Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Molecule-level graphdiyne coordinated transition metals as new class of bifunctional electrocatalysts for oxygen reduction and oxygen electrode reactions

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Supplementary Figures

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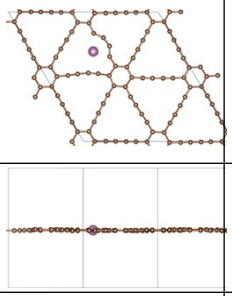
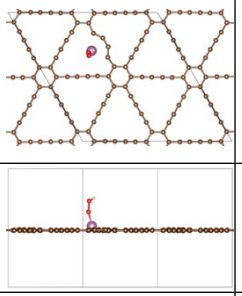
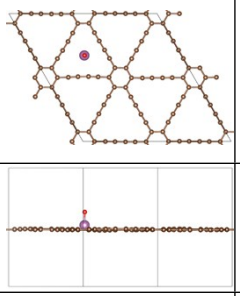
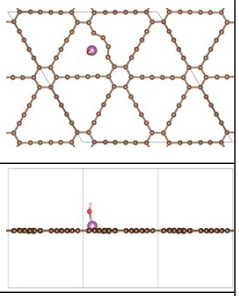
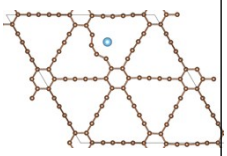
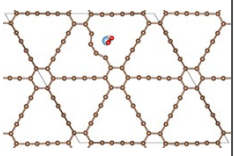
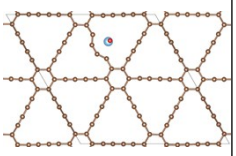
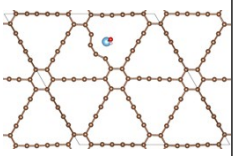
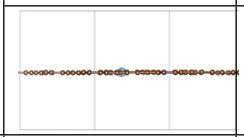
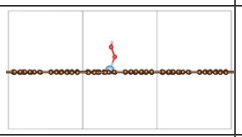
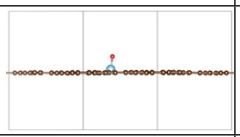
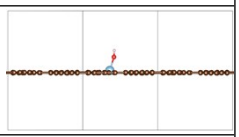
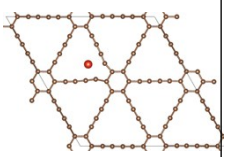
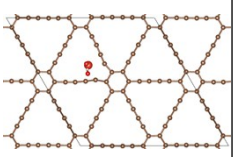
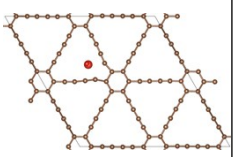
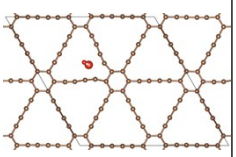
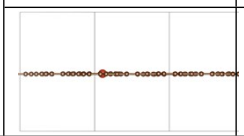
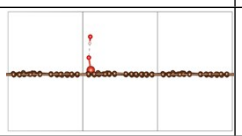
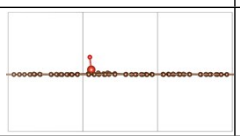
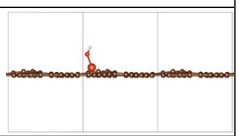
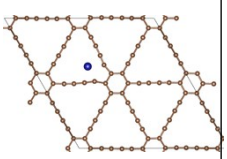
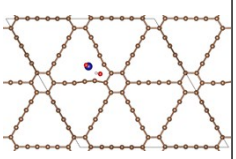
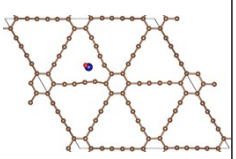
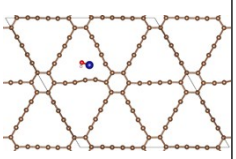
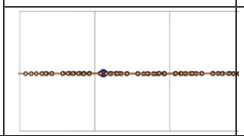
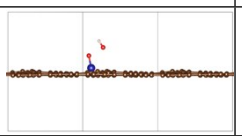
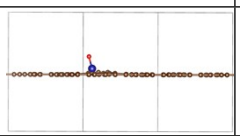
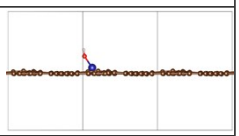
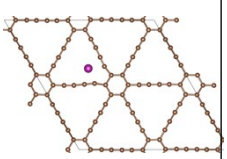
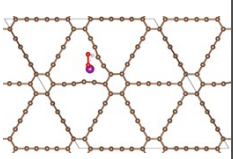
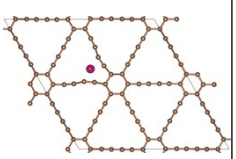
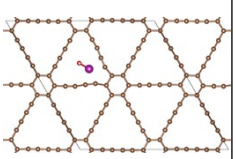
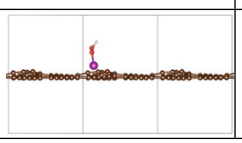
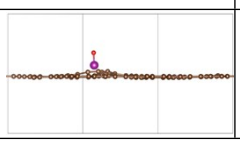
