

Supporting Information

Single-atom Pd Directly Anchored on Biphenylene: A Promising Bifunctional Electrocatalyst for Overall Water Splitting

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Note 1

The HER and OER activities were evaluated by the calculation of the Gibbs free energy change ΔG of the adsorptions of intermediates based on the computational hydrogen electrode (CHE) model developed by Nørskov and co-workers: ^{S1}

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S + \Delta G_{\text{U}} - \Delta G_{\text{pH}} \quad (\text{S1})$$

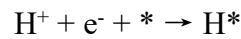
where ΔE is the adsorption energy of a given system. ΔE_{ZPE} and ΔS are zero-point energy and entropy differences between the adsorbed state and the free-standing state. $\Delta G_{\text{U}} = -eU$, in which e is the amount of charge transfer and U is the potential applied on the electrode. $\Delta G_{\text{pH}} = -k_{\text{B}}T\ln[\text{H}^+]$, where k_{B} is the Boltzmann constant and $\ln[\text{H}^+]$ is the logarithm of hydrogen ions concentration. Herein, all calculations were performed under the standard conditions $T = 300 \text{ K}$.^{S2}

Additionally, the ΔE is defined as the following formula:

$$\Delta E = E_{\text{total}} - (E_{\text{sub}} + E_{\text{mol}}) \quad (\text{S2})$$

where E_{sub} and E_{mol} are energies of the substrates and adsorbed molecules, respectively. With this definition, the more negative the ΔE value is, the more stable the adsorption structure is.

For hydrogen evolution reaction:



in which the $*$ represent the surface site and the calculated reaction free energy (ΔG_{H^*}) can be calculated by:

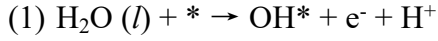
$$G_{\text{H}^*} = G_{\text{H}^*} - \frac{1}{2}G_{\text{H}_2} - G^* + 0.059 \times \text{pH} - eU \quad (\text{S3})$$

The theoretical overpotential η^{HER} is given by:

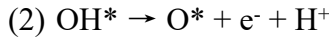
$$\eta^{HER} = -\frac{|\Delta G_{H^*}|}{e} \quad (S4)$$

The optimal value for HER is $\Delta G_{H^*} = 0$, which means that the smaller the $|\Delta G_{H^*}|$, the better HER performance of the material.^{S3}

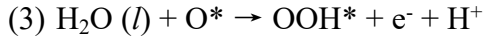
The oxygen evolution reaction (OER) is considered as four elementary steps. The Gibbs free energy (ΔG) for each step was calculated as follows:



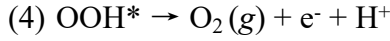
$$\Delta G_1 = G_{\text{OH}^*} + \frac{1}{2}G_{\text{H}_2} - G_{\text{H}_2\text{O}} - G^* - 0.059 \times \text{pH} - eU \quad (S5)$$



$$\Delta G_2 = G_{\text{O}^*} + \frac{1}{2}G_{\text{H}_2} - G_{\text{OH}^*} - 0.059 \times \text{pH} - eU \quad (S6)$$



$$\Delta G_3 = G_{\text{OOH}^*} + \frac{1}{2}G_{\text{H}_2} - G_{\text{H}_2\text{O}} - G_{\text{O}^*} - 0.059 \times \text{pH} - eU \quad (S7)$$



$$\Delta G_4 = 2G_{\text{H}_2\text{O}} + G^* - \frac{3}{2}G_{\text{H}_2} - G_{\text{OOH}^*} + 4.92 - 0.059 \times \text{pH} - eU \quad (S8)$$

The overpotential for OER is obtained by:

$$\eta^{OER} = \frac{\max(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4)}{e} - 1.23 \text{ V} \quad (S9)$$

Additionally, the adsorption energies were calculated by the following equation:

$$E_{ad} = E_{\text{TM@Bip}} - E_{\text{Bip}} - E_{\text{TM}} \quad (S10)$$

where $E_{\text{TM@Bip}}$, E_{Bip} , and E_{TM} are the energies of TM@Bip, Bip, and single metal atom, respectively.

Additionally, the U_{diss} is defined as the following formula: ^{S4}

$$U_{\text{diss}} = U_{\text{diss}}^0(\text{TM}, \text{bulk}) - (E_{\text{TM@Bip}} - E_{\text{Bip}} - E_{(\text{TM}, \text{bulk})})/ne \quad (S11)$$

where $E_{\text{TM@Bip}}$, E_{Bip} , and $E_{(\text{TM}, \text{bulk})}$ represent the energies of TM@Bip, the Bip

monolayer, and the metal atom in its most stable bulk structure, respectively.

