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Electronic Supplementary Information

Penta-BCN monolayer: a metal-free photocatalyst with high carrier mobility for water splitting

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Table S1. Zero-point energy correction (E_{ZPE}), entropy contribution (TS, T = 298.15 K), total energy (E), and the Gibbs free energy (G) of molecules and adsorbates in this study.

Species	E_{ZPE} (eV)	-TS (eV)	E (eV)	G(eV)
H_2	0.27	-0.40	-6.76	-6.89
H_2O	0.56	-0.67	-14.22	-14.33
OH*	0.35	-0.01	-432.46	-423.12
O*	0.09	-0.03	-426.28	-426.22
OOH*	0.36	-0.01	-436.01	-435.66
H*	0.25	-0.01	-423.88	-423.64

In the aqueous solution, the OER process generally involves four-electron oxidation steps, which can be written as:

$$H_2O + * \rightarrow OH^* + H^+ + e^- \quad (1)$$

$$OH^* \rightarrow O^* + H^+ + e^- \quad (2)$$

$$O^* + H_2O \rightarrow OOH^* + H^+ + e^- \quad (3)$$

$$OOH^* \rightarrow * + O_2 + H^+ + e^- \quad (4)$$

where * denotes the adsorption site, OH*, O* and OOH* denote the adsorbed intermediates.

Meanwhile, the HER process with two-electron pathways, including a fast proton/electron transfer step and a fast hydrogen release step, can be written as:

$$* + H^+ + e^- \rightarrow H^* \quad (5)$$

$$H^* + H^+ + e^- \rightarrow * + H_2 \quad (6)$$

We used a 3×3×1 supercell to explore the catalytic activity of the penta-BCN monolayer with the computational hydrogen electrode (CHE) model.[1] Then, considering the effect of electrode potential (U) and pH, the free energy change (ΔG) for OER and HER electrochemical steps can be expressed as:

$$\Delta G_1 = G_{OH^*} + 1/2G_{H2} - G_{H2O} - G^* - \Delta G_U - \Delta G_{pH} \quad (7)$$

$$\Delta G_2 = G_{O^*} + 1/2G_{H2} - G_{OH^*} - \Delta G_U - \Delta G_{pH} \quad (8)$$

$$\Delta G_3 = G_{OOH^*} + 1/2G_{H2} - G_{H2O} - G_{O^*} - \Delta G_U - \Delta G_{pH} \quad (9)$$

$$\Delta G_4 = G^* + 1/2G_{H2} + G_{O2} - G_{OOH^*} - \Delta G_U - \Delta G_{pH} \quad (10)$$

$$\Delta G_5 = G_{H^*} - 1/2G_{H2} - G^* - \Delta G_U + \Delta G_{pH} \quad (11)$$

$$\Delta G_6 = G^* + 1/2G_{H2} - G_{H^*} - \Delta G_U + \Delta G_{pH} \quad (12)$$

where the G^*, G_{OH^*}, G_{O^*}, and G_{OOH^*} are the free energies of *, OH*, O*, and OOH*, respectively. G_{H2O} and G_{H2} are the free energies of H_2O and H_2 molecules, respectively. The Gibbs free energy (G) can be calculated by

$$G = E + E_{ZPE} - TS \quad (13)$$

in which E represents the total energy from DFT calculation. E_{ZPE} and TS are zero-point energy and entropy correction, respectively. $\Delta G_U = -n_e U$, where n_e denotes the number of electrons and U is the electrode potential. $\Delta G_{pH} = k_B T \times \ln 10 \times pH$ and here the value of pH is set to be zero.

Reference

1 J. K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard and H. Jonsson, *J. Phys. Chem. B*, 2004, **108**, 17886–17892.