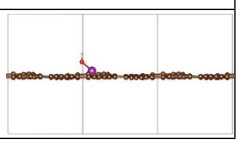
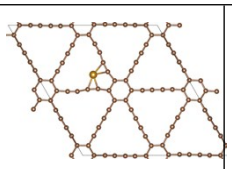
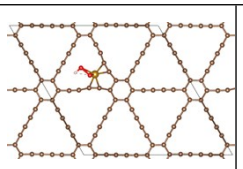
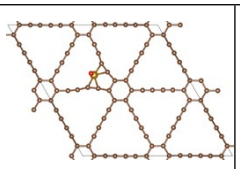
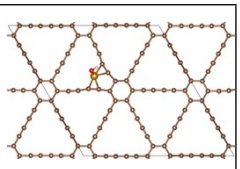
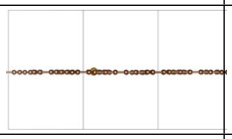
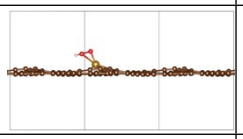
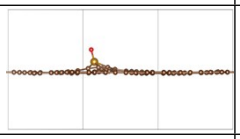
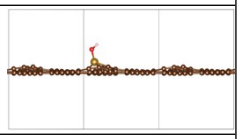
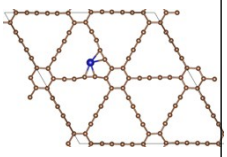
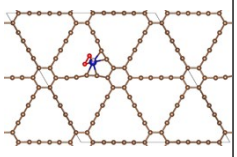
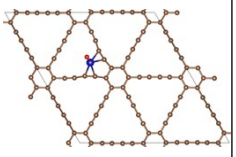
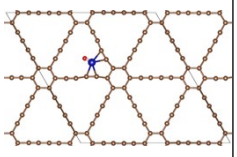
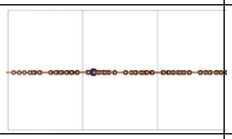
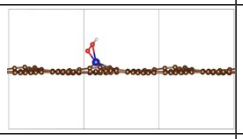
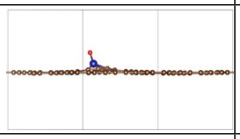
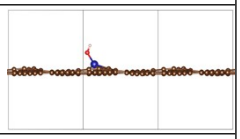
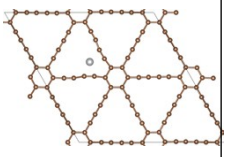
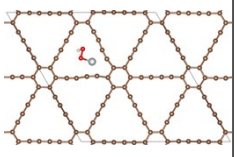
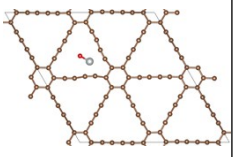
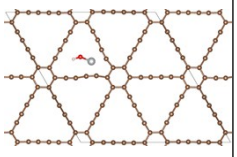
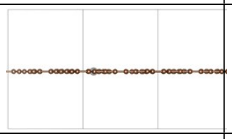
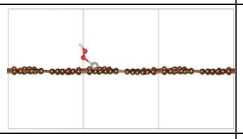
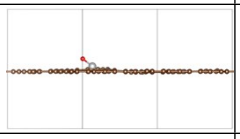
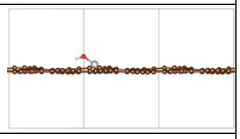
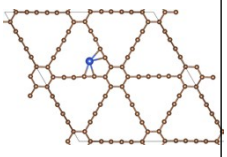
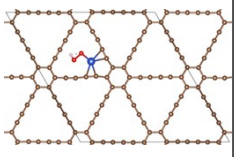
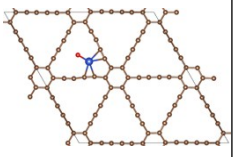
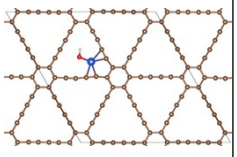
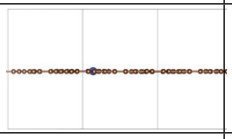
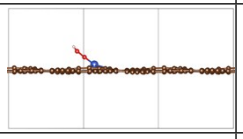
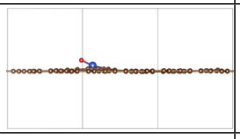
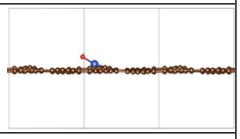
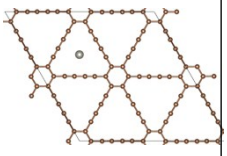
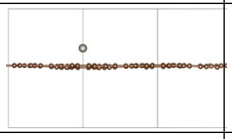
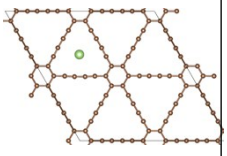
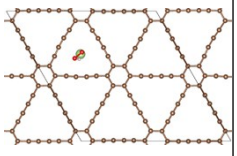
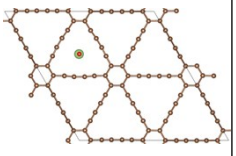
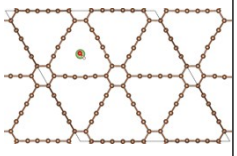
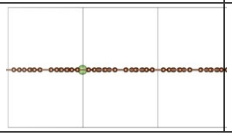
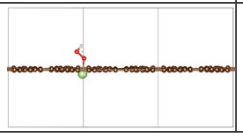
Sc@GDY				
Ti@GDY				
				