$U_{diss}^0(TM,bulk)$ and n stand for the standard dissolution potential of bulk metal and the number of electrons involved in the dissolution, respectively.

In the volcano curve, the exchange current (i_0) base on the Nørskov's assumption was calculated by:

$$i_0 = -ek_0 \frac{1}{1 + \exp(-|\Delta G_{H^*}| / k_B T)} \quad (S12)$$

where k_0 is the rate constant. As there are no experimental data available, k_0 was set to 1.

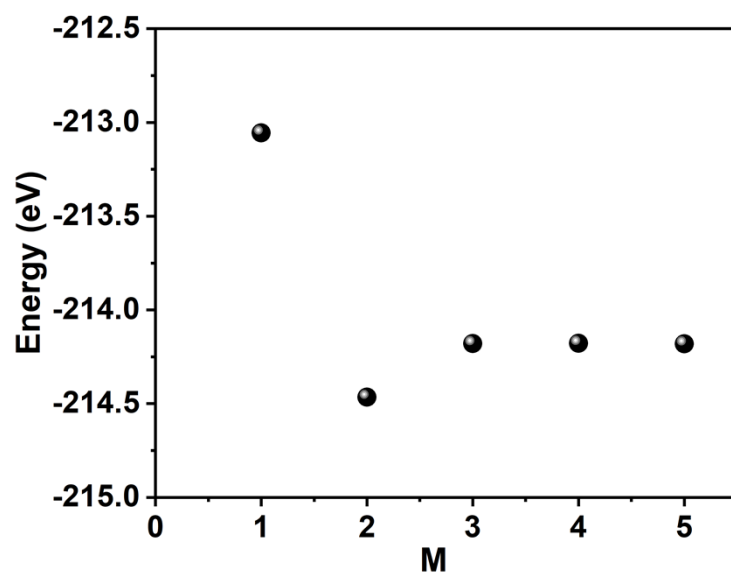


Fig. S1 Total energies for Pd@Bip calculated as a function of M for calculations using M x M x 1 k points.

