Complementary Effects of External Strain, Functionalization and Vacancy Defects Towards Enhanced HER Activity in Transition Metal Phosphorous based Tri-chalcogenide Monolayers

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Supporting Information Available

Activity calculated at different coverages

Table S1: Computed adsorption energy (E_{ads}) and free energy ($\Delta G_{\mathrm{H^*}}$) values on S site of pristine pristine FePS$_3$ for different hydrogen coverages (θ). $\theta = 1$ corresponds corresponds to the full monolayer coverage where all the available S sites are occupied with H atoms.

θ	E_{ads} (eV)	$\Delta G_{\mathrm{H^*}}$ (eV)
0.08	1.28	1.52
0.33	0.89	1.13
0.5	−1.82	−1.58
0.66	1.11	1.35
1	−2.44	−2.20

Formation energies of the functionalized surfaces

In order to check the energetic feasibility of whether it is possible to substitute S by X, and to create a S-vac system we have calculated their formation energies as per the following equation.

$$E_{\mathrm{f}} = E_{\mathrm{T}}(\mathrm{X} : \mathrm{FePS_3}) - E_{\mathrm{T}}(\mathrm{FePS_3}) - \mu_X + \mu_S, \tag{1}$$

where $E_{\mathrm{T}}(\mathrm{X} : \mathrm{FePS_3})$ and $E_{\mathrm{T}}(\mathrm{FePS_3})$ are the total energies of the functionalized and pristine systems respectively. μ_X and μ_S are the chemical potentials of the dopant element and S in their respective reference states. For each dopant element as well as S, we consider two extreme possibilities for their reference states. One is their isolated atomic states, and the other one their most stable state. For C, P and S the most stable state is taken as their most stable solid phases. For N and O it is their molecular, gaseous states, $i.e.$, N_2 and O_2. It is worth mentioning that since binding energy of the O_2 molecule is not correctly reproduced by the usual approximations in DFT, the chemical potential of oxygen has been calculated from the reaction free energy of the $H_2O \rightarrow 1/2\ O_2 + H_2$ reaction.

Thus the chemical potential of each element involved can vary over the range from their atomic energy to that at their respective stable states, and one can plot the formation energy of the functionalized layer as a function of two chemical potentials (except for the S-vac system when it is a function of μ_S alone). Instead of going into this (unnecessary though straightforward) exercise, we calculate the formation energy for each functionalized system in four limiting cases as described and given Tables S2- S5.

Table S2: Case I: Reference states of both X and S are their atomic states.

System	E_{f} (eV)
P: FePS$_3$	+0.48
C: FePS$_3$	−2.39
N: FePS$_3$	−0.68
O: FePS$_3$	−2.64
S-vac: FePS$_3$	+5.36

Table S3: Case II: Reference states of both X and S are their respective most stable states. See text above for details.

System	E_{f} (eV)
P: $FePS_3$	+1.835
C: $FePS_3$	+4.458
N: $FePS_3$	+1.734
O: $FePS_3$	−2.077
S-vac: $FePS_3$	+1.242

Table S4: Case III: Reference state of X is its most stable state, but that of S is its atomic state.

System	E_{f} (eV)
P: $FePS_3$	+5.953
C: $FePS_3$	+5.852
N: $FePS_3$	+8.576
O: $FePS_3$	+2.041
S-vac: $FePS_3$	+5.36

Table S5: Case IV: Reference state of X is its atomic state, but that of S is its stable solid state.

System	E_{f} (eV)
P: $FePS_3$	−3.638
C: $FePS_3$	−4.798
N: $FePS_3$	−6.508
O: $FePS_3$	−6.758
S-vac: $FePS_3$	+1.242

The important point to note is that all the systems except S-vac: $FePS_3$ has negative E_f under some conditions. In particular, if the reference state of the dopant is its gaseous state, and that of S is its solid state, all doped layers have negative E_f. Therefore, controlling the experimental conditions appropriately, it is possible to substitute S by and C, N, O or P. On the other hand, creating a vacancy defect in a crystalline material is not expected to make it more stable. Therefore, it is not surprising that S-vac: $FePS_3$ does not have a negative E_f in any situation.