V@GDY				
				
Cr@GDY				
				
Mn@GDY				
				

Fe@GDY				
				
Co@GDY				
				
Ni@GDY				
				
Cu@GDY				
				
Zn@GDY		-	-	-
		-	-	-
Ga@GDY				
				

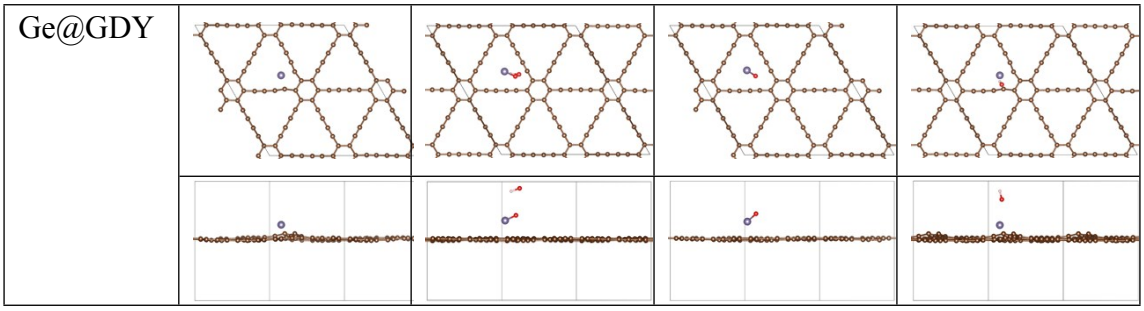


Fig. S1. Optimized stable geometries of TM@GDY and adsorption configurations of oxygenated intermediates on the surface of various TM@GDY sheets. The brown, red, and white balls represent C, O, and H atoms, respectively.

The captured Ge atom is located above the surface of GDY and is out of the GDY plane with a distance of 2.46 Å, when the Ge@GDY captures the OOH, O and OH. Thus, we take no account of Ge@GDY in the following ORR and OER calculations.