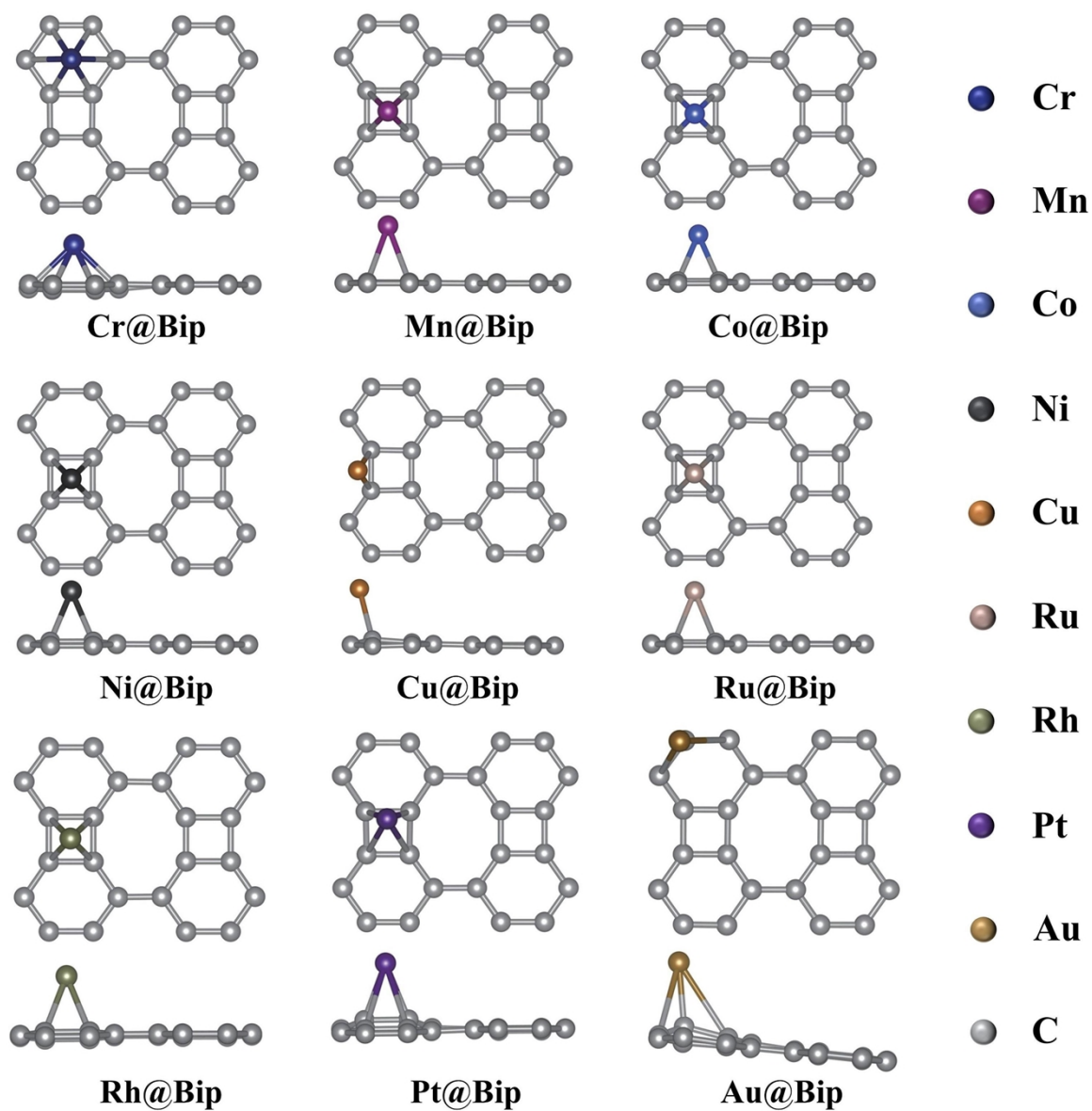


Fig. S2 Top and side views of the optimal structures of TM@Bip.

Table S1. Calculated adsorption energies (E_{ad} in eV), dissolution potential (U_{diss} in eV), nearest neighbor bond lengths (l in Å), Bader charge for the TM atoms (Q_{TM} in e), and total magnetic moment (M in μ_{B}). The negative values represent the loss of electrons, respectively.

Systems	E_{ad} (eV)	U_{diss} (eV)	l (Å)	Q_{TM} (e)	M (μ_{B})
V@Bip	-3.05	-0.04	-	-	-
Cr@Bip	-3.90	0.36	2.05	-1.01	3.60
Mn@Bip	-2.46	0.89	2.23	-0.56	4.89
Fe@Bip	0.54	-	-	-	-
Co@Bip	-3.11	1.14	1.97	-0.47	0.40
Ni@Bip	-2.49	0.97	2.02	-0.44	0.00
Cu@Bip	-2.56	0.48	2.09	-0.28	0.49
Ru@Bip	-3.88	0.40	2.09	-0.32	0.69
Rh@Bip	-2.57	0.36	2.12	-0.23	0.00
Pd@Bip	-2.00	0.42	2.25	-0.28	0.00
Ag@Bip	0.78	-	-	-	-
Ir@Bip	-4.27	-0.20	-	-	-
Pt@Bip	-2.98	0.44	2.06	-0.16	0.00
Au@Bip	-2.06	1.01	2.14	-0.11	0.58

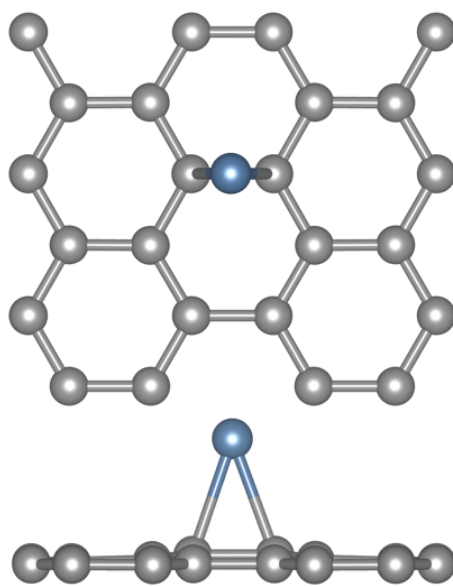


Fig. S3 Top and side views of Pd@GR. Pd, blue; C, gray.

