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

Transition Metal Single–atom Supported on Hexagonal $ZnIn_2S_4$ Monolayer for Hydrogen Evolution Reaction

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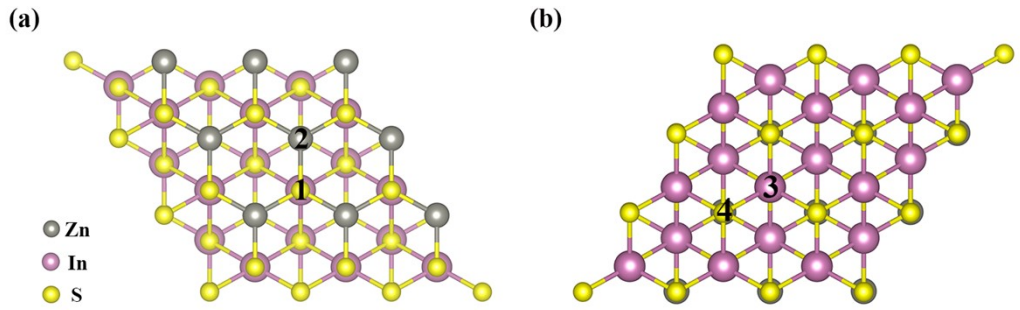

Figure S1. Four possible sites for a single H atom adsorbed on ZIS, including S atop site and Zn atop site on Zn–S plane are labeled by numbers 1and 2, respectively, In atop site and S atop site on In–S plane are labeled by numbers 3 and 4, respectively.

Table S1. The reaction Gibbs free energy of hydrogen adsorption (ΔG_{H^*}) of a single H atom adsorbed at three different sites of ZIS. Sites 1, 3, 4 represent S atop site on Zn–S plane, In atop site, and S atop site on In–S plane, respectively. After optimization, the H atom of the Zn atop site (site 2 in Figure S1) moves to the S atop site (site 1) on Zn–S plane.

Sites	site 1	site 3	site 4
ΔG_{H^*} (eV)	2.07	3.78	4.42

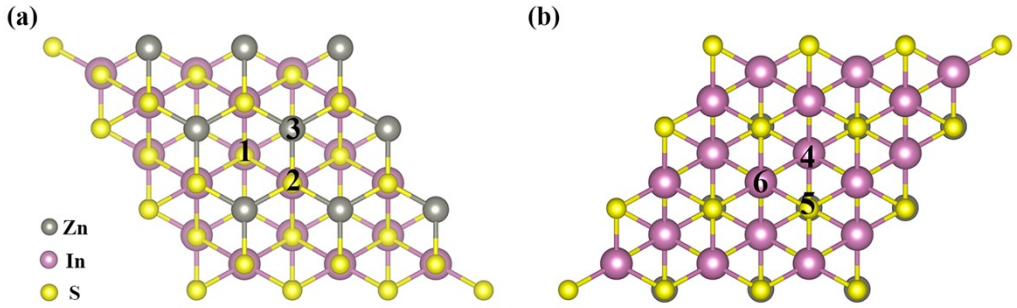

Figure S2. Six possible sites for a single TM atom supported on ZIS, including Zn–S hollow site, S atop site on Zn–S plane, Zn atop site, In–S hollow site, S atop site on In–S plane and In atop site, are labeled by numbers 1, 2, 3,4, 5 and 6, respectively.

Table S2. The binding energies of the Hf single atom adsorbed at six different sites of ZIS. Sites 1, 2, 3, 4, 5 and 6 represent Zn–S hollow site, S atop site on Zn–S plane, Zn atop site, In–S hollow site, S atop site on In–S plane and In atop site, respectively.

Sites	site 1	site 2	site 3	site 4	site 5	site 6
E_{ads} (eV)	−7.01	−2.16	4.90	−0.28	−1.30	−6.67

Table S3. The sum of the covalent radii of the isolated TM and S atoms ($r_{TM} + r_S$)

	Hf–S	Ta–S	W–S	Re–S	Os–S	Ir–S	Pt–S	Au–S
$r_{TM}+r_S$(Å)	2.55	2.49	2.40	2.34	2.32	2.25	2.26	2.27

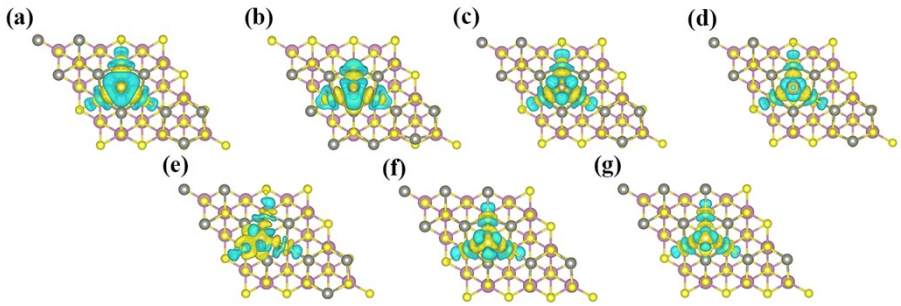

Figure S3. The top views of 3D charge density difference isosurfaces (a) Hf@ZIS, (b) Ta@ZIS, (c) W@ZIS, (d) Re@ZIS, (e) Os@ZIS, (f) Ir@ZIS, and (g) Pt@ZIS.