catalysts

Supporting Information

Noble metal single-atom coordinated to nitrogen, oxygen, and carbon as electrocatalysts for oxygen evolution

Table S1. Gibbs free energy change (ΔG) for each OER reaction step on MN_4-C, MO_4-C and MC_4-C (M = Ir, Ru) in vacuum.

		ΔG (eV)					
step	**Process**	**IrN_4-C**	**IrO_4-C**	**IrC_4-C**	**RuN_4-C**	**RuO_4-C**	**RuC_4-C**
1	H_2O (l) → OH*	0.96	1.72	−0.42	−0.01	0.40	−0.26
2	OH* → O*	1.53	1.22	0.42	0.68	1.12	0.18
3	O* → OOH*	1.48	1.74	2.66	2.22	1.85	2.96
4	OOH* → O_2 (g)	0.95	0.25	2.26	2.03	1.55	2.04
Total ΔG	$2H_2O$ (l) → O_2 (g)	4.92	4.92	4.92	4.92	4.92	4.92

Table S2. The *d*-band center of M atom on MN_4-C, MO_4-C and MC_4-C (M = Ir, Ru).

Systems	***d*-band center (eV)**	**Systems**	***d*-band center (eV)**
IrN_4-C	−1.86	RuN_4-C	−1.07
IrO_4-C	−2.02	RuO_4-C	−1.10
IrC_4-C	−2.60	RuC_4-C	−1.81

Table S3. Bader charges of IrN_4, IrO_4-C, IrC_4-C. The ZVAL represents the number of valent electrons in each atomic sphere.

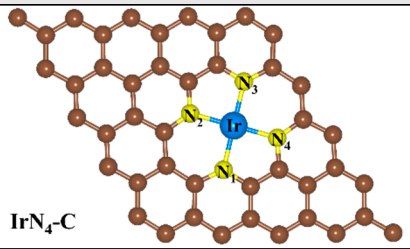
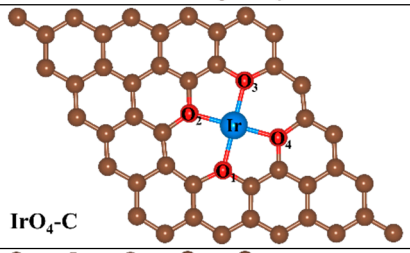
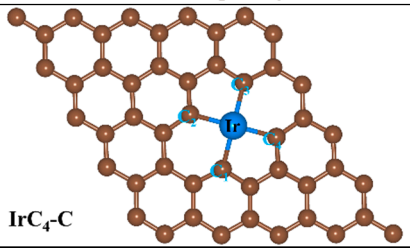
Systems	Atom	Calculated valence electrons	ZVAL	Net charge (|e|)
 IrN_4-C	N_1	6.21	5.00	−1.21
	N_2	6.14		−1.14
	N_3	6.21		−1.21
	N_4	6.16		−1.16
	Ir	8.28	9.00	0.72
 IrO_4-C	O_1	7.10	6.00	−1.10
	O_2	7.10		−1.10
	O_3	7.09		−1.09
	O_4	7.09		−1.09
	Ir	8.39	9.00	0.61
 IrC_4-C	C_1	4.17	4.00	−0.17
	C_2	4.17		−0.17
	C_3	4.16		−0.16
	C_4	4.17		−0.17
	Ir	8.44	9.00	0.56

Table S4. Bader charges of RuN_4, RuO_4-C, RuC_4-C. The ZVAL represents the number of valent electrons in each atomic sphere.

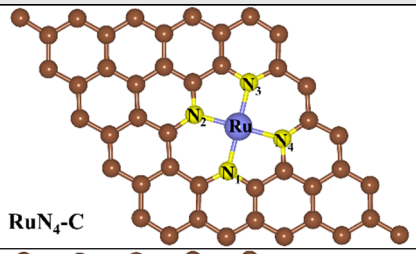
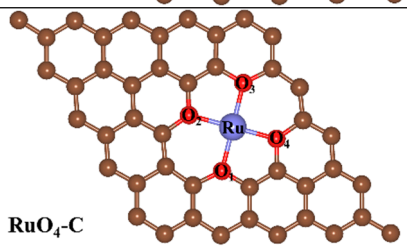
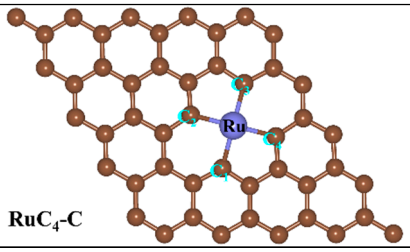
Systems	Atom	Calculated valence electrons	ZVAL	Net charge (|e|)
 **RuN_4-C**	N_1	6.21	5.00	−1.21
	N_2	6.07		−1.07
	N_3	6.18		−1.18
	N_4	6.17		−1.17
	Ru	7.18	8.00	0.82
 **RuO_4-C**	O_1	7.11	6.00	−1.11
	O_2	7.11		−1.11
	O_3	7.11		−1.11
	O_4	7.11		−1.11
	Ru	7.46	8.00	0.54
 **RuC_4-C**	C_1	4.12	4.00	−0.12
	C_2	4.09		−0.09
	C_3	4.13		−0.13
	C_4	4.09		−0.09
	Ru	7.35	8.00	0.65