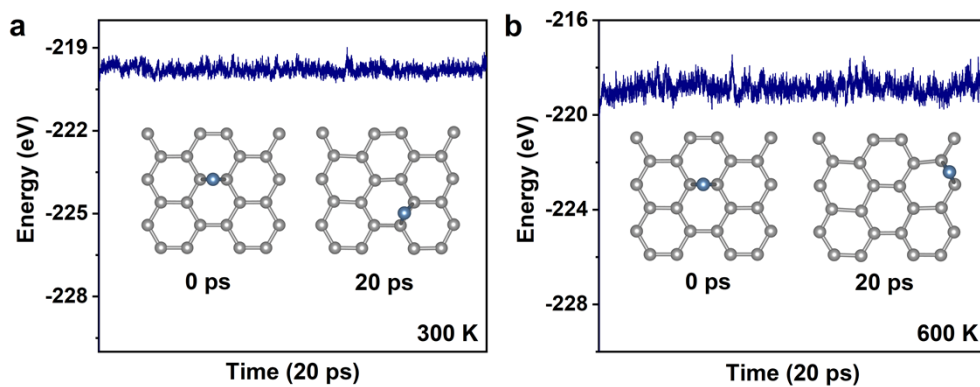


Fig. S4 The total energy change of Pd@GR at 300 K and 600K during 20 ps AIMD simulations. Pd, blue; C, gray.

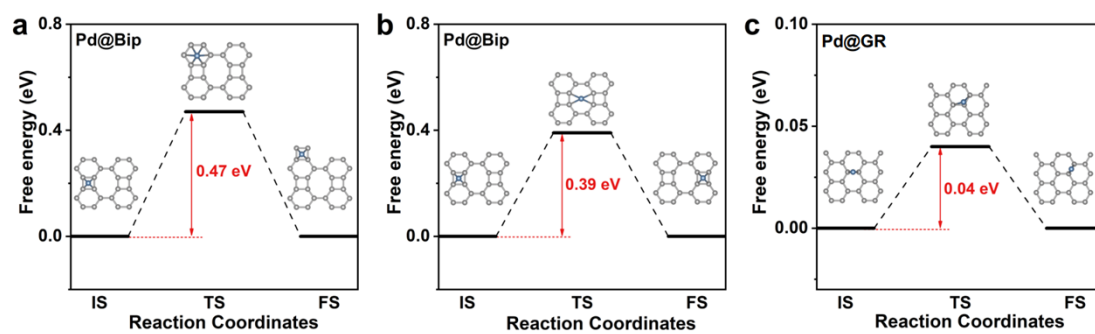


Fig. S5 From left to right: the optimized geometries of initial state (IS), transition state (TS), final state (FS), and the potential energy profile of Pd atom diffusion on (a) and (b) Bip, and (c) GR surfaces. Pd, blue; C, gray.

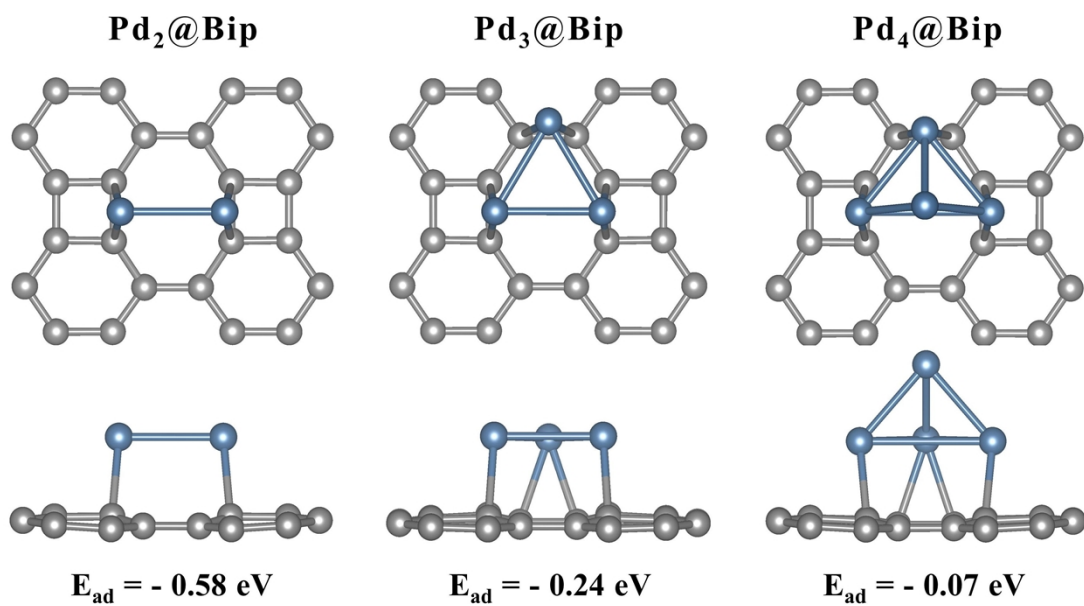


Fig. S6 The optimized structures and adsorption energies of Pd₂₋₄ clusters anchored on Bip. Pd, blue; C, gray.