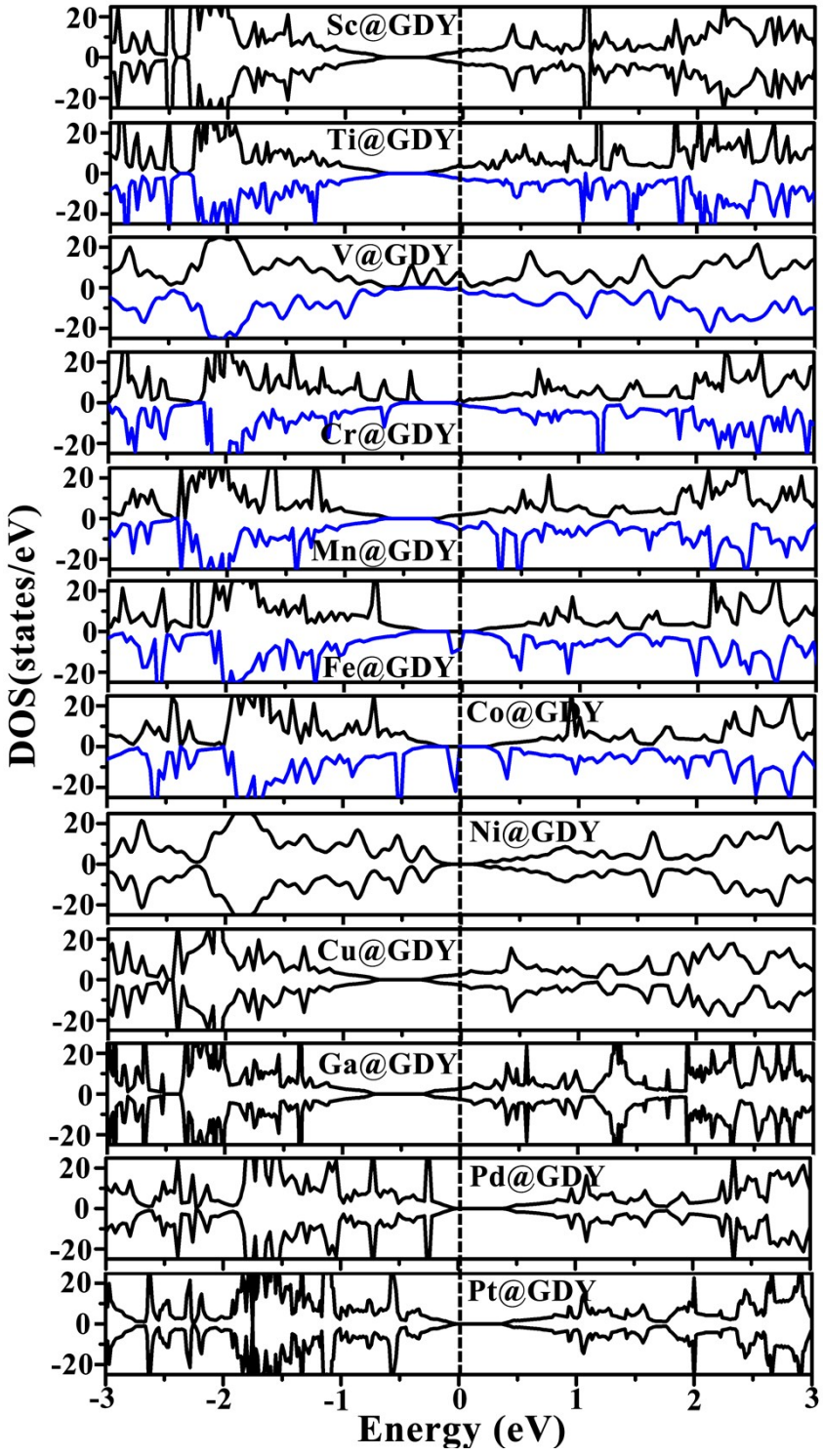


Fig. S2. The total density of states of TM@GDY systems.

The DOS of the considered TM@GDY systems shows that the Ni@GDY, Pd@GDY and Pt@GDY monolayers exhibit semiconductor, the Fe@GDY and Co@GDY monolayers exhibit half-metal character, and other TM@GDY systems exhibit metal character.

Supplementary Tables

Table S1 Zero point energy (*ZPE*) corrections and entropic contributions (at 298.15 K) to the free energies on TM@GDY systems.