Table S5. Gibbs free energy change (ΔG) for each OER reaction step on MN_4-C, MO_4-C and MC_4-C (M = Ir, Ru) with an implicit solvent model.

		ΔG (eV)					
step	**Process**	**IrN_4-C**	**IrO_4-C**	**IrC_4-C**	**RuN_4-C**	**RuO_4-C**	**RuC_4-C**
1	H_2O (l) → OH*	0.84	1.55	−0.54	−0.16	0.14	−0.31
2	OH* → O*	1.39	0.93	0.46	0.72	1.01	0.29
3	O* → OOH*	1.56	1.94	2.57	2.16	1.90	2.81
4	OOH* → O_2 (g)	1.13	0.50	2.42	2.21	1.87	2.13
Total ΔG	$2H_2O$ (l) → O_2 (g)	4.92	4.92	4.92	4.92	4.92	4.92

Table S6. The calculated total energies (E) and thermodynamic quantities for the gas phase H_2 species (T = 298.15 K, P = 1 bar), and free H_2O at the 298.15 K, 0.035 bar.

Species	**E (eV)**	**ZPE−TS (eV)**	**G (eV)**
H_2(g)	−6.76	−0.05	−6.80
H_2O(l)	−14.22	−0.00	−14.22

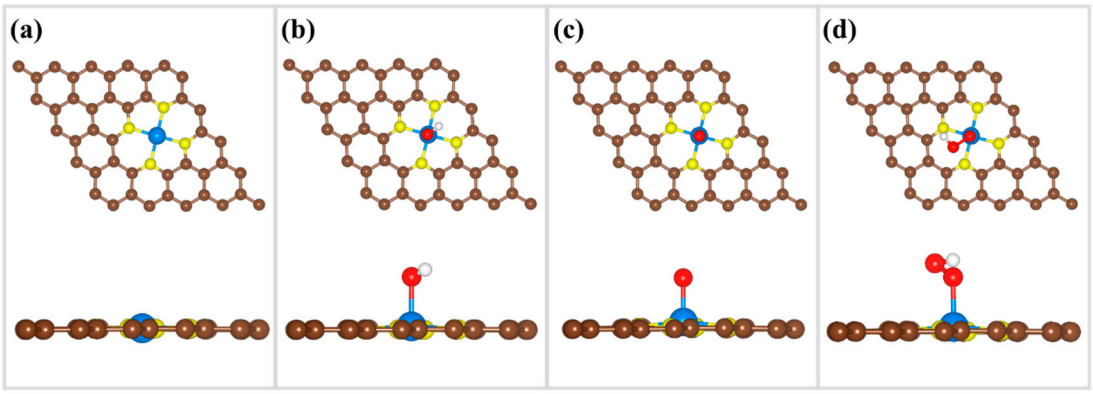


Figure S1. Optimized structures of (a) IrN_4-C catalyst and (b-d) OER intermediates along the pathway on IrN_4-C. Ir, C, N, H and O atoms are presented with blue, brown, yellow, white and red circles, respectively.