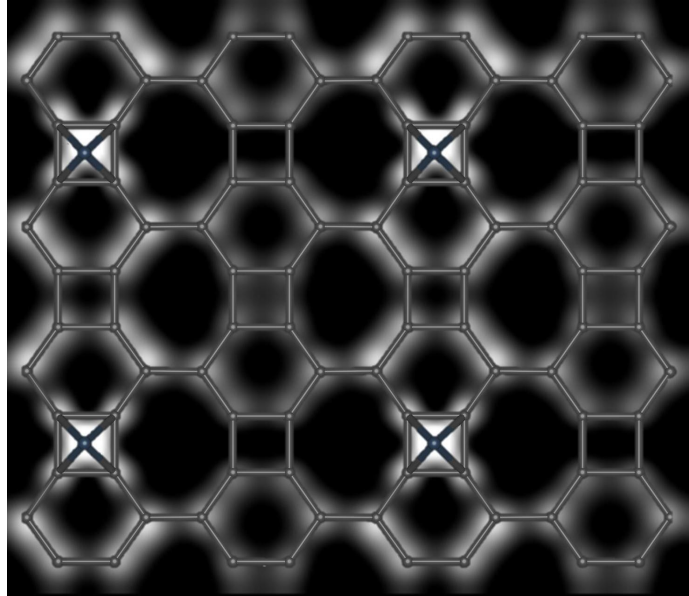


Fig. S7 Simulated STM images for Pd@Bip. Image taken at the bias voltage (V_s) of -2.5 V.