Systems	Species	*O	*O_2	*OH	*OOH	O_2	H_2	H_2O
Mn@GDY	Δ*ZPE*	0.09	0.14	0.34	0.39	0.10	0.27	0.56
	*T*Δ*S*	0.03	0.16	0.09	0.21	0.64	0.41	0.67
Ni@GDY	Δ*ZPE*	0.09	0.14	0.35	0.40	0.10	0.27	0.56
	*T*Δ*S*	0.03	0.15	0.09	0.21	0.64	0.41	0.67

Table S2 Binding energy (E_b) of TM atom and GDY, cohesive energy of bulk metal (E_{coh}), energy difference (ΔE_b) between binding energy (E_b) and cohesive energy (E_{coh}), total magnetic moments (M_{tot}) and the amounts of charge (ΔQ) transmitted from the TM atoms to the GDY monolayers ('-' means losing electrons) of TM @ GDY structure.

Systems	Sc@GDY	Ti@GDY	V@GDY	Cr@GDY	Mn@GDY
E_b (eV)	6.49	6.39	5.33	3.92	4.11
E_{coh}(eV)	4.19	5.46	5.37	4.01	3.86
ΔE_b(eV)	2.30	0.93	-0.04	-0.08	0.25
ΔQ (e)	+1.43	+1.28	+1.04	+0.89	+0.83
$M_{tot}(\mu_B)$	0	1.15	2.55	3.64	3.54
Systems	Fe@GDY	Co@GDY	Ni@GDY	Cu@GDY	Zn@GDY
E_b (eV)	5.02	5.56	6.75	3.80	0.92
E_{coh}(eV)	4.78	5.36	4.90	3.51	1.12
ΔE_b(eV)	0.24	0.20	1.85	0.29	-0.20
ΔQ (e)	+0.50	+0.61	+0.49	+0.47	-
$M_{tot}(\mu_B)$	2	1	0	0	0
Systems	Ga@GDY	Ge@GDY	Pd@GDY	Pt@GDY	-
E_b (eV)	3.64	3.81	4.42	4.98	-
E_{coh}(eV)	2.31	3.73	3.74	4.86	-
ΔE_b(eV)	1.33	0.08	0.68	0.12	-
ΔQ (e)	+0.67	-	+0.71	+0.11	-
$M_{tot}(\mu_B)$	0	0	0	0	-

Table S3 Gibbs adsorption free energy values (eV) of key oxygenated intermediates involved in the ORR on TM@GDY structures.

Systems	Δ*G**OOH(eV)	Δ*G**O(eV)	Δ*G**OH(eV)
Sc@GDY	0.26	-1.70	-1.91
Ti@GDY	-0.30	-2.91	-2.35
V@GDY	-0.49	-2.77	-2.68
Cr@GDY	0.10	-2.05	-1.38
Mn@GDY	0.77	-1.70	-1.02
Fe@GDY	0.65	-1.10	-0.83
Co@GDY	1.64	-0.22	-0.57
Ni@GDY	1.52	0.21	0.01
Cu@GDY	1.23	1.02	-0.50
Ga@GDY	1.66	1.38	-0.27
Pd@GDY	2.11	1.76	0.69
Pt@GDY	1.81	1.15	0.21

Table S4 Onset overpotentials of OER and ORR, *d*-band center for TM@GDY structures.

Systems	η^{ORR} (V)	η^{OER} (V)	*d*-band (eV)
Sc@GDY	2.14	-1.28	1.33
Ti@GDY	2.58	-1.94	0.58
V@GDY	2.32	-1.64	0.70
Cr@GDY	1.62	-1.47	0.60
Mn@GDY	1.25	-1.86	-0.50
Fe@GDY	1.07	-1.07	-0.60
Co@GDY	0.81	-0.60	-1.20
Ni@GDY	0.23	-0.63	-0.90
Cu@GDY	0.73	-0.84	-3.60
Ga@GDY	0.51	-0.98	-0.27
Pd@GDY	0.53	-0.39	-0.75
Pt@GDY	0.23	-0.27	-2.17

Supplementary note

Note S1

According to the developed theories for metal or other catalyst surfaces, the ORR electrocatalytic activity descriptors of a given catalyst are governed by the adsorption free energies of ORR intermediates including OOH*, O*, and OH*. The Gibbs adsorption free energy values of the different oxygenated intermediates (ΔG_{*O2}, ΔG_{*OOH}, ΔG_{*O}, and ΔG_{*OH}) are calculated as the following four reactions, respectively.