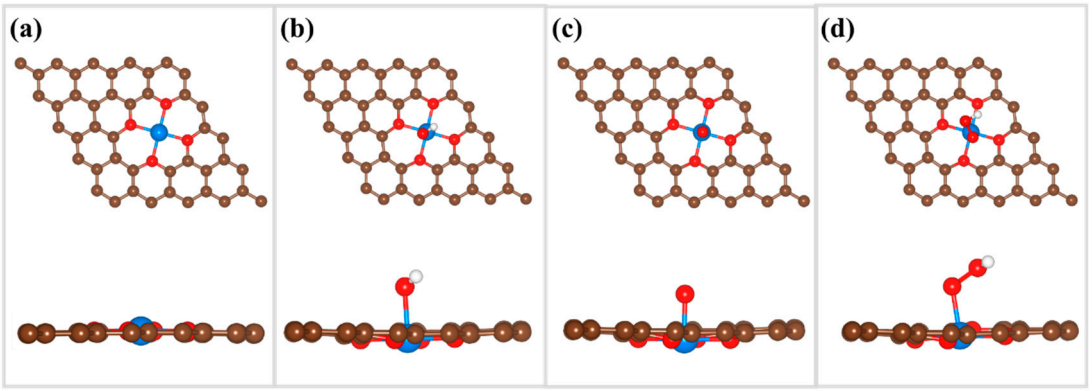


Figure S2. Optimized structure of (a) IrO_4-C catalyst and (b-d) OER intermediates along the pathway on IrO_4-C. Ir, C, H and O atoms are presented with blue, brown, white and red circles, respectively.

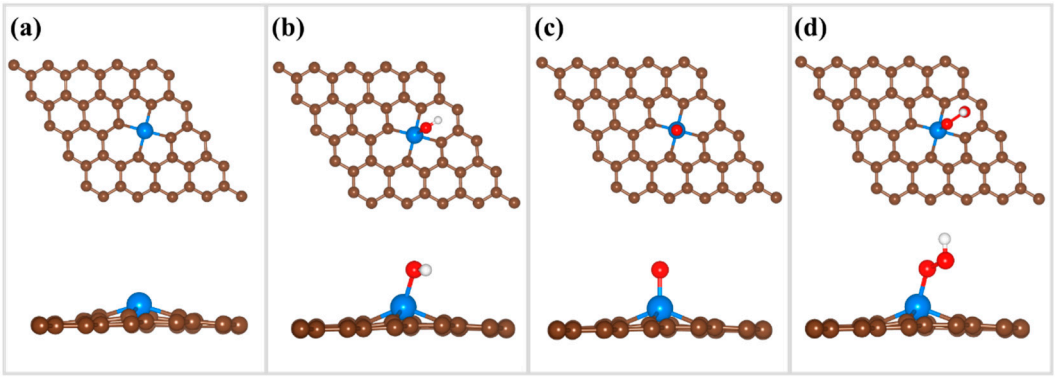


Figure S3. Optimized structure of (a) IrC_4-C catalyst and (b-d) OER intermediates along the pathway on IrC_4-C. Ir, C, H and O atoms are presented with blue, brown, white and red circles, respectively.

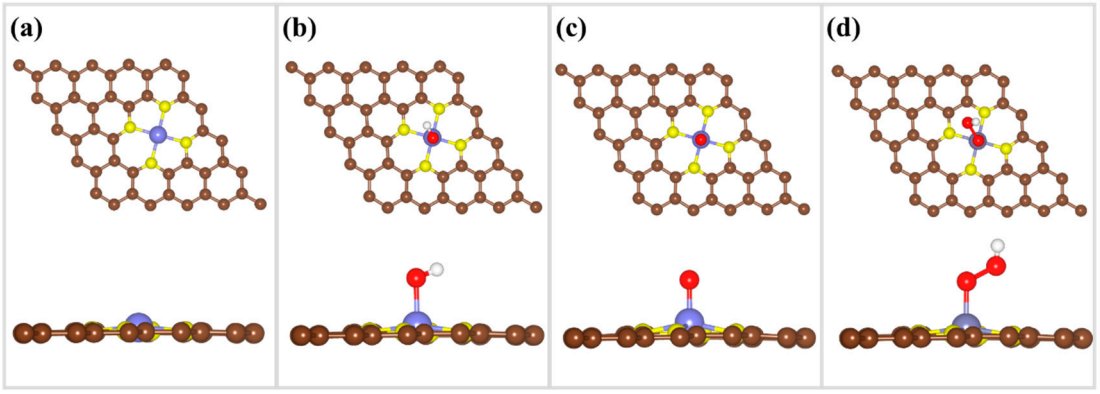


Figure S4. Optimized structure of (a) RuN_4-C catalyst and (b-d) OER intermediates along the pathway on RuN_4-C. Ru, C, N, H and O atoms are presented with purple, brown, yellow, white and red circles, respectively.

