Supporting Information for:

From the single-atom limit to the mixed-metal phase: Finding the optimum condition for activating the basal plane of a FePSe$_3$ monolayer towards HER

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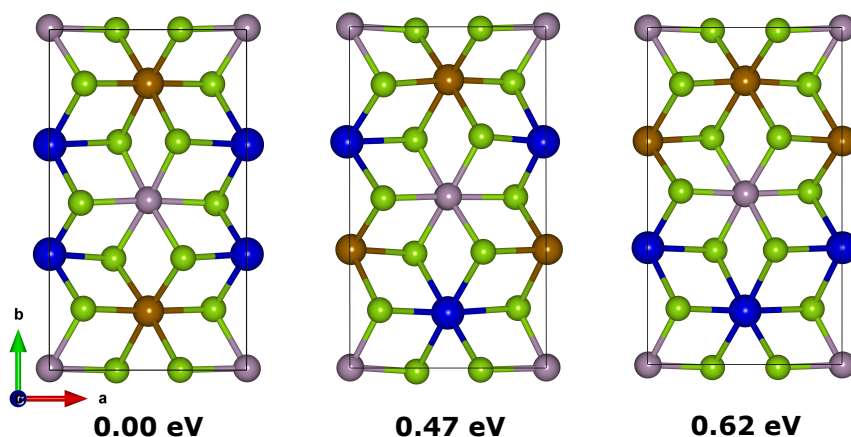
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0.00 eV   **0.47 eV**   **0.62 eV**

Figure S1: Optimized structures of FeTcP$_2$Se$_6$ monolayer. The number given below the structures denote the relative energies with respect to the most stable configuration.

Table S1: Lattice parameter of pristine and TM-doped (25%) $FePSe_3$ monolayers.

System	a (Å)
Pristine	6.28
3d–TM	
Sc-FePSe$_3$	6.34
Ti-FePSe$_3$	6.30
V-FePSe$_3$	6.29
Cr-FePSe$_3$	6.29
Mn-FePSe$_3$	6.30
Co-FePSe$_3$	6.29
Ni-FePSe$_3$	6.24
Cu-FePSe$_3$	6.25
Zn-FePSe$_3$	6.27
4d–TM	
Y-FePSe$_3$	6.39
Zr-FePSe$_3$	6.32
Nb-FePSe$_3$	6.33
Mo-FePSe$_3$	6.29
Tc-FePSe$_3$	6.30
Ru-FePSe$_3$	6.24
Rh-FePSe$_3$	6.24
Pd-FePSe$_3$	6.26
Ag-FePSe$_3$	6.28
Cd-FePSe$_3$	6.32

Table S2: Variation of ΔG_{H^*} (in eV) on 6.25% Sc doped FePSe$_3$ monolayer with applied biaxial tensile strain.

% Strain	Site							
	P2	Se3	P1	P3	Se5	Se6	Se7	Se8
0	0.35	1.08	0.38	0.35	1.59	0.66	1.19	1.29
1	0.30	0.92	0.42	0.32	1.02	0.64	1.05	1.16
2	0.21	0.49	0.32	0.24	0.61	0.48	0.58	0.64
3	0.23	0.35	0.31	0.29	0.52	0.48	0.59	0.56
4	0.20	0.22	0.21	0.24	0.42	0.37	0.39	0.40
5	0.14	−0.05	0.18	0.18	0.27	0.23	0.19	0.13

HER pathways

The Volmer-Heyrovsky pathway involves the following two reaction steps:

(1) $2H^+ + 2e^- + * \longrightarrow H^+ + e^- + H^*$

(2) $H^+ + e^- + H^* \longrightarrow H_2(g) + *.$
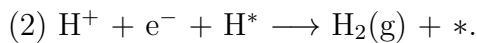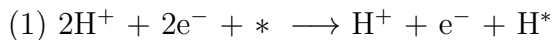
The free energy changes at these intermediate steps at a finite bias and zero pH can be expressed as ΔG_1 and ΔG_2, which are defined as follows.
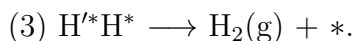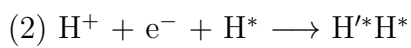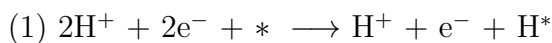
$$\Delta G_1 = G(H^+ + e^-) + G(H^*) - G(2H^+ + 2e^-) - G(*) = \Delta G_{H^*} + eU,$$

and

$$\Delta G_2 = G(H_2(g)) + G(*) - G(H^+ + e^-) - G(H^*) = -\Delta G_{H^*} + eU.$$

The values of ΔG_1 and ΔG_2 depend on ΔG_{H^*}, the applied bias (U) with respect to the reversible hydrogen electrode (RHE), and the electric charge (e).

Another pathway is Volmer–Tafel pathway, in which the intermediate reaction steps are:

(1) $2H^+ + 2e^- + * \longrightarrow H^+ + e^- + H^*$

(2) $H^+ + e^- + H^* \longrightarrow H'^*H^*$

(3) $H'^*H^* \longrightarrow H_2(g) + *.$

H^* indicates the first H adsorbed at a particular site, and H'^* is the second H which gets adsorbed at a neighbouring site in the presence of first adsorbed H. Free energy changes for these intermediate steps can be written as follows:

$$\Delta G_1 = \Delta G_{H^*} + eU,$$

$$\Delta G_2 = \Delta G_{H'^*} + eU,$$

and

$$\Delta G_3 = \Delta G(H'^*H^*) - G(*) - G(H_2(g)) = -\Delta G_{H^*} - \Delta G_{H'^*}.$$

Here, ΔG_{H^*} is the adsorption free energy of the first H and $\Delta G_{H'^*}$ is the adsorption free energy of the second H at the neighbouring site in presence of the first adsorbed H.
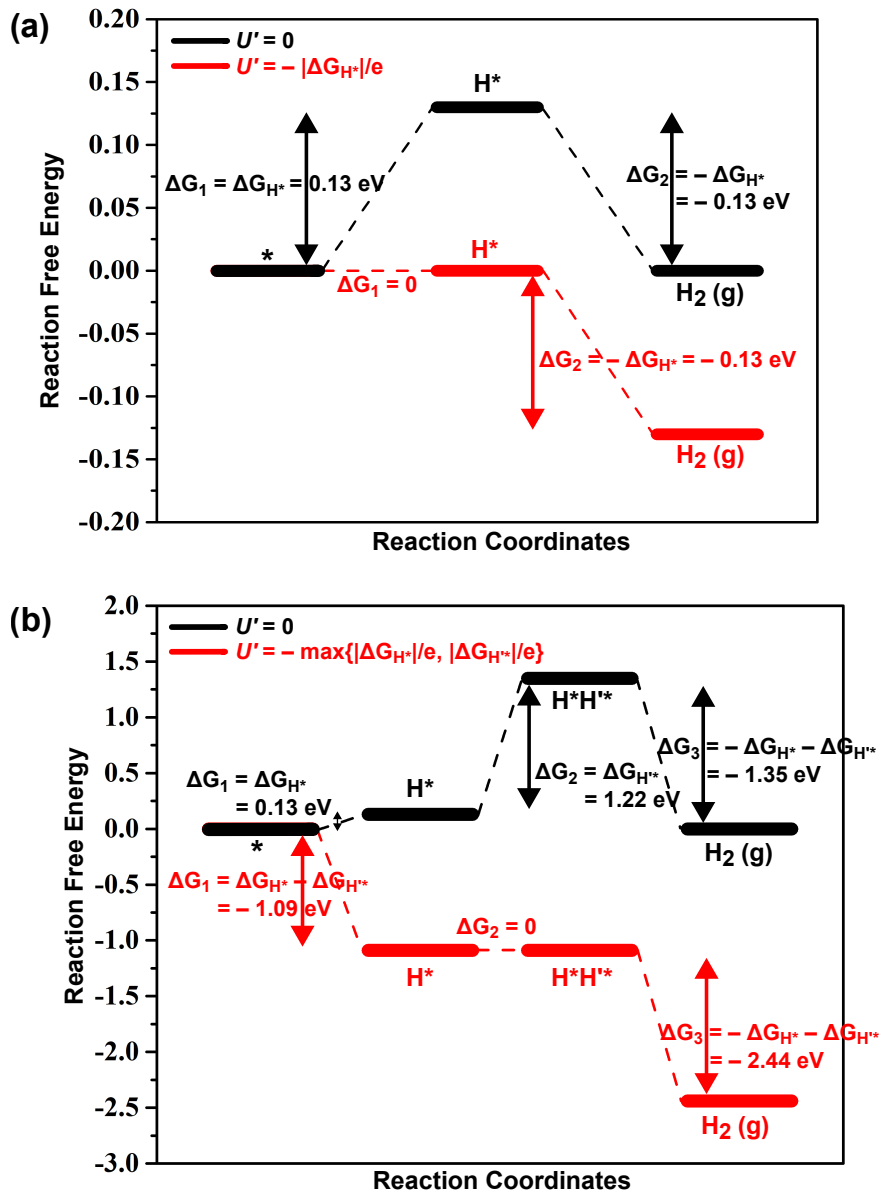
Figure S2: (a) Volmer-Heyrovsky and (b) Volmer-Tafel reaction pathways for the most active site of 25% Tc doped FePSe$_3$ monolayer.