$$*+3OH^- \leftrightarrow *OOH+H_2O \quad \Delta G_{OOH*}=G_{*OOH}+G_{H2O}-G^*-3G_{OH^-} \tag{1}$$

$$*+2OH^- \leftrightarrow *O+H_2O \quad \Delta G_{O*}=G_{*O}+G_{H2O}-G^*-2G_{OH^-} \tag{2}$$

$$*+OH^- \leftrightarrow *OH \quad \Delta G_{OH*}=G_{*OH}-G^*-G_{OH^-} \tag{3}$$

Then, the ORR and OER reaction pathway on the strongest TM@GDY models were calculated. In alkaline media, the four electron ORR pathway could be summarized by the following elementary steps:

$$O_2+*+H_2O+e^- \leftrightarrow *OOH+OH^- \tag{SR$_1$}$$

$$*OOH+e^- \leftrightarrow *O+OH^- \tag{SR$_2$}$$

$$*O+H_2O+e^- \leftrightarrow *OH+OH^- \tag{SR$_3$}$$

$$*OH+e^- \leftrightarrow * + OH^- \tag{SR$_4$}$$

where * stands for an adsorption site on catalysts.

At electrode potential U^0, the ΔG for each step can be calculated by the following relations.

$$\Delta G_1 = G_{*OOH} + G_{OH^-} - G_{O2} - G_* - G_{H2O} + eU^0$$

$$= G_{*OOH} + G_{H2O} - G^* - 3G_{OH^-} - G_{H2O} + 3G_{OH^-} + G_{OH} - G_{O2} - G_{H2O} + eU^0$$

$$= \Delta G_{OOH*} - 2G_{H2O} + 4G_{OH^-} - G_{O2} + eU^0$$

$$= \Delta G_{OOH*} - 4eU^0 + eU^0$$

$$= \Delta G_{OOH*} - 3eU^0 \tag{4}$$

$$\Delta G_2 = G_{*O} + G_{OH^-} - G_{*OOH} + eU^0$$

$$= G_{*O} + G_{H2O} - G^* - 2G_{OH^-} - G_{H2O} + G^* + 2G_{OH^-} + G_{OH} - G_{*OOH} + eU^0$$

$$= \Delta G_{O^*} - G_{H2O} + G^* + 2G_{OH^-} + G_{OH} - (G_{*OOH} + G_{H2O} - G^* - 3G_{OH^-}) + G_{H2O} - G^* - 3G_{OH^-} + eU^0$$

$$= \Delta G_{O^*} - G_{H2O} + G^* + 2G_{OH^-} + G_{OH} - \Delta G_{OOH^*} + G_{H2O} - G^* - 3G_{OH^-} + eU^0$$

$$= \Delta G_{O^*} - \Delta G_{OOH^*} + eU^0 \quad (5)$$

$$\Delta G_3 = G_{*OH} + G_{OH^-} - G_{*O} - G_{H2O} + eU^0$$

$$= G_{*OH} - G^* - G_{OH^-} + G^* + G_{OH^-} + G_{OH^-} - (G_{*O} + G_{H2O} - G^* - 2G_{OH^-}) + G_{H2O} - G^* - 2G_{OH^-} - G_{H2O} + eU^0$$

$$= \Delta G_{OH^*} + G^* + G_{OH^-} + G_{OH} - \Delta G_{O^*} + G_{H2O} - G^* - 2G_{OH^-} - G_{H2O} + eU^0$$

$$= \Delta G_{OH^*} - \Delta G_{O^*} + eU^0 \quad (6)$$

$$\Delta G_4 = G_{OH^-} + G_* - G_{OH^*} + eU^0$$

$$= G_{OH^-} + G_* - (G_{*OH} - G^* - G_{OH^-}) - G^* - G_{OH^-} + eU^0$$

$$= -\Delta G_{OH^*} + eU^0 \quad (7)$$

In alkaline media, the OER pathway could be summarized as,

$$*+OH \leftrightarrow *OH^- + e^- \quad (SR_a)$$

$$*OH + OH^- \leftrightarrow *O + H_2O + e^- \quad (SR_b)$$

$$*O + OH^- \leftrightarrow *OOH + e^- \quad (SR_c)$$

$$*OOH + OH^- \leftrightarrow * + O_2(g) + H_2O + e^- \quad (SR_d)$$

where * stands for an adsorption site on catalysts.

