Electronic Supplementary Material (ESI) for Nanoscale.

Theoretical Insight into Single Rh Atom Anchored on N-Doped γ-Graphyne as Excellent Bifunctional Electrocatalyst for OER and ORR: Electronic Regulation of Graphite Nitrogen

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1. Calculation details of reaction mechanism, free energies, and overpotentials

1.1 Reaction mechanism

The OER process consists of four elementary steps as follows,[1]

$$H_2O(l) + * \rightarrow OH^* + H^+ + e^- \quad \text{(S1-1)}$$

$$OH^* \rightarrow O^* + H^+ + e^- \quad \text{(S1-2)}$$

$$H_2O(l) + O^* \rightarrow OOH^* + H^+ + e^- \quad \text{(S1-3)}$$

$$OOH^* \rightarrow O_2(g) + * + H^+ + e^- \quad \text{(S1-4)}$$

and the ORR progress is regarded as the reverse reaction of OER and is described as follows,[2]

$$O_2(g) + * + H^+ + e^- \rightarrow OOH^* \quad \text{(S2-1)}$$

$$OOH^* + H^+ + e^- \rightarrow H_2O(l) + O^* \quad \text{(S2-2)}$$

$$O^* + H^+ + e^- \rightarrow OH^* \quad \text{(S2-3)}$$

$$OH^* + H^+ + e^- \rightarrow H_2O(l) + * \quad \text{(S2-4)}$$

where $*$ represents the activate site on the catalysts surface and O^*, OH^*, and OOH^* are the adsorbed intermediates.

1.2 Free energies

The reaction free energies of OER/ORR four elementary steps (ΔG_1, ΔG_2, ΔG_3, and ΔG_4) are calculated by[3]

$$\Delta G_1 = G_{OH^*} + G_{H^+ + e^-} - G_{H_2O(l)} - G_* \quad \text{(S3-1)}$$

$$\Delta G_2 = G_{O^*} + G_{H^+ + e^-} - G_{OH^*} \quad \text{(S3-2)}$$

$$\Delta G_3 = G_{OOH^*} + G_{H^+ + e^-} - G_{H_2O(l)} - G_{O*} \quad \text{(S3-3)}$$

$$\Delta G_4 = G_* + G_{O_{2(g)}} + G_{H^+ + e^-} - G_{OOH^*} \quad \text{(S3-4)}$$

The Gibbs adsorption free energies of OER/ORR intermediates (ΔG_{OH^*}, ΔG_{O^*}, and ΔG_{OOH^*}) are calculated by[4]

$$\Delta G_{OH^*} = G_{OH^*} - G_* - G_{H_2O(l)} + \frac{1}{2}G_{H_2(g)} \quad \text{(S4-1)}$$

$$\Delta G_{O^*} = G_{O^*} - G_* - G_{H_2O(l)} + G_{H_2(g)} \quad \text{(S4-2)}$$

$$\Delta G_{OOH^*} = G_{OOH^*} - G_* - 2G_{H_2O(l)} + \frac{3}{2}G_{H_2(g)} \quad \text{(S4-3)}$$