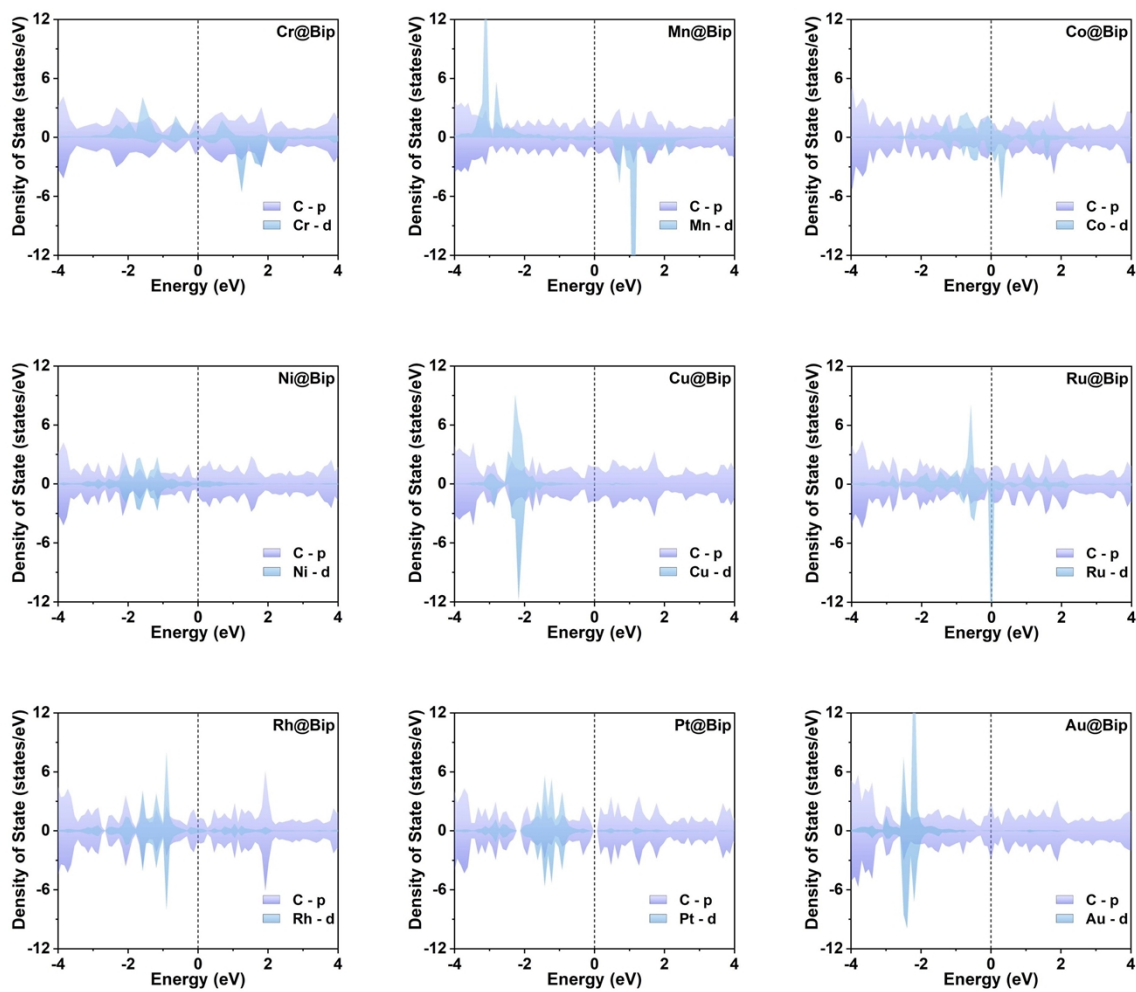


Fig. S8 Projected density of the states (PDOS) of TM@Bip. The s orbitals of C and TM atoms contribute insignificantly, therefore the PDOS mainly focus on the p orbitals of C and the d orbitals of TM atoms.

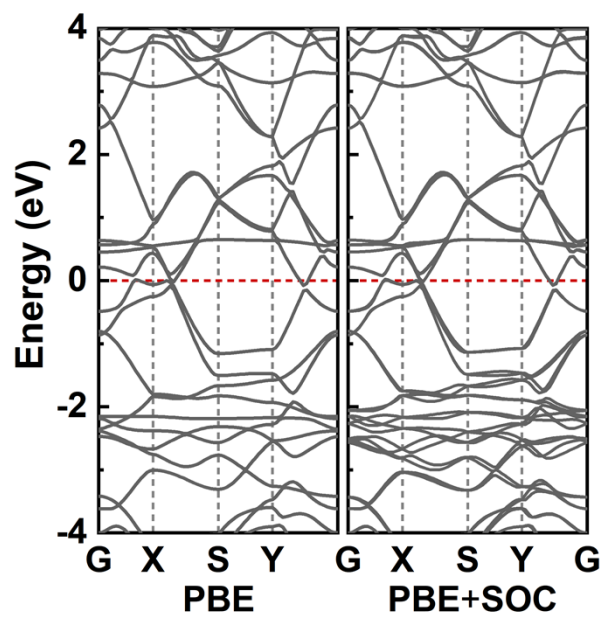


Fig. S9 Band structures for the Pd@Bip without (a) and with (b) spin-orbit coupling (SOC).

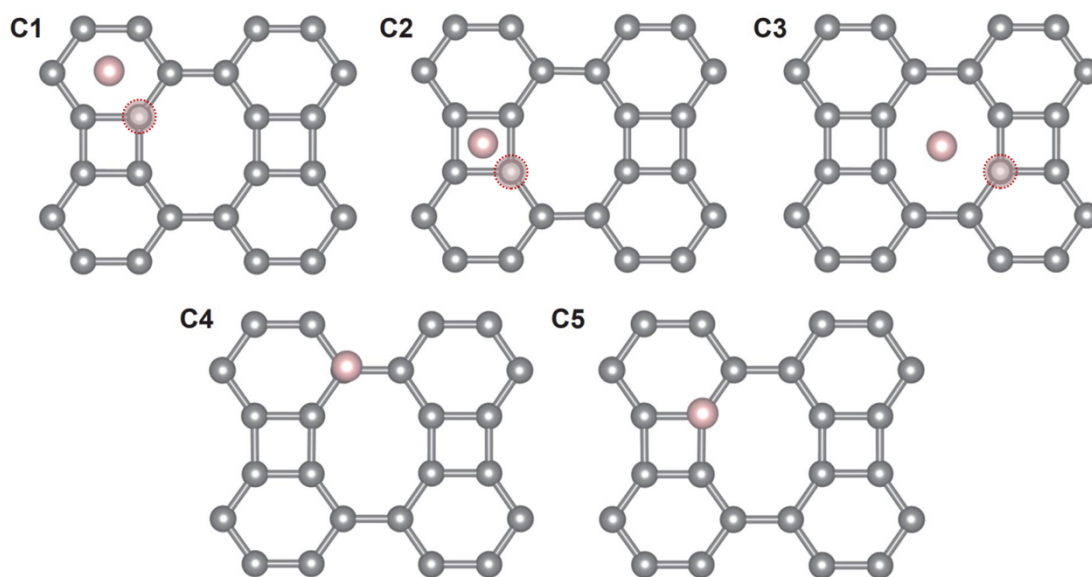


Fig. S10 The structures of H atom adsorbed on Bip of C1, C2, C3, C4, and C5 sites.