Table S3: Total magnetic moment (M_{total}) and magnetic moment of each dopant atom (M_{dopant}) in pristine and TM-FePSe$_3$ monolayers at different doping concentrations. Fe with ↑-spin is replaced by another TM atom.

| System	25%		12.5%		6.25%	
	M_{total}	M_{dopant}	M_{total}	M_{dopant}	M_{total}	M_{dopant}
Sc-FePSe$_3$	−3.78	−0.10	−3.10	0.06	−3.07	0.05
Ti-FePSe$_3$	−2.01	1.68				
V-FePSe$_3$	−1.00	2.79				
Cr-FePSe$_3$	0.01	3.83				
Mn-FePSe$_3$	0.86	4.47				
FePSe$_3$	0.00	3.53				
Co-FePSe$_3$	−2.73	1.13				
Ni-FePSe$_3$	−2.03	1.30				
Cu-FePSe$_3$	−3.01	0.24				
Zn-FePSe$_3$	−3.77	0.00				
Y-FePSe$_3$	−3.79	−0.03	−3.11	0.03	−3.08	0.02
Zr-FePSe$_3$	−3.79	0.24	−3.74	−0.21	−2.48	0.62
Nb-FePSe$_3$	−0.89	2.69				
Mo-FePSe$_3$	−1.66	2.40	−1.72	2.32	−1.71	2.36
Tc-FePSe$_3$	−0.94	2.69	−0.92	2.74	−0.92	2.74
Ru-FePSe$_3$	−3.77	−0.03				
Rh-FePSe$_3$	−2.90	0.66	−2.90	0.68	−2.90	0.69
Pd-FePSe$_3$	−2.20	0.83				
Ag-FePSe$_3$	−3.02	0.08				
Cd-FePSe$_3$	−3.77	0.00				