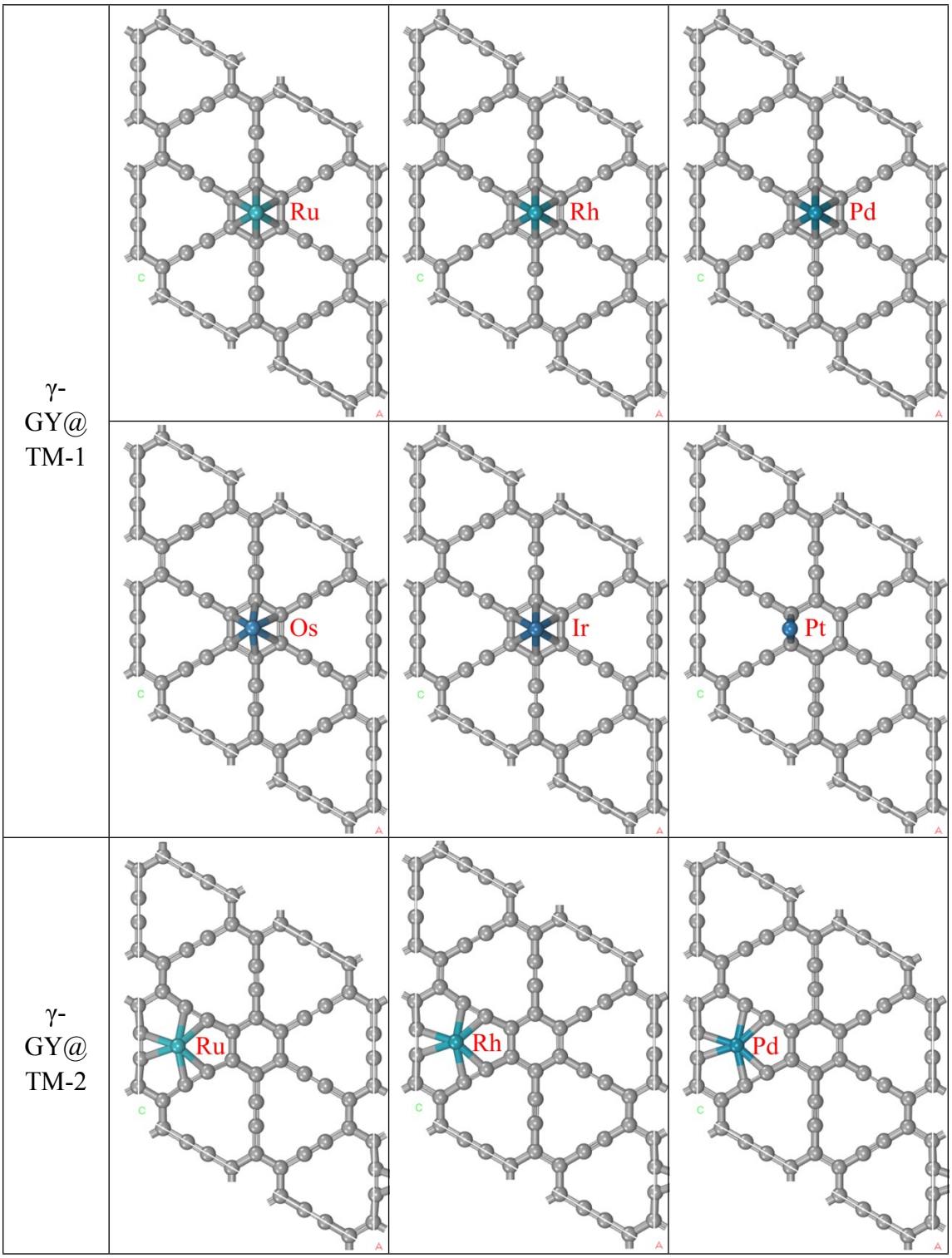
1.3 Overpotentials

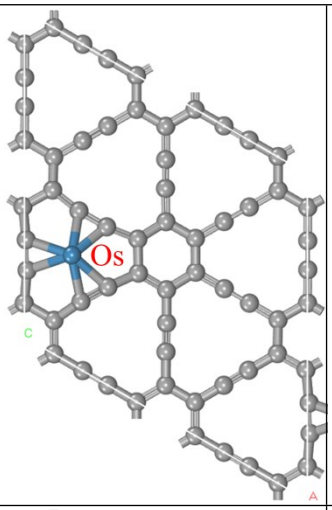
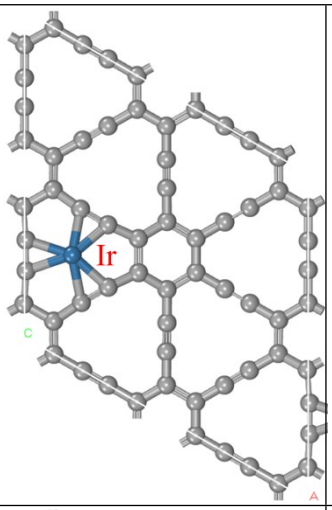
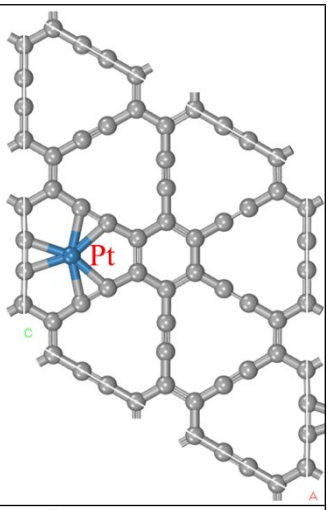
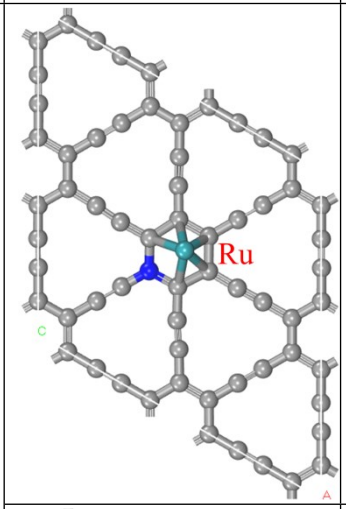
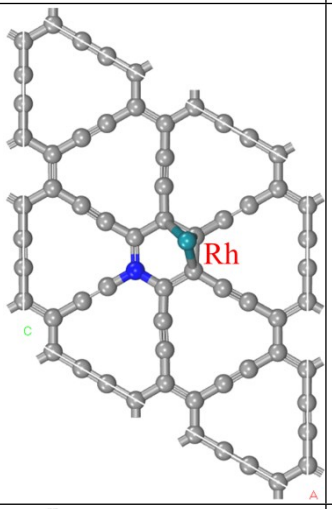
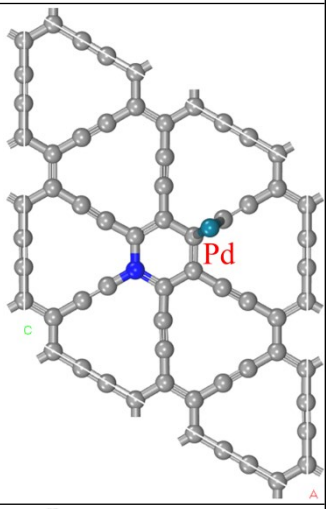
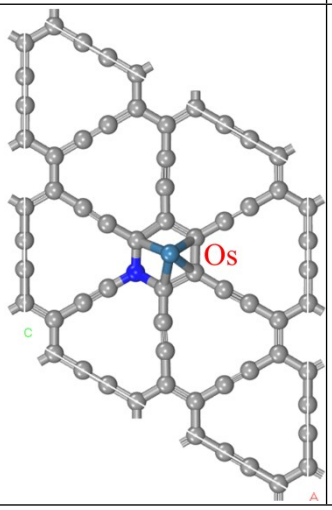
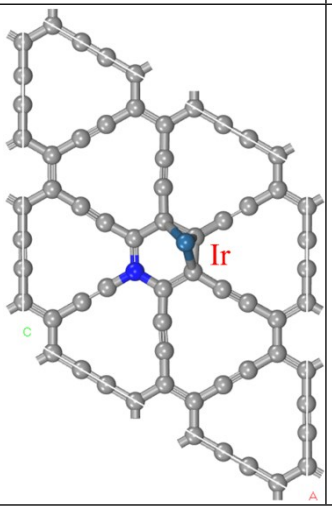
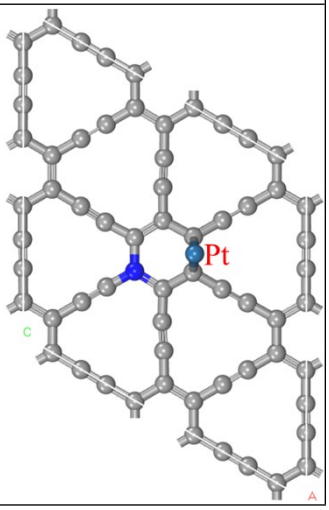
The theoretical OER and ORR overpotentials (η^{OER} and η^{ORR}) are determined by the rate-limiting steps,[5]