At electrode potential U^0, the ΔG for each step can be calculated by the following relations.

$$\Delta G_a = G_{OH^*} - eU^0 - G_{OH^-} - G_*$$

$$= G_{*OH} - G^* - G_{OH^-} + G^* + G_{OH^-} - eU^0 - G_{OH^-} - G_*$$

$$= \Delta G_{OH^*} - eU^0$$

$$= -\Delta G_4 \quad (8)$$

$$\Delta G_b = G_{*O} + G_{H2O} - eU^0 - G_{*OH} + G_{OH^-}$$

$$= G_{*O} + G_{H2O} - G^* - 2G_{OH^-} + G^* + 2G_{OH^-} - eU^0 - (G_{*OH} - G^* - G_{OH-}) - G^* - G_{OH-} + G_{OH-}$$

$$= \Delta G_{O^*} + G^* + 2G_{OH^-} - eU^0 - \Delta G_{OH^*} - G^* - G_{OH^-} + G_{OH^-}$$

$$= \Delta G_{O^*} - \Delta G_{OH^*} - eU^0$$

$$= -\Delta G_3 \quad (9)$$

$$\Delta G_c = G_{*OOH} - eU^0 - G_{*O} - G_{OH-}$$

$$= G_{*OOH} + G_{H2O} - G^* - 3G_{OH^-} - G_{H2O} + G^* + 3G_{OH^-} - eU^0 - (G_{*O} + G_{H2O} - G^* - 2G_{OH-}) + G_{H2O} - G^* - 2G_{OH^-} - G_{OH-}$$

$$= \Delta G_{OOH^*} - G_{H2O} + G^* + 3G_{OH^-} - eU^0 - \Delta G_{O^*} + G_{H2O} - G^* - 2G_{OH^-} - G_{OH^-}$$

$$= \Delta G_{OOH^*} - \Delta G_{O^*} - eU^0$$

$$= -\Delta G_2 \quad (10)$$

$$\Delta G_d = G_* + G_{H2O} + G_{O2} - eU^0 - G_{*OOH} - G_{OH^-}$$

$$= G_* + G_{H2O} + G_{O2} - eU^0 - (G_{*OOH} + G_{H2O} - G^* - 3G_{OH^-}) + G_{H2O} - G^* - 3G_{OH^-} - G_{OH^-}$$

$$= -\Delta G_{OOH^*} + 2G_{H2O} - 4G_{OH^-} + G_{O2} - eU^0$$

$$= -\Delta G_{OOH^*} + 4eU^0 - eU^0$$

$$= -\Delta G_{OOH^*} + 3eU^0$$

$$= -\Delta G_1 \quad (11)$$

The onset overpotential (η) which used to evaluate the performance of ORR and OER can be obtained as follows.

$$\eta^{ORR} = \max[\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4]/e - 0.22eV \quad (12)$$

$$\eta^{OER} = \max[\Delta G_a, \Delta G_b, \Delta G_c, \Delta G_d]/e + 0.22eV \quad (13)$$

The relationship for the Gibbs free energy and the *OOH, *O, and *OH intermediates for the different TM@GDY monolayers can be expressed as the following two reactions.

$$\Delta G_{OOH^*} = 0.84\Delta G_{OH^*} + 1.67 \quad (14)$$

$$\Delta G_{O^*} = 1.50\Delta G_{OH^*} + 0.75 \quad (15)$$

Based on the linear relationship between ΔG_{*OOH}, ΔG_{*O} and ΔG_{*OH}, the equations describing the ORR process for the dual volcano plot are therefore.

$$\eta^{ORR}=0.84\Delta G\text{OH}^* +0.085 \quad \Delta\text{GOH}^* \geq 0.082 \text{ eV} \tag{16}$$

$$\eta^{ORR}=-\Delta G\text{OH}^* +0.235 \quad \Delta\text{GOH}^* \leq 0.082 \text{ eV} \tag{17}$$

The equations describing the OER process for the dual volcano plot are therefore.

$$\eta^{OER}=0.66\Delta G\text{OH}^* -0.245 \quad \Delta G\text{OH}^* \leq 0.146 \text{ eV} \tag{18}$$

$$\eta^{OER}=-0.50\Delta G\text{OH}^* -0.075 \quad 0.146 \text{ eV} \leq \Delta G\text{OH}^* \leq 1.5 \text{ eV} \tag{19}$$

$$\eta^{OER}=-\Delta G\text{OH}^* +0.675 \quad \Delta G\text{OH}^* \geq 1.5 \text{ eV} \tag{20}$$