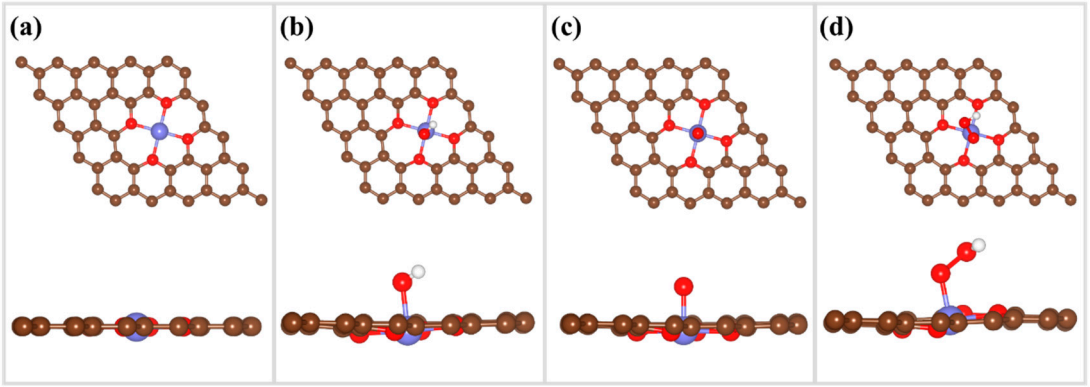


Figure S5. Optimized structure of (a) RuO_4-C catalyst and (b-d) OER intermediates along the pathway on RuO_4-C. Ru, C, H and O atoms are presented with purple, brown, white and red circles, respectively.

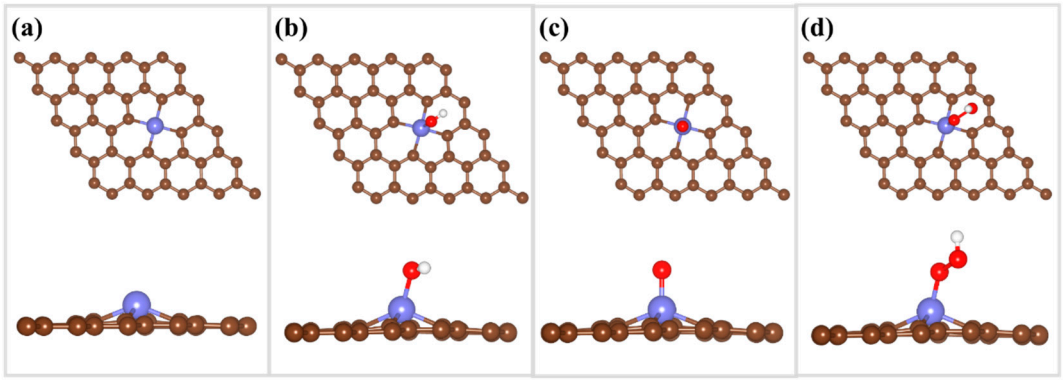


Figure S6. Optimized structure of (a) RuC_4-C catalyst and (b-d) OER intermediates along the pathway on RuC_4-C. Ru, C, H and O atoms are presented with purple, brown, white and red circles, respectively.

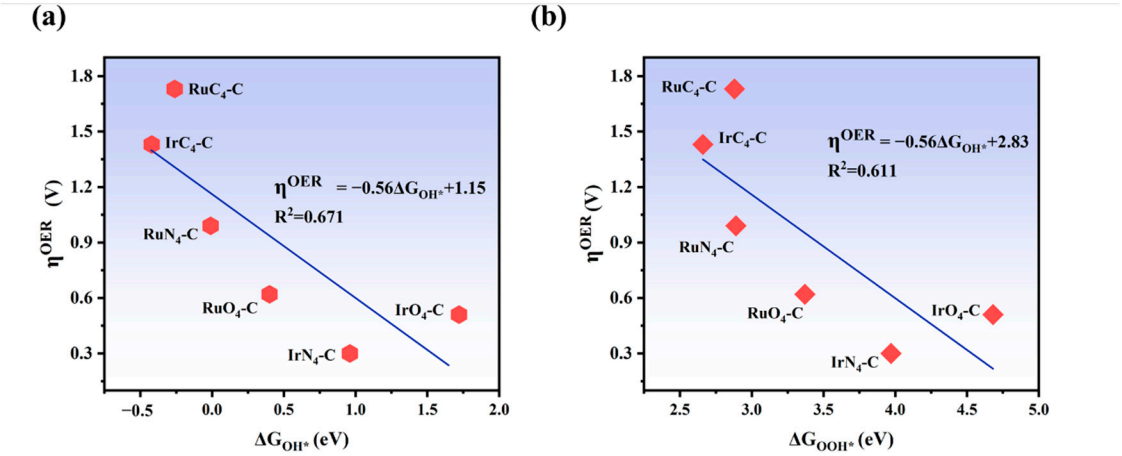


Figure S7. The scaling relationship between (a) $\triangle G_{OH^*}$ *vs.* η^{OER}, (b) $\triangle G_{OOH^*}$ *vs.* η^{OER} on MN_4-C, MO_4-C and MC_4-C (M = Ir, Ru).