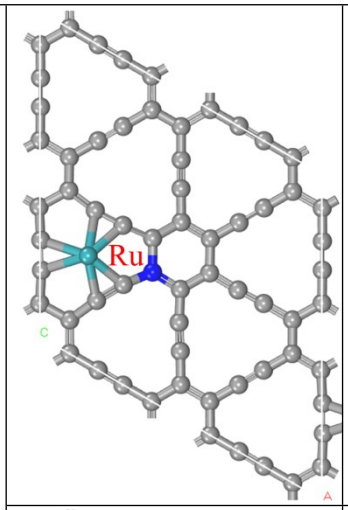
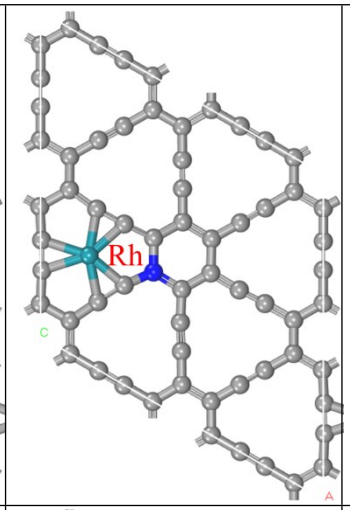
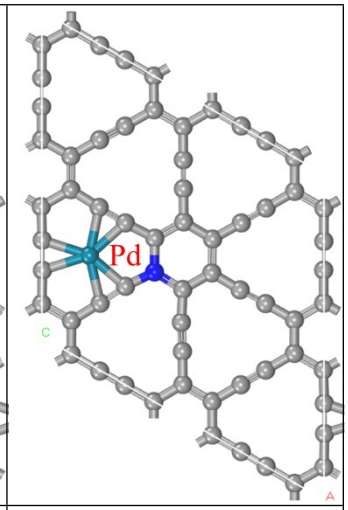
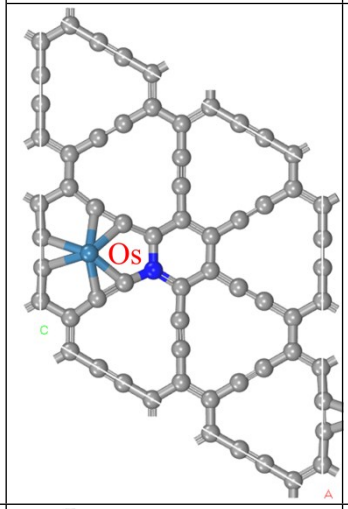
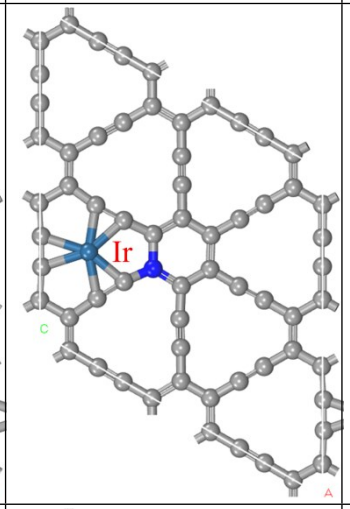
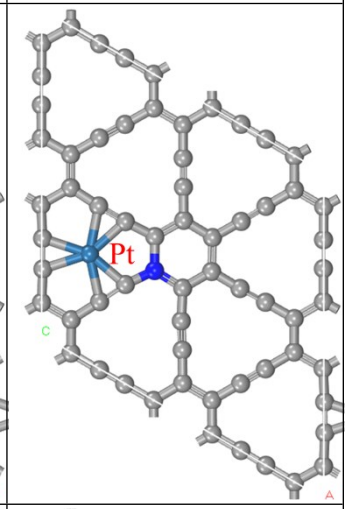
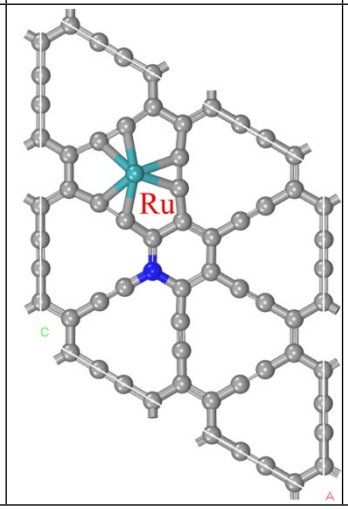
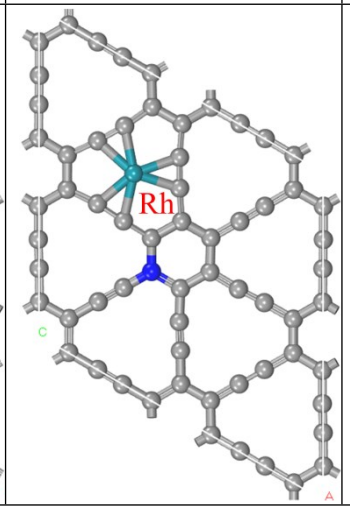
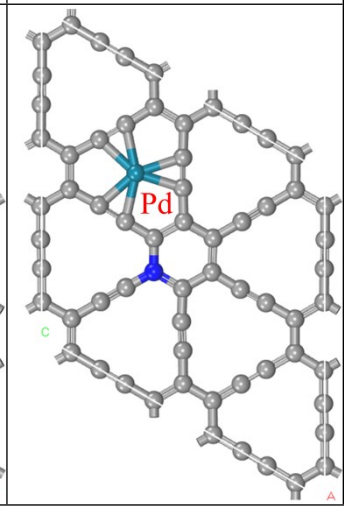
$$\eta^{OER} = \max\left[\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\right]/e - 1.23V \quad \text{(S5)}$$

$$\eta^{ORR} = 1.23V - \min\left[\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\right]/e \quad \text{(S6)}$$