The pink spheres represent hydrogen atoms and the red dashed circles represent the final adsorption site for H*. Pd, blue; C, gray; H, pink.

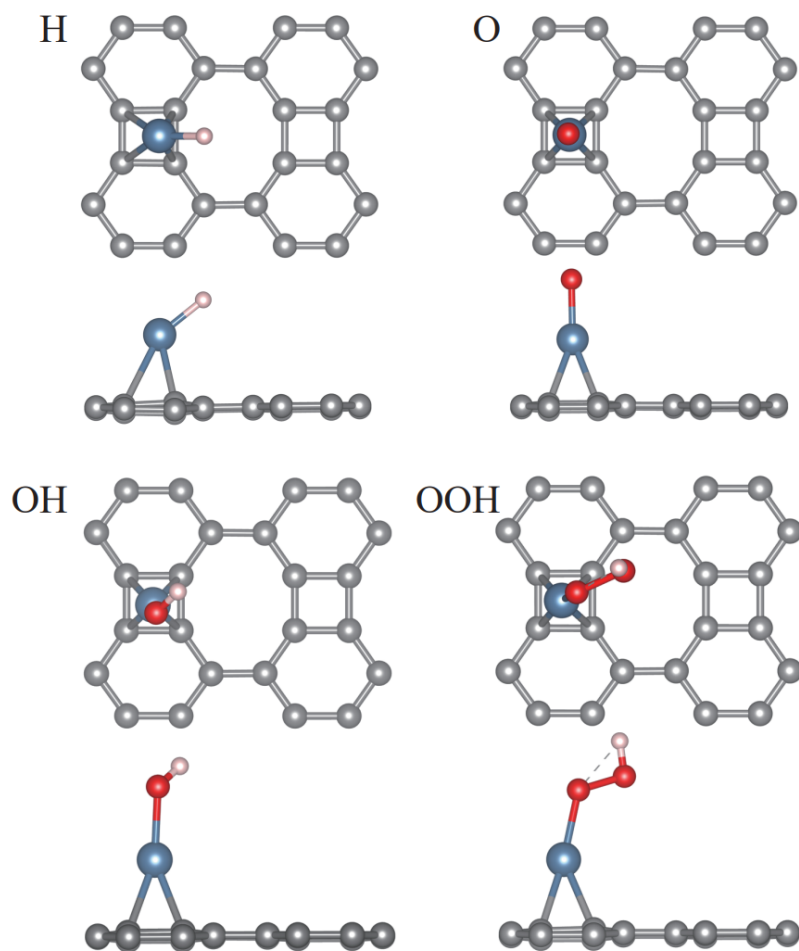


Fig. S11 The adsorption configurations of HER/OER intermediate states for Pd@Bip.

Pd, blue; C, gray; O, red; H, pink.

