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

Supporting Information

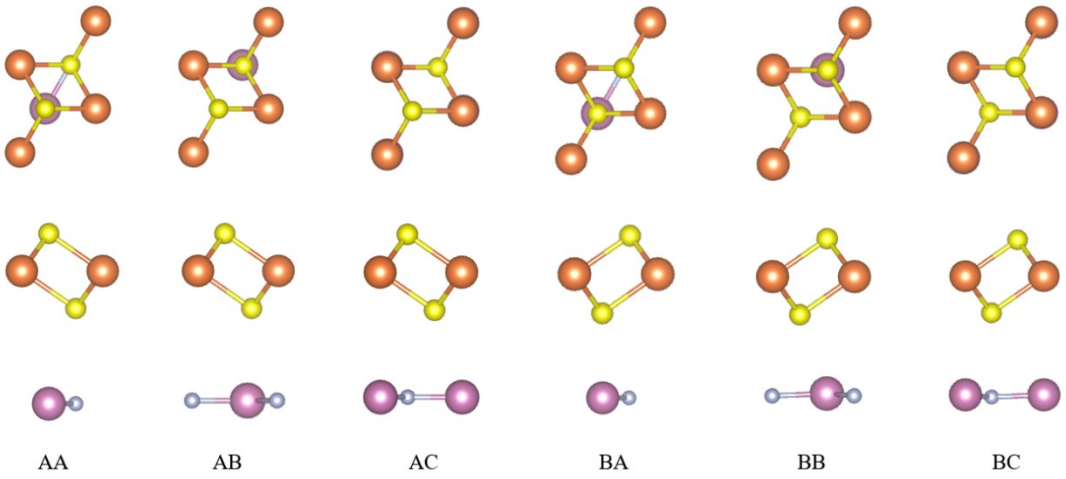

Fig. S1 Six configurations of InN/XS_2 (X=Zr, Hf) heterojunctions

Table S1. Lattice constants, binding energies, and interlayer spacings of six configurations for InN/XS_2 (X=Zr, Hf) heterostructures

Configuration	AA	AB	AC	BA	BB	BC
Lattice constant /Å	3.64	3.63	3.64	3.64	3.65	3.64
E_b (meV/Å^2)	-60.07	-63.39	-64.30	-67.60	-63.07	-59.05
Interlayer distance/Å	3.25	3.11	3.09	3.05	3.09	3.35

Configuration	AA	AB	AC	BA	BB	BC
Lattice constant /Å	3.62	3.63	3.62	3.62	3.63	3.62
E_b (meV/Å^2)	-70.54	-73.67	-74.82	-77.43	-74.18	-69.53
Interlayer distance/Å	3.33	3.19	3.18	3.12	3.17	3.42

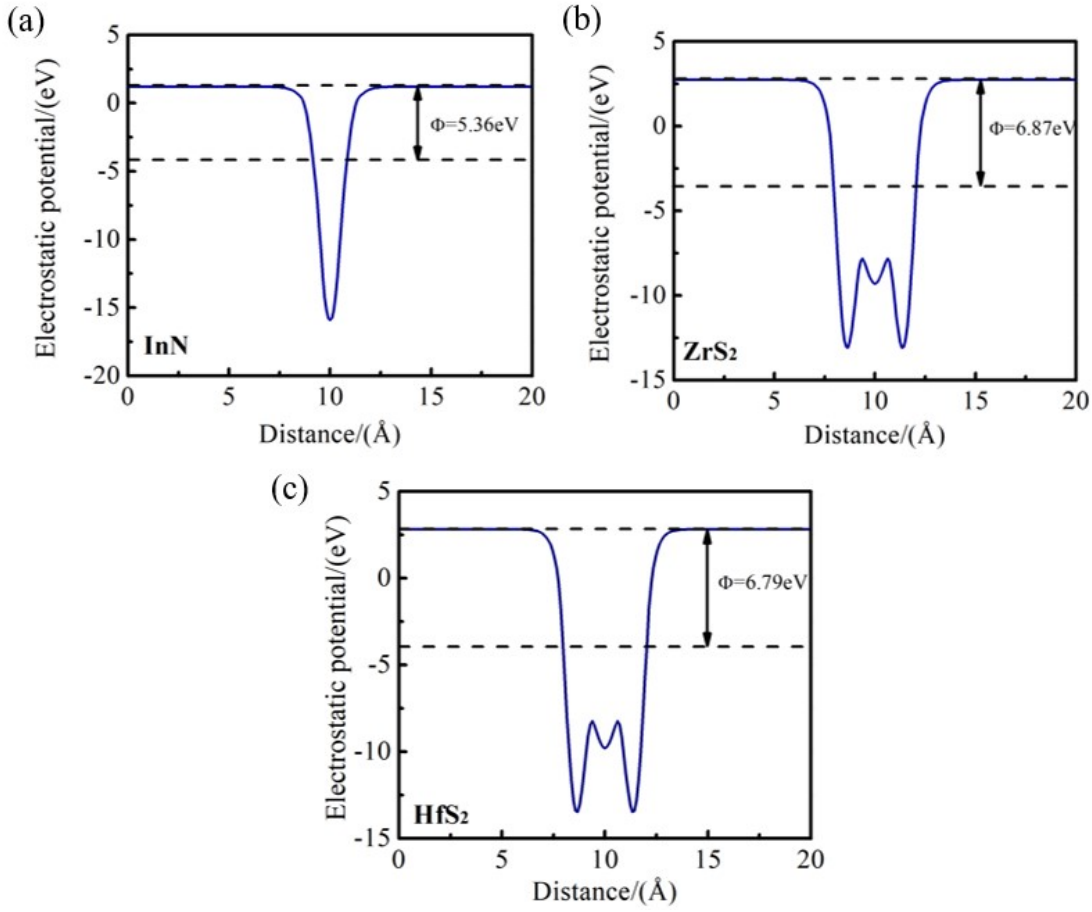

Fig. S2 The variation of Electrostatic potential along z-direction of InN, ZrS2, and HfS2 monolayers

The HER/OER process

The change in Gibbs free energy in HER and OER are calculated according to the formula，

$$\Delta G = \Delta E + \Delta E_{\mathrm{zpe}} - T\Delta S \tag{1}$$

where ΔE indicates the change in total energies, ΔE_{zpe} and ΔS is the change of zero-point energies and entropic contributions, respectively.