2. Figures



			
graN-γ-GY @TM-1			
			

graN-γ-GY@TM-2			
			
graN-γ-GY@TM-3			

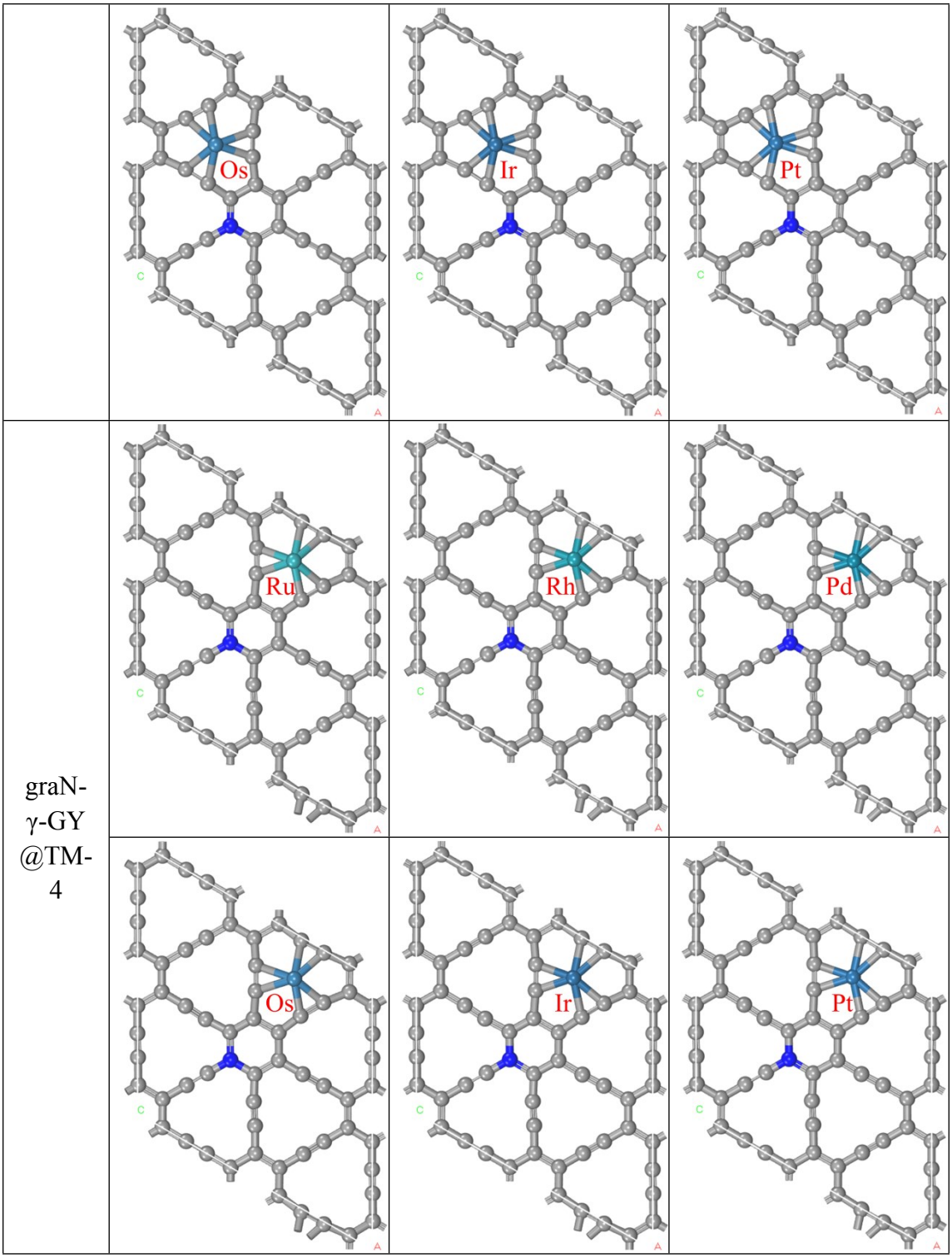


Fig. S1 Top view of optimized structures of TM atoms supported on the different sites of γ-GY and graN-γ-GY substrates.

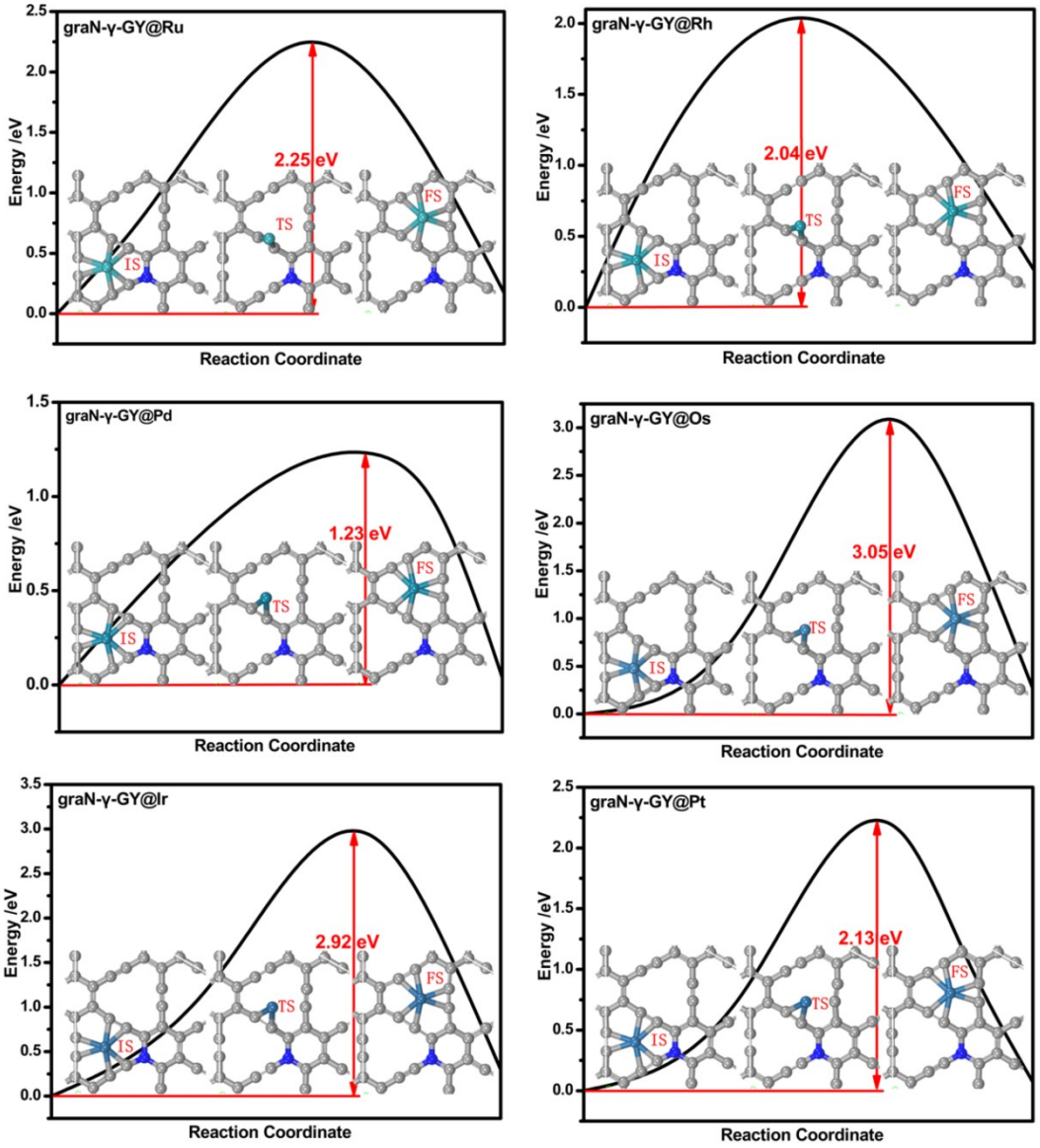


Fig. S2 Minimum energy pathways of TM atoms to diffuse to the neighboring site in graN-γ-GY and the optimized structures of the initial state (IS), transition state (TS), and final state (FS).

