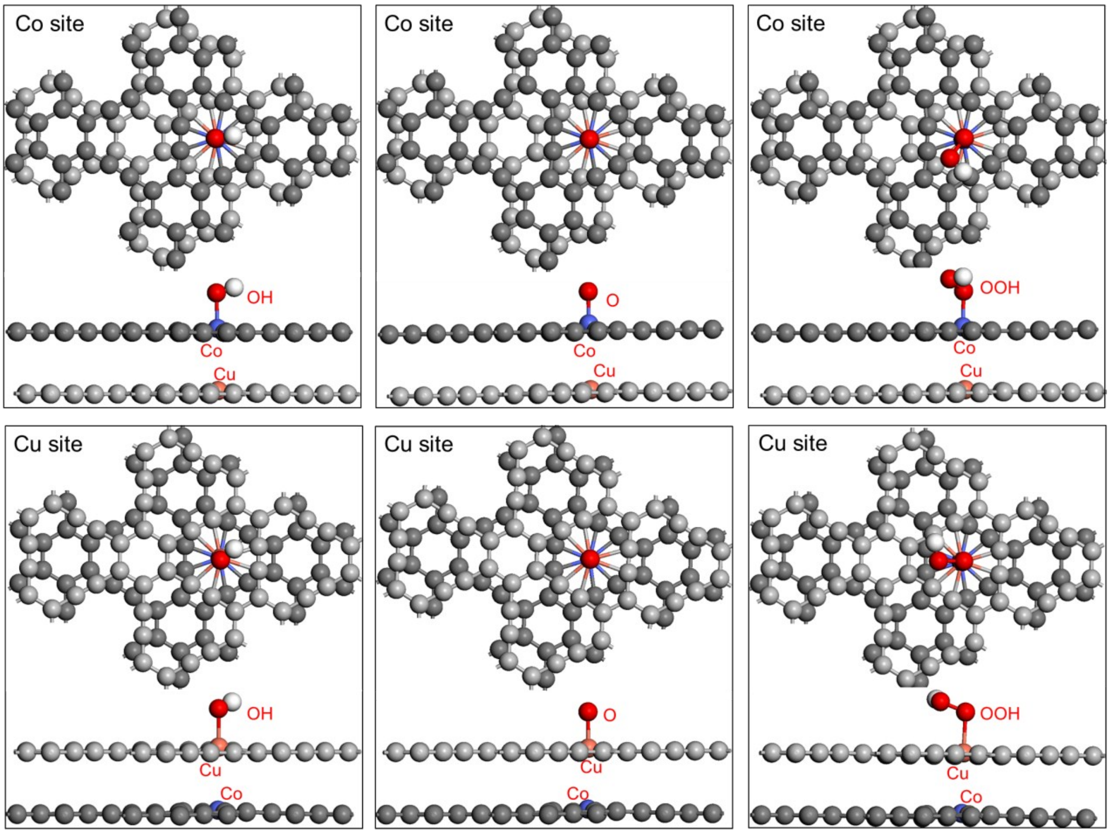

Figure S12. Adsorption configurations of OH, O, and OOH intermediates on the Co and Cu sites of the Co@GY/Cu@GY catalyst for OER. White, red, light grey, grey, blue, andorange balls represent H, O, C, C, Co, and Cu atoms, respectively.

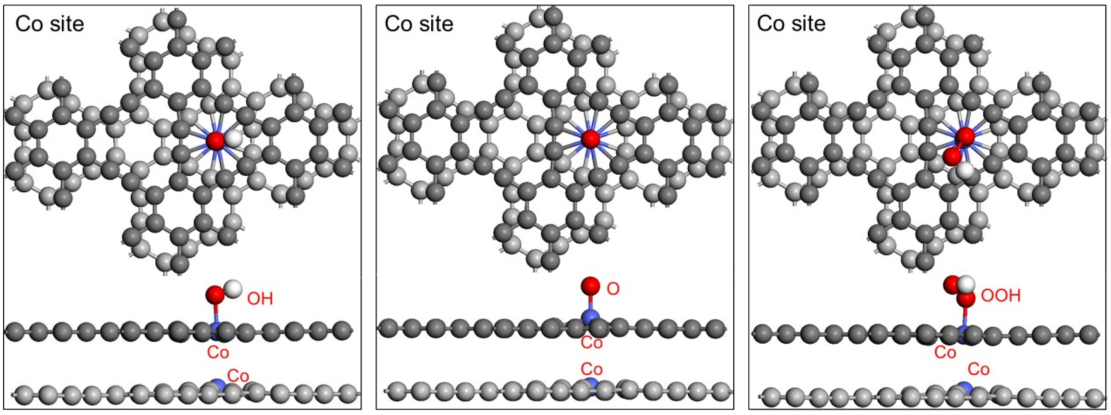

Figure S13. Adsorption configurations of OH, O, and OOH intermediates on the Co site of the Co@GY/Co@GY catalyst for OER. White, red, light grey, grey, and blue balls represent H, O, C, C, and Co atoms, respectively.