The process of HER can be divided into two steps，

$$* + \mathrm{H^+} + \mathrm{e^-} \rightarrow \mathrm{H^*} \tag{2}$$

$$\mathrm{H^*} + \mathrm{H^+} + \mathrm{e^-} \rightarrow \mathrm{H_2} + * \tag{3}$$

The process of OER can be considered as four steps，

$$* + \mathrm{H_2O} \rightarrow \mathrm{OH^*} + \mathrm{H^+} + \mathrm{e^-} \tag{4}$$

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

$$O^* + H_2O \rightarrow OOH^* + H^+ + e^- \quad (6)$$

$$OOH^* \rightarrow * + O_2 + H^+ + e^- \quad (11)$$

where * is the adsorbed materials, O^*, OH^*, OOH^* are the adsorbed intermediates of OER, and H^* represents the adsorbed intermediates of HER.

Heteroatom doping is an effective case to improve HER efficiency, which can simultaneously tune the active site and electrochemical surface area (ECSA). Taking InN/ZrS_2 as an example, the HER efficiency of InN doped with a single metal atom was studied by DFT calculation with 4 × 4 × 1 supercell, investigating the substitution of In atoms in InN by different metal atoms. The formation energies of these different structures were firstly calculated to evaluate their structural stability. The formula is $E_f = E_{tot} - E_{InN} - E_i$, where E_{tot} is the total energy of InN doped with metal atoms, and E_{InN} is the energy of InN with one In vacancy, E_i is the energy of a metal atom relative to its bulk metal. The calculated results are shown in Table S2. The negative value of the calculated results indicates that the structure can exist stably.

Table S2. Formation energies of structures doped with different metal single atoms

Metal	Cr	Mo	W	Pt
E_f(eV)	-19.78	-21.91	-22.71	-11.69
Metal	Al	Ge	Sn	Pb
E_f(eV)	-13.42	-13.16	-12.22	-10.43

The HER process of the single-metal doped structure was studied, the HER activity was judged by ΔG. Fig. S4 shows the HER reaction process on the catalyst.

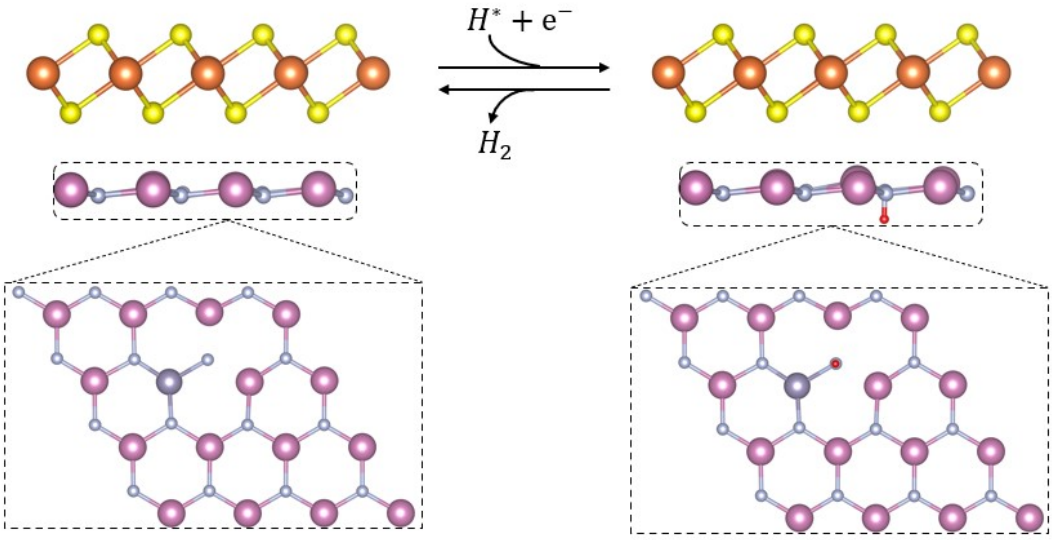

Fig. S4 Adsorption configurations of intermediate species involved in the HER process, the orange, yellow, pink, white, red, and gray atoms represent Zr, S, In, N, H, and doped atoms, respectively

Table S3. The calculated energy barriers at different cut-off energies with k-mesh fixed at 3×3×1

ENCUT (eV)	300	350	400	450	500	520	550	570
Barrier (eV)	-0.0652	-0.1052	-0.1181	-0.1204	-0.1231	-0.1268	-0.1257	-0.1232
Difference	-0.0401	-0.0129	-0.0023	-0.0027	-0.0037	0.0011	0.0025	\

Table S4. The calculated energy barriers at different k-mesh with ENCUT fixed at 500 eV

K-points	1×1×1	3×3×1	5×5×1	7×7×1
Barrier (eV)	-0.1951	-0.1231	-0.1233	-0.1144
Difference	0.0720	-0.0002	0.0089	\