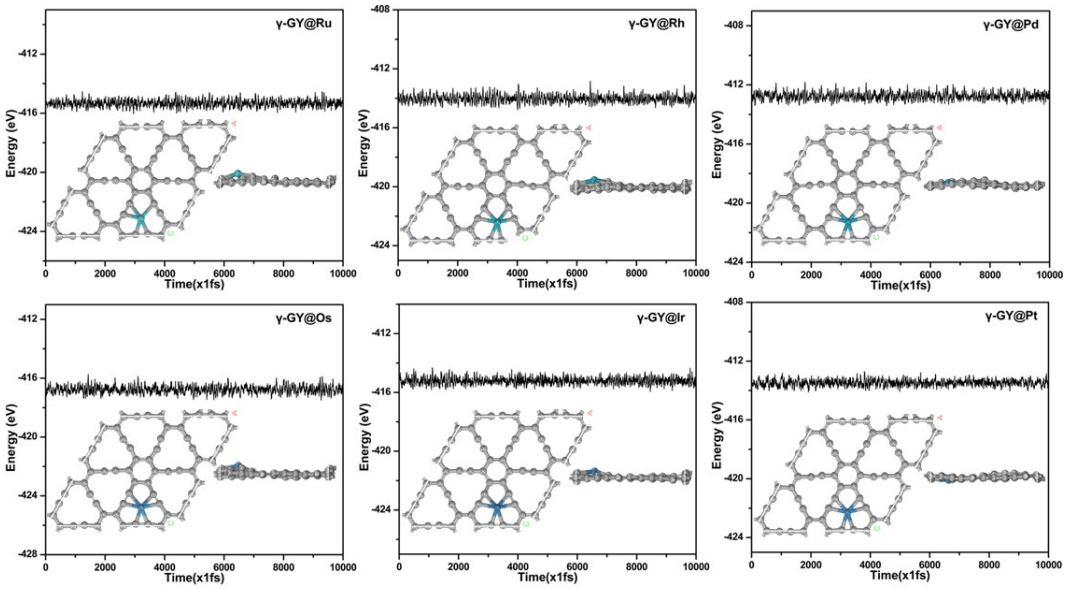


Fig. S3 AIMD simulations of γ-GY@M catalysts with a time step of 1fs at the temperature of 300K.

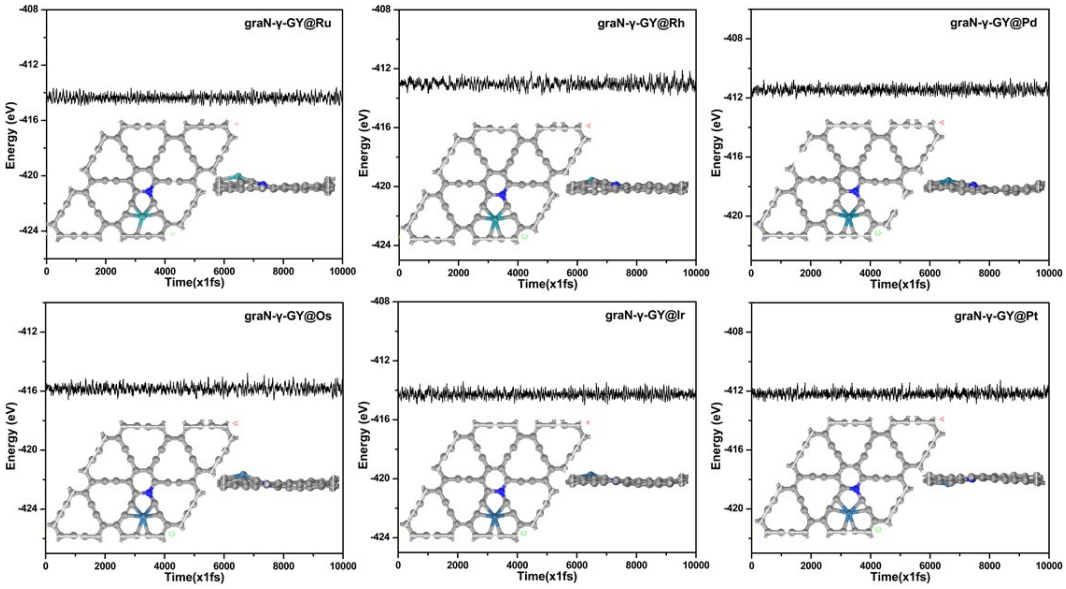
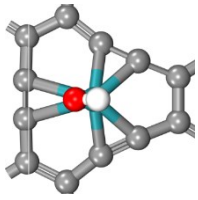
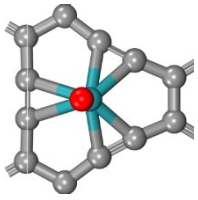
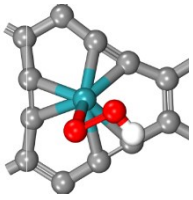


Fig. S4 AIMD simulations of graN-γ-GY@M catalysts with a time step of 1fs at the temperature of 300K.