Comparison of experimental and theoretically calculated data: lattice parameters and bond lengths

The data for calculated and experimentally measured lattice parameters along with the different bond lengths is tabulated in Table S6. In order to have a clear picture different bond lengths are depicted in Fig. 1. There are three different Fe-Fe bonds, three different Fe-S bonds and two different S-S bonds which are in good agreement with the experimentally measured data.

Table S6: Comparison between computed and experimentally measured lattice parameters (a) and bond lengths (d).

Parameters	Calculated value (Å)	Experimental value (Å)
a	5.99	5.93
$d_{Fe\uparrow-Fe\uparrow}$	3.5	3.42
$d_{Fe\downarrow-Fe\downarrow}$	3.42	3.42
$d_{Fe\uparrow-Fe\downarrow}$	3.46	3.44
$d_{Fe-S}(1)$	2.54	2.54
$d_{Fe-S}(2)$	2.58	2.55
$d_{Fe-S}(3)$	2.61	2.56
$d_{S-S}(1)$	3.43	3.41
$d_{S-S}(2)$	3.47	3.43

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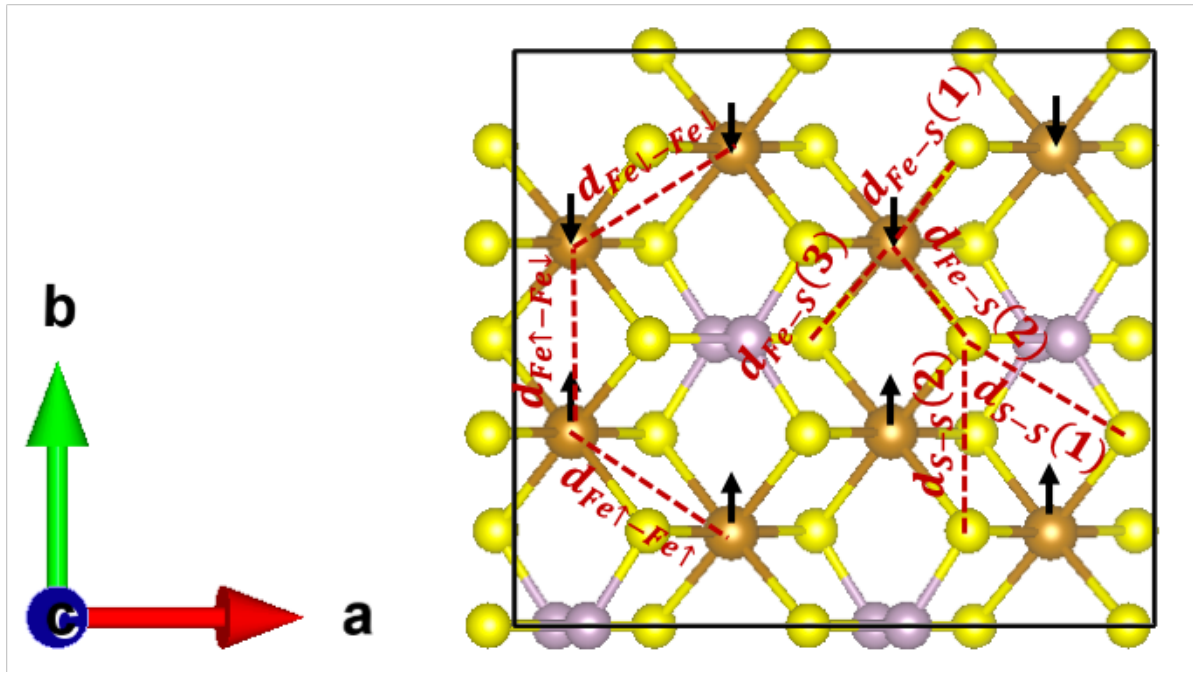
Figure S 1: Red dashed lines depict different bond lengths between Fe, P and S atoms in pristine FePS$_3$ system. The black ↑ and ↓ represent Fe atoms with majority up (↑) spin and down (↓) spin respectively.