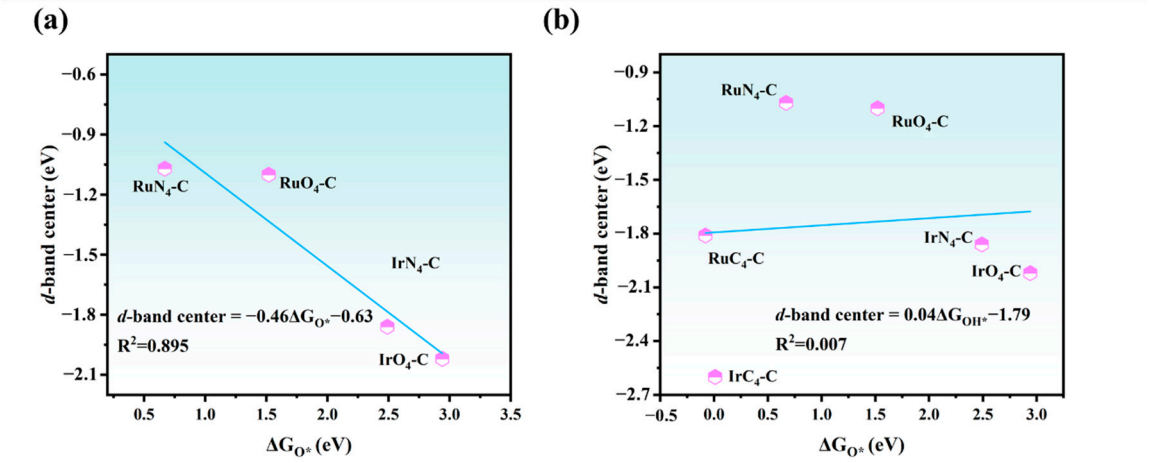


Figure S8. The scaling relationship between △G$_{O*}$ *vs. d*-band center on MN$_4$-C, MO$_4$-C and MC$_4$-C (M = Ir, Ru).

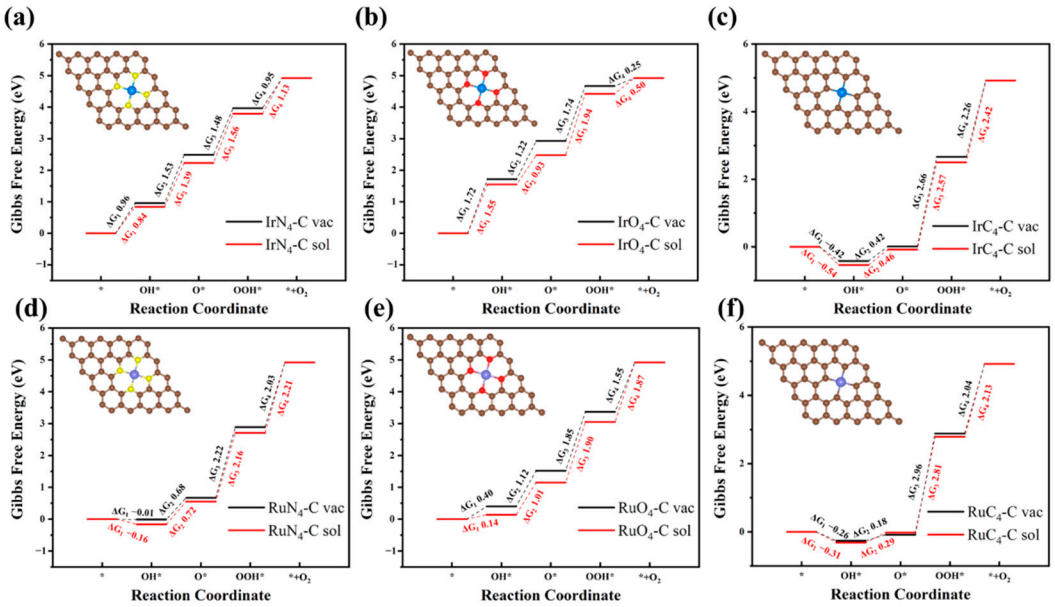


Figure S9. Free energy diagrams of OER processes on (a) IrN$_4$-C, (b) IrO$_4$-C, (c) IrC$_4$-C, (d) RuN$_4$-C, (e) RuO$_4$-C and (f) RuC$_4$-C in vacuum (black lines) and implicit solvent model (red lines), respectively. H, C, O, N, Ir and Ru atoms are represented with white, brown, red, yellow, blue and purple circles.