	OH^*	O^*	OOH^*
γ-GY@Ru			

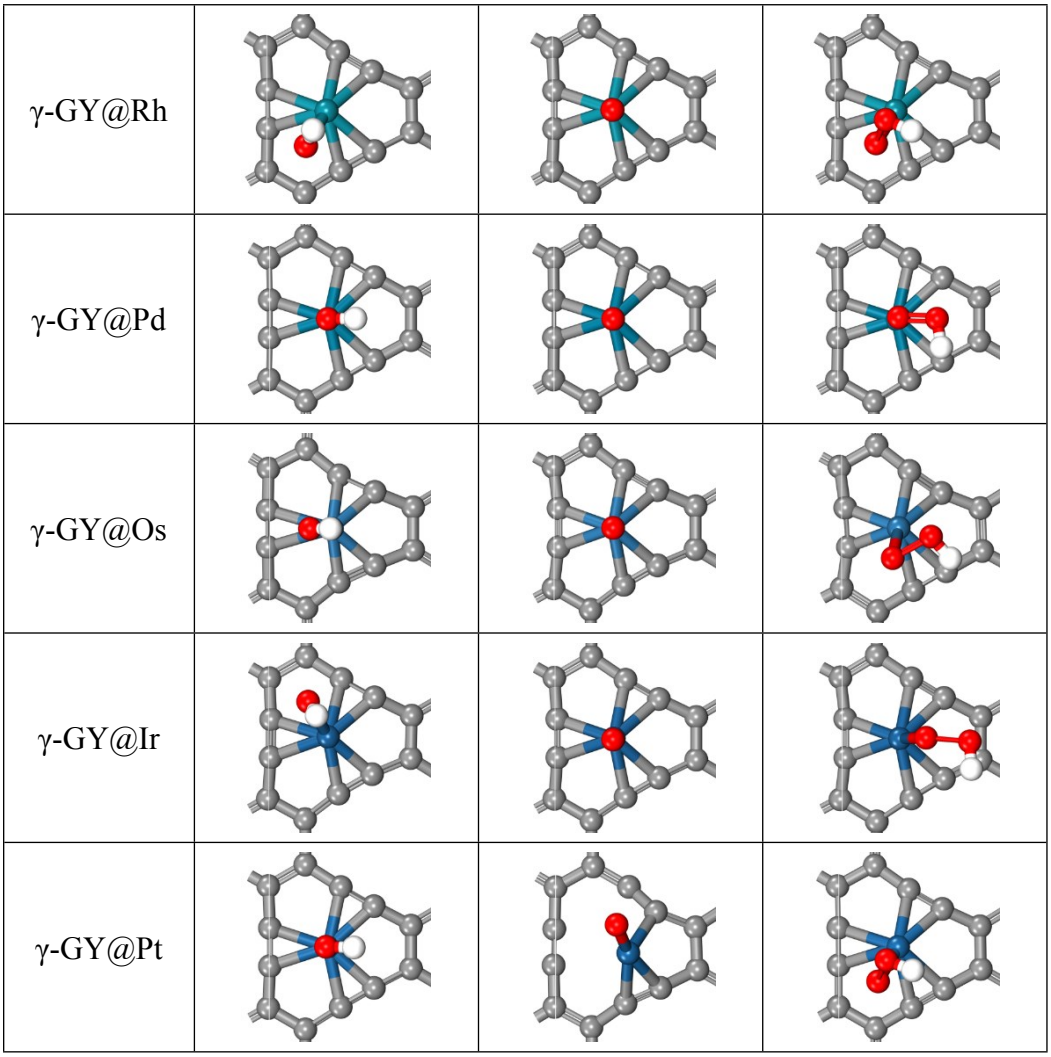


Fig. S5 Optimized structures of the OH^*, O^*, and OOH^* adsorption intermediates in γ-GY@TM.

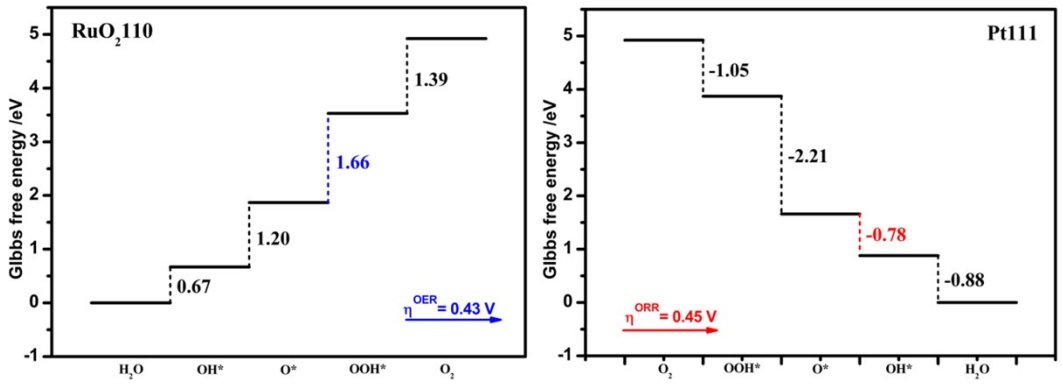


Fig. S6 Calculated Gibbs free energies of RuO_2 for OER and Pt for ORR at zero potential (U=0). The blue line and red line are the potential-determining steps for OER and ORR, respectively.

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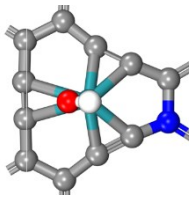
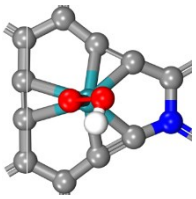
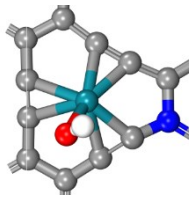
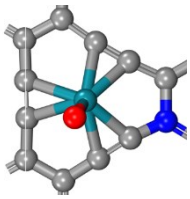
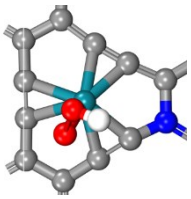
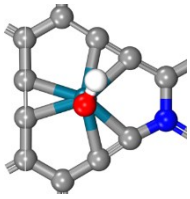
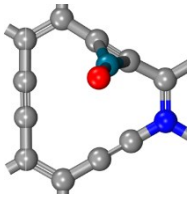
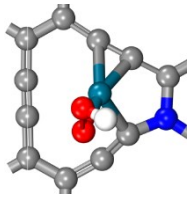
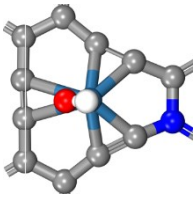
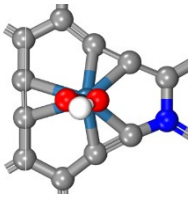
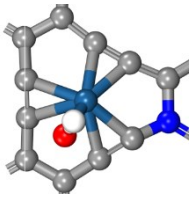
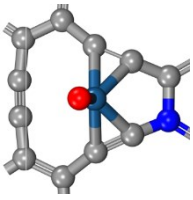
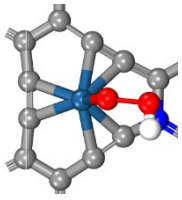
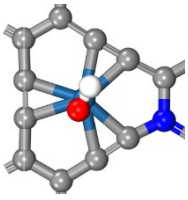
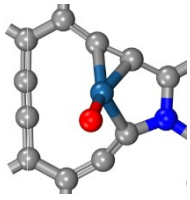
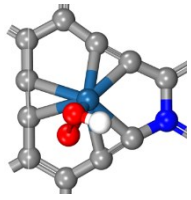
graN-γ-GY@Ru			
graN-γ-GY@Rh			
graN-γ-GY@Pd			
graN-γ-GY@Os			
graN-γ-GY@Ir			
graN-γ-GY@Pt			

Fig. S7 Optimized structures of the OH^*, O^*, and OOH^* adsorption intermediates in graN-γ-GY@TM.