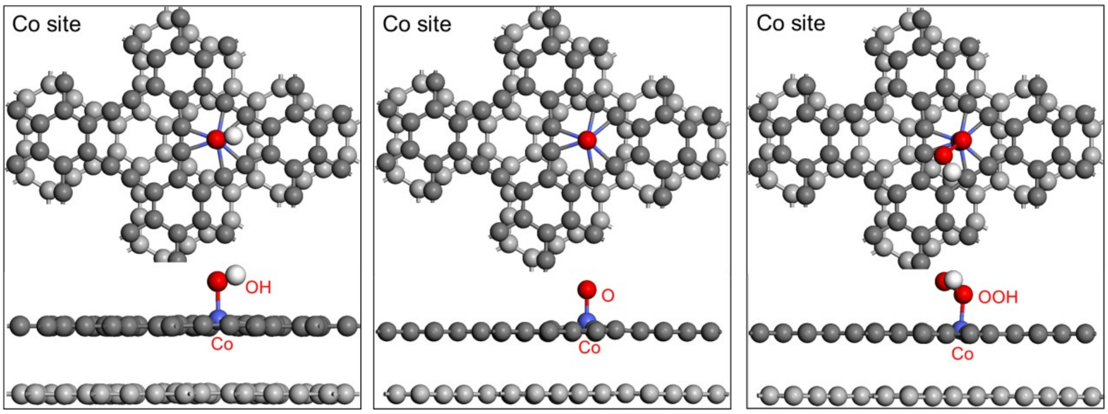

Figure S14. Adsorption configurations of OH, O, and OOH intermediates on the Co site of the Co@GY/GY catalyst for OER. White, red, light grey, grey, and blue balls represent H, O, C, C, and Co atoms, respectively.

Table S1 Vibrational frequencies of the intermediates adsorbed on Co@GY catalysts.

System	Vibration Frequencies (cm^{-1})
H*- Co@GY	390.66, 392.07, 2129.41
HO*- Co@GY	171.71, 185.91, 202.28, 549.43, 944.16, 3639.02
O*- Co@GY	190.5, 191.79, 735.99
HOO*- Co@GY	104.51, 142.18, 173.45, 276.49, 353.87, 520.01, 832.4, 1325.4, 3570.09

Table S2 The zero-point energy (ZPE) and entropic corrections (TS) in determining the free energy of reactants, intermediates, and products adsorbed on catalysts at 298K. For the adsorbates, the ZPE value is not sensitive to the metal and coordination since they have close value.

Species	ZPE(eV)	TS(eV)
H_2O	0.56	0.67
H_2	0.27	0.41
H*	0.16	0
O*	0.05	0
HO*	0.36	0
HOO*	0.40	0

Table S3 Calculated Gibbs free energy changes (eV) of the H atom binding on the Co (ΔG_H (Co)), C1 (ΔG_H (C1)), TM (ΔG_H (TM)) and C2 (ΔG_H (C2)) atoms for the Co@GY/TM@GY catalysts.

Co@GY/TM@GY	ΔG_H (Co)	ΔG_H (C1)	ΔG_H (TM)	ΔG_H (C2)
Co@GY/Mn@GY	1.514	−0.345	1.635	0.359
Co@GY/Fe@GY	1.112	0.412	1.009	0.378
Co@GY/Co@GY	0.600	0.396	0.600	0.396
Co@GY/Ni@GY	0.117	0.255	0.967	−0.613
Co@GY/Cu@GY	0.082	0.146	2.248	0.050
Co@GY/GY	−0.056	0.100	-	0.414

Table S4 Calculated over-potential on Co and TM atoms sites for the Co@GY/TM@GY and the over-potential of TM@GY catalysts on the previous study[5].

Co@GY/TM@GY	η^{OER} (V)		TM@GY[5]	η^{OER} (V)[5]
	Co site	TM site		
Co@GY/Mn@GY	0.92	2.96	Mn@GY	1.84
Co@GY/Fe@GY	0.98	1.62	Fe@GY	1.41
Co@GY/Co@GY	0.55	0.55	Co@GY	0.55
Co@GY/Ni@GY	0.38	0.86	Ni@GY	0.93
Co@GY/Cu@GY	0.78	1.21	Cu@GY	0.98
Co@GY/GY	0.53	-	GY	1.54

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