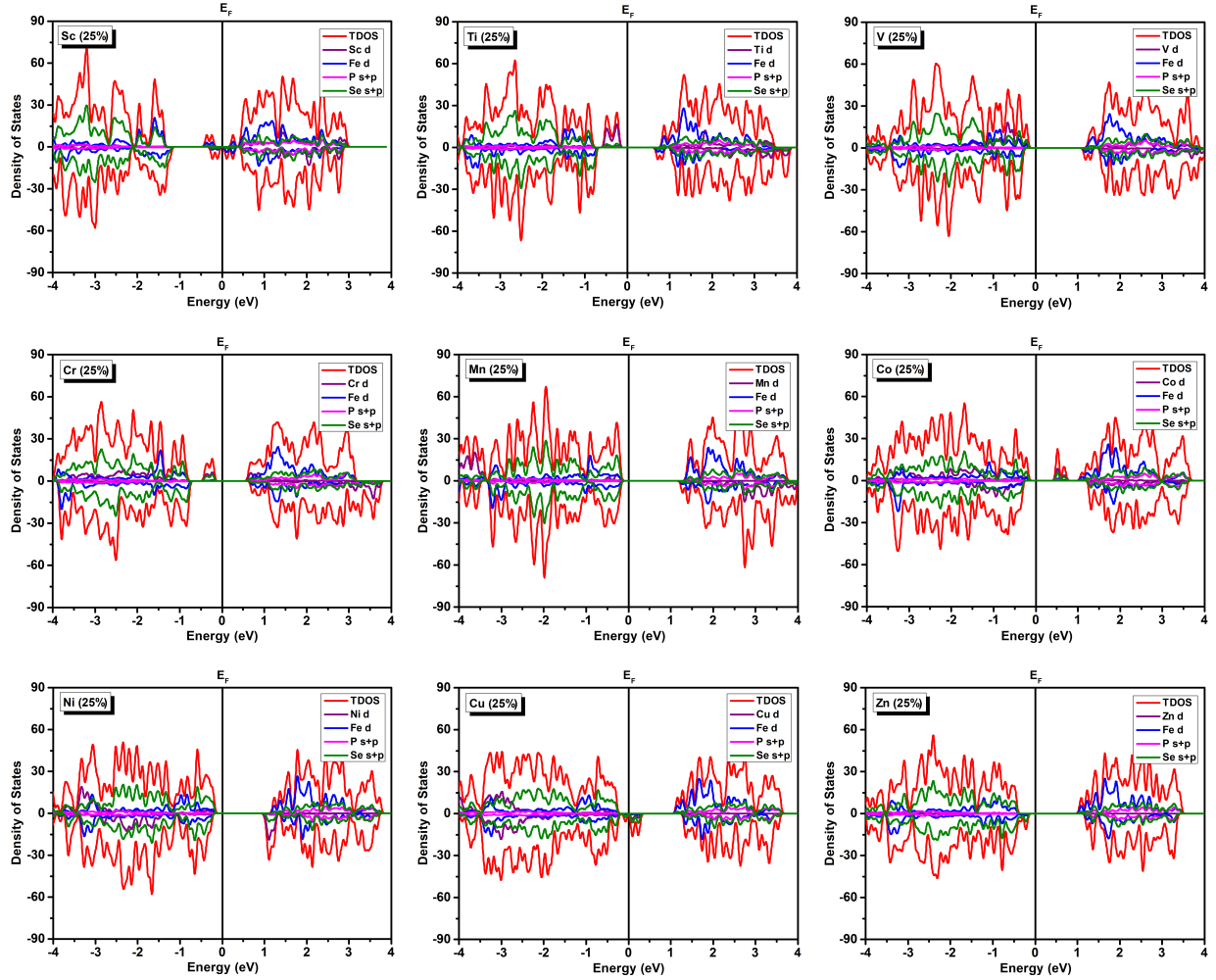
Figure S3: Total as well as the partial DOS of 3d TM-doped FePSe$_3$ monolayer with 25% doping concentration. E$_F$ denotes the Fermi energy and is represented by a black colored solid vertical line.
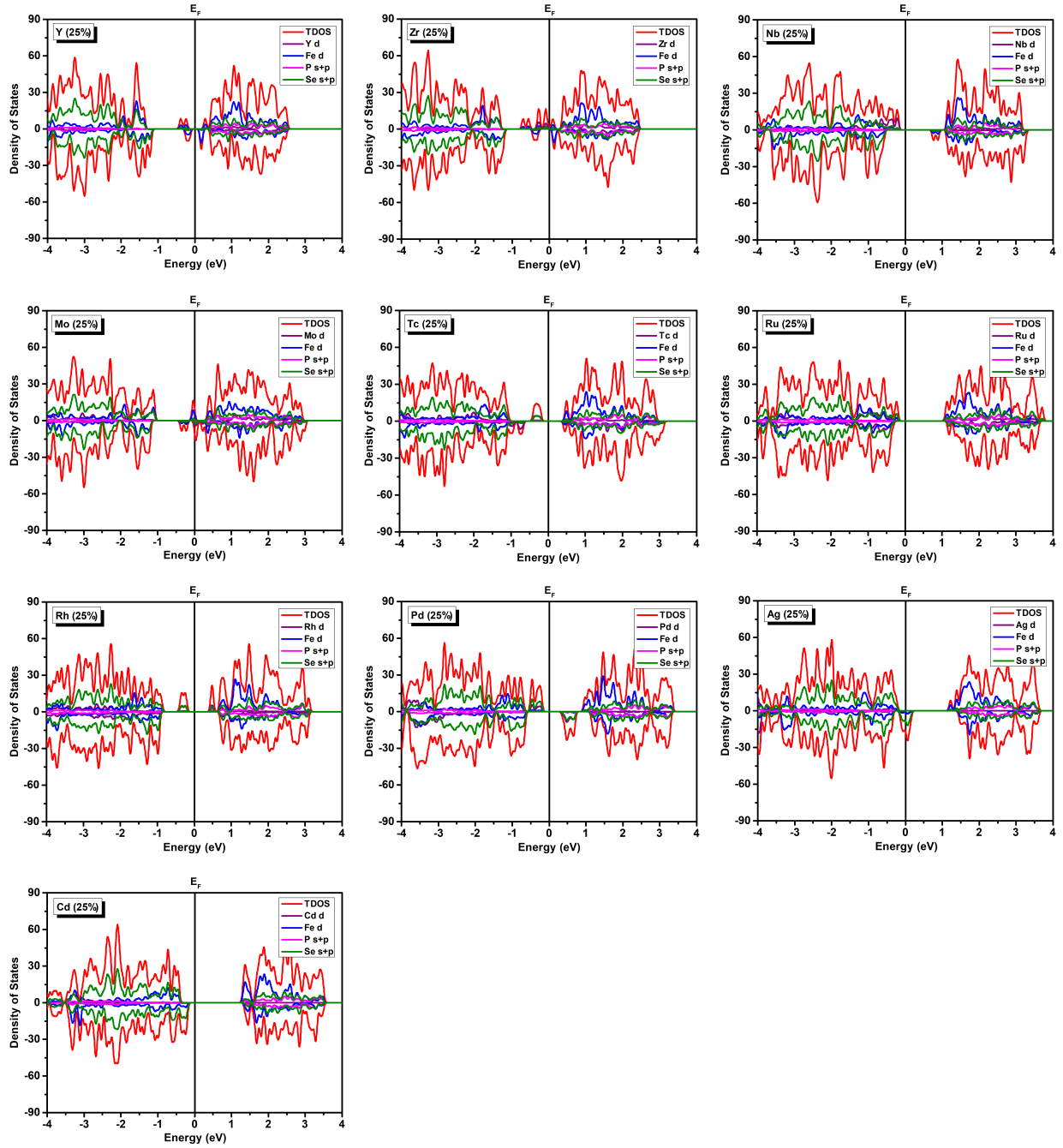
Figure S4: Total as well as the partial DOS of 4d TM-doped FePSe$_3$ monolayer with 25% doping concentration. E$_F$ denotes the Fermi energy and is represented by a black colored solid vertical line.