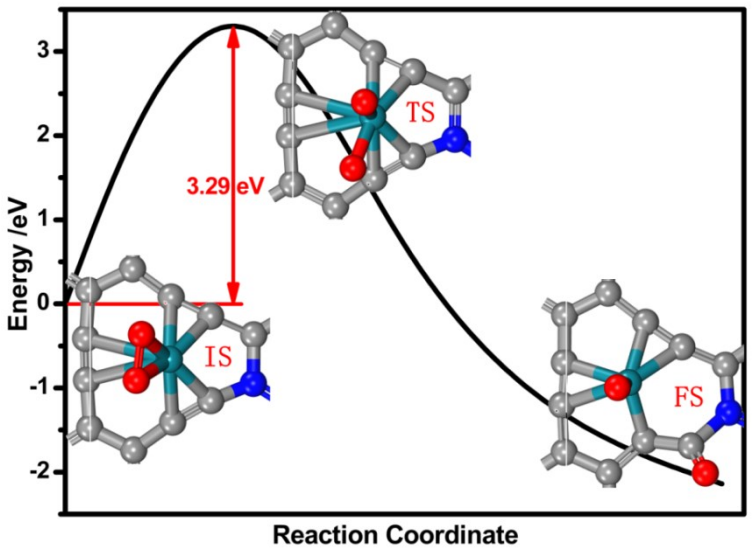


Fig. S8 Minimum energy pathways for the dissociation of O_2 into two separate O^* species and the optimized structures of the initial state (IS), transition state (TS), and final state (FS).

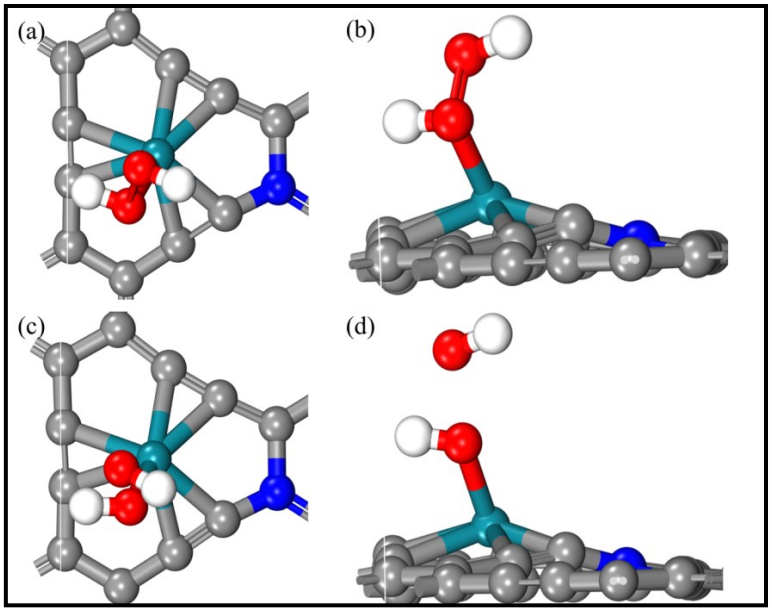


Fig. S9 (a) Top view and (b) side view of optimized before optimization. (c) Top view and (d) side view of optimized structures for the protonation of the unprotonated O atom in OOH^* intermediate.

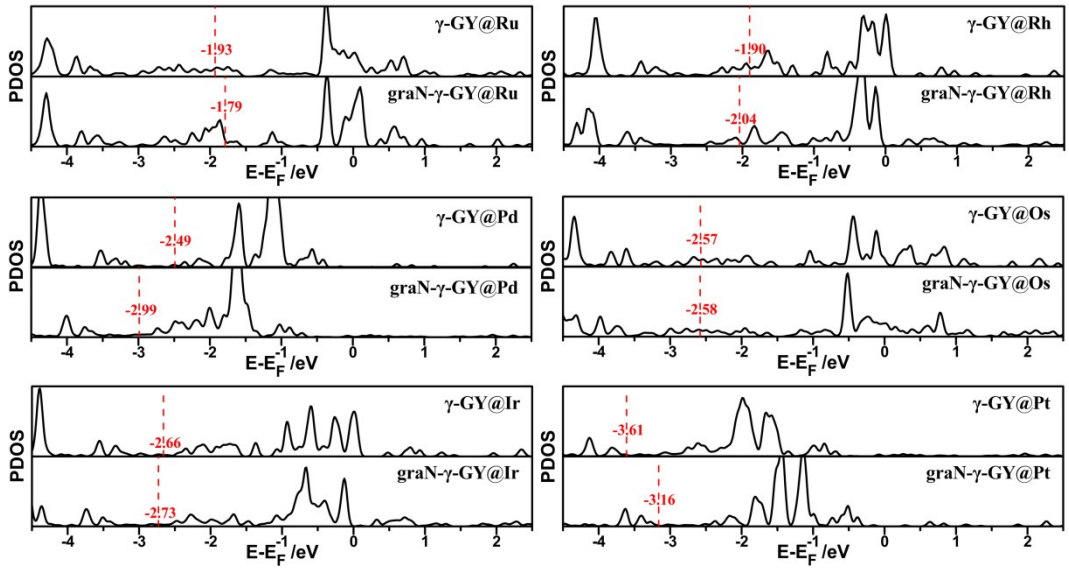


Fig. S10. The changes of d-band center for metal atoms before and after N doping.

3. Tables

Table S1. Energy difference between without and with DFT+U.

	ΔG_1(eV)	ΔG_2(eV)	ΔG_3(eV)	ΔG_4(eV)	η^{OER}(V)	η^{ORR}(V)
DFT	0.90	1.33	1.50	1.19	0.27	0.33
DFT+U	0.84	1.35	1.49	1.24	0.26	0.39
difference	0.06	0.02	0.01	0.05	0.01	0.06

Table S2. The calculated E, ZPE, and S for H_2 and H_2O.