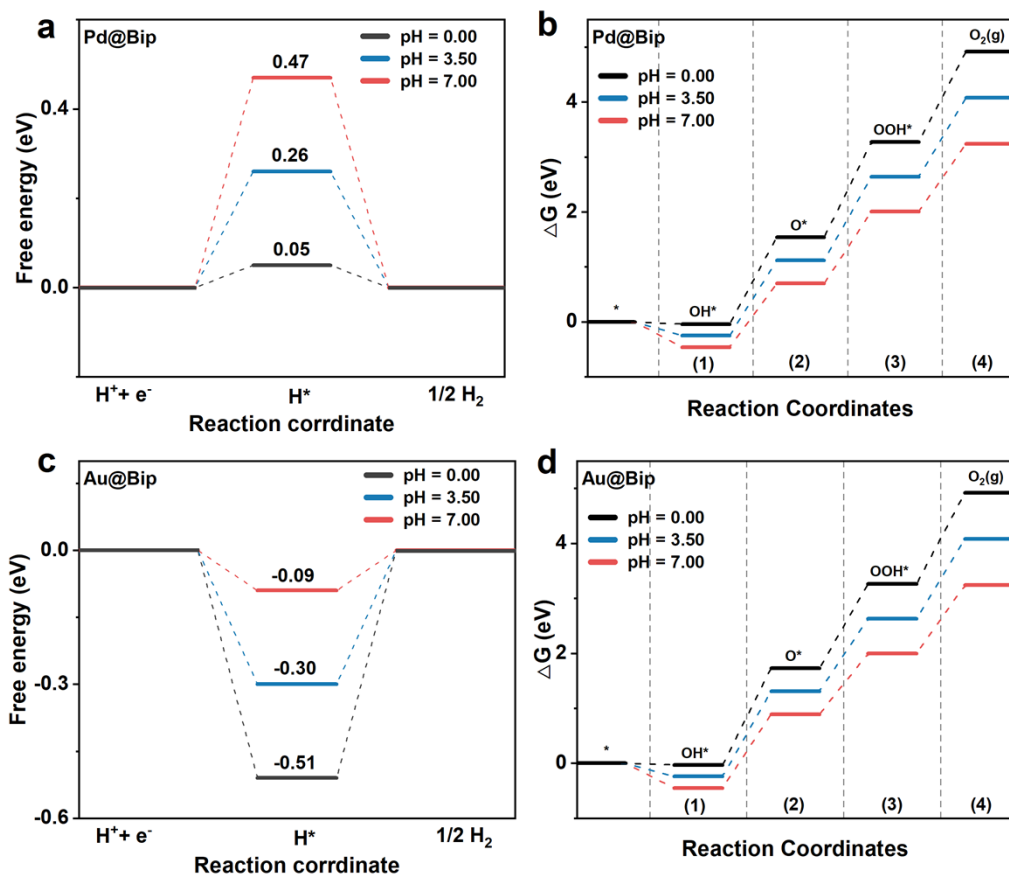


Fig. S12 Gibbs free energy change diagram of HER and OER for Pd@Bip and Au@Bip under different pH at 300 K.

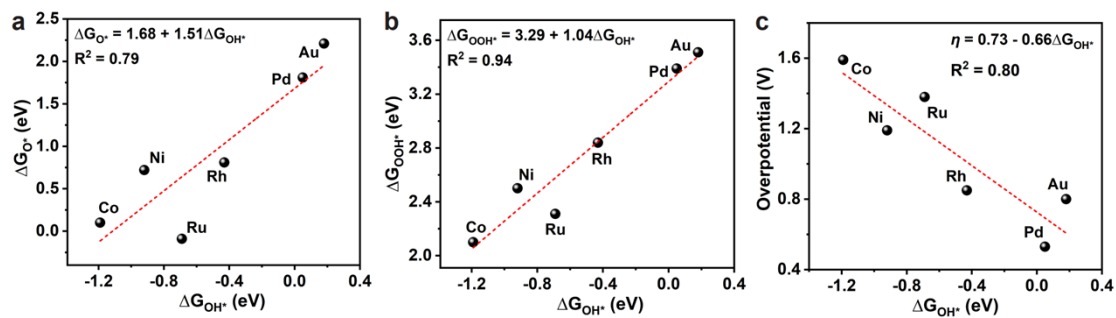


Fig. S13 The relationship between ΔG_{OH^*} and (a) ΔG_{O^*} ; (b) ΔG_{OOH^*} ; (c) overpotential of TM@Bip at 300 K.

Reference

- S1. J. K. Nørskov, T. Bligaard, A. Logadottir, J. Kitchin, J. G. Chen, S. Pandalov and U. Stimming, *J. Electrochem. Soc.*, 2005, **152**, J23.
- S2. I. C. Man, H. Y. Su, F. Calle-Vallejo, H. A. Hansen, J. I. Martínez, N. G. Inoglu, J. Kitchin, T. F. Jaramillo, J. K. Nørskov and J. Rossmeisl, *ChemCatChem*, 2011, **3**, 1159-1165.
- S3. M. Umer, S. Umer, M. Zafari, M. Ha, R. Anand, A. Hajibabaei, A. Abbas, G. Lee and K. S. Kim, *J. Mater. Chem. A*, 2022, **10**, 6679-6689.
- S4. J. Wu and Y.-X. Yu, *Int. J. Hydrog. Energy*, 2023, **48**, 5961-5975.