	E	ZPE	S
H_2	-6.76	0.36	0.0014
H_2O	-14.22	0.67	0.0022

Table S3. The calculated ΔE, ΔZPE, and ΔS for all the intermediates.

	ΔE	ΔZPE	ΔS
γ-GY@Ru-O	-0.11	-0.20	-0.0007
γ-GY@Ru-OH	-0.76	-0.08	-0.0013
γ-GY@Ru-OOH	2.57	-0.33	-0.0019
γ-GY@Rh-O	1.79	-0.21	-0.0005
γ-GY@Rh-OH	0.27	-0.09	-0.0012
γ-GY@Rh-OOH	3.06	-0.29	-0.0020
γ-GY@Pd-O	4.10	-0.27	-0.0009
γ-GY@Pd-OH	1.78	-0.16	-0.0013
γ-GY@Pd-OOH	4.48	-0.30	-0.0018
γ-GY@Os-O	-0.74	-0.20	-0.0007
γ-GY@Os-OH	-1.19	-0.07	-0.0013
γ-GY@Os-OOH	2.29	-0.26	-0.0020
γ-GY@Ir-O	1.60	-0.21	-0.0005
γ-GY@Ir-OH	0.13	-0.08	-0.0013
γ-GY@Ir-OOH	3.13	-0.31	-0.0020
γ-GY@Pt-O	3.08	-0.21	-0.0006
γ-GY@Pt-OH	1.93	-0.16	-0.0013
γ-GY@Pt-OOH	4.58	-0.26	-0.0019
graN-γ-GY@Ru-O	0.00	-0.20	-0.0007
graN-γ-GY@Ru-OH	-0.78	-0.08	-0.0013
graN-γ-GY@Ru-OOH	2.23	-0.31	-0.0019

graN-γ-GY@Rh-O	2.27	-0.21	-0.0006
graN-γ-GY@Rh-OH	0.65	-0.09	-0.0011
graN-γ-GY@Rh-OOH	3.44	-0.26	-0.0018
graN-γ-GY@Pd-O	3.73	-0.22	-0.0005
graN-γ-GY@Pd-OH	2.27	-0.11	-0.0009
graN-γ-GY@Pd-OOH	4.65	-0.27	-0.0017
graN-γ-GY@Os-O	-0.48	-0.20	-0.0007
graN-γ-GY@Os-OH	-1.10	-0.07	-0.0013
graN-γ-GY@Os-OOH	2.02	-0.31	-0.0019
graN-γ-GY@Ir-O	1.51	-0.20	-0.0007
graN-γ-GY@Ir-OH	0.52	-0.08	-0.0012
graN-γ-GY@Ir-OOH	3.65	-0.30	-0.0020
graN-γ-GY@Pt-O	2.05	-0.21	-0.0006
graN-γ-GY@Pt-OH	1.23	-0.13	-0.0012
graN-γ-GY@Pt-OOH	3.87	-0.26	-0.0018

Table S4. The calculated adsorption energies (eV), ΔE_{ads}, of different transition metals anchored at different sites of γ-GY and graN-γ-GY.

	Ru	Rh	Pd	Os	Ir	Pt
γ-GY@TM-1	-3.17	-2.95	-1.59	-2.70	-2.16	-2.83
γ-GY@TM-2	-4.66	-4.63	-3.28	-5.56	-5.44	-4.95
graN-γ-GY@TM-1	-2.92	-3.14	-1.88	-2.75	-2.70	-2.49
graN-γ-GY@TM-2	-4.53	-4.79	-3.00	-5.59	-5.67	-4.70
graN-γ-GY@TM-3	-4.37	-4.54	-2.96	-5.32	-5.38	-4.62
graN-γ-GY@TM-4	-4.37	-4.54	-2.94	-5.38	-5.40	-4.61

Table S5. The calculated cohesive energies (eV), ΔE_{ads}, and the difference between adsorption energies and cohesive energies, $\Delta E_{ads} - \Delta E_{coh}$, of different transition metals anchored at site 2 of γ-GY and graN-γ-GY.

	Ru	Rh	Pd	Os	Ir	Pt
ΔE_{coh}	-6.63	-5.96	-3.61	-8.27	-7.33	-5.50
$\Delta E_{ads} - \Delta E_{coh}$ (γ-GY@TM-2)	1.97	1.33	0.34	2.70	1.88	0.55
$\Delta E_{ads} - \Delta E_{coh}$ (graN-γ-GY@TM-2)	2.10	1.17	0.62	2.67	1.66	0.81

Table S6. Comparison of the calculated OER and ORR overpotentials for recently reported electrocatalysts in theoretical studies.

Catalyst	η^{OER}	η^{ORR}	Reference
graN-γ-GY@Rh	0.27 V	0.33 V	This work
$(H2NMe_2)_2M_2(Cl_2dhbq)_3$	0.41 V	0.46 V	6
Rh-VCC	0.35 V	0.27 V	4
Black phosphorus	0.70 V	0.69 V	7
$Co_3(HITP)_2$	0.36 V	0.73 V	5
Fe-TCNQ-Cl	0.55 V	0.27 V	8
$Co_1/g\text{-}C_3N_4$	0.50 V	0.59 V	9
Nb_2CF_2–VF–Pt	0.37 V	0.40 V	10
Ir-N_4-bPC	0.21 V	0.21V	11
Rh-N_4-bPC	0.62V	0.33V	11
spN-doped graphdiynes	0.40 V	0.49 V	12
Ni@GDY	0.29 V	0.40 V	13

Table S7. Calculated adsorption Gibbs free energy changes (eV) of the O*, OH*, and OOH* intermediates on γ-GY@M and graN-γ-GY@M.

	ΔG_{O*}	ΔG_{OH*}	ΔG_{OOH*}
γ-GY@Ru	-0.11	-0.45	2.81
graN-γ-GY@Ru	-0.01	-0.48	2.48
γ-GY@Rh	1.73	0.54	3.38
graN-γ-GY@Rh	2.23	0.90	3.73
γ-GY@Pd	4.09	2.01	4.71
graN-γ-GY@Pd	3.66	2.45	4.90
γ-GY@Os	-0.74	-0.87	2.63
graN-γ-GY@Os	-0.48	-0.79	2.28
γ-GY@Ir	1.53	0.42	3.42
graN-γ-GY@Ir	1.51	0.81	3.95
γ-GY@Pt	3.06	2.16	4.87
graN-γ-GY@Pt	2.02	1.46	4.15

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