

Chalcogen Composition Driven Enhancement of Catalytic Efficiency in Zirconium based Monolayers: Insight from Reaction Coordinate Mapping

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1 d-band center Analysis

The d-band center theory proposed by Nørskov and Hammer is a theoretical model for explaining substance adsorption on catalysts. This theory suggests that the adsorption capacity of a catalyst is mainly influenced by the position of the d-orbital center of the metal atom in the catalyst when a bond is formed with the adsorbed material. It also elucidates the connections between a catalyst's electronic structure and its adsorption capacity, as well as for revealing the catalyst's strong coordination ability and electrocatalytic performance based on changes in energy levels and electronic structures. Additionally, the incorporation of dopants, vacancies, strains, and heterostructures can be used to regulate the d-band centers of the catalyst atoms. In our work, we investigated the d-band center to find out the relation with HER activity. The plots for projected density of states (PDOS) of 'd' orbital of Zr atoms with d-band center are represented in Fig. 3 (a), (b) & (c) for functionalized ZrS₂, ZrSe₂ and ZrTe₂ monolayers, respectively and the values of d -band center are noted in Tab. 6 in supplementary information. In our analysis, we observed a correlation between the d-band center's proximity to the Fermi level and its efficacy in promoting the HER. Our findings indicate that as the d-band center moves further away from the Fermi level, its catalytic activity decreases. Our research shows a similar trend between the HER activity and the d-band center. In the comparison

of HER activities for the functionalized ZrS_2 monolayers, P-doped case shows good HER activity as compared to C and N doped cases which also reflected into d-band center as shown in Fig. 3 (a) in the supplementary information. The d-band center for P-doped ZrS_2 case is nearest to the Fermi level while for the C and N doped ZrS_2 cases, it shift away from the Fermi level as results they are less active as compared to P-doped. We also observed the similar trend for functionalized ZrSe_2 and ZrTe_2 monolayer and the d-band center of P-doped ZrSe_2 and N-doped ZrTe_2 are the closest to the Fermi level as shown in Fig 3 (b) and Fig 3 (c) in the supplementary information, respectively and identified as the good HER catalyst.

Figure 1: Side and top views of doped ZrSe_2 structure: (a), (b) for C doped (C - brown color atom); (c), (d) for N doped (N - light blue color atom); and (e), (f) for P doped (P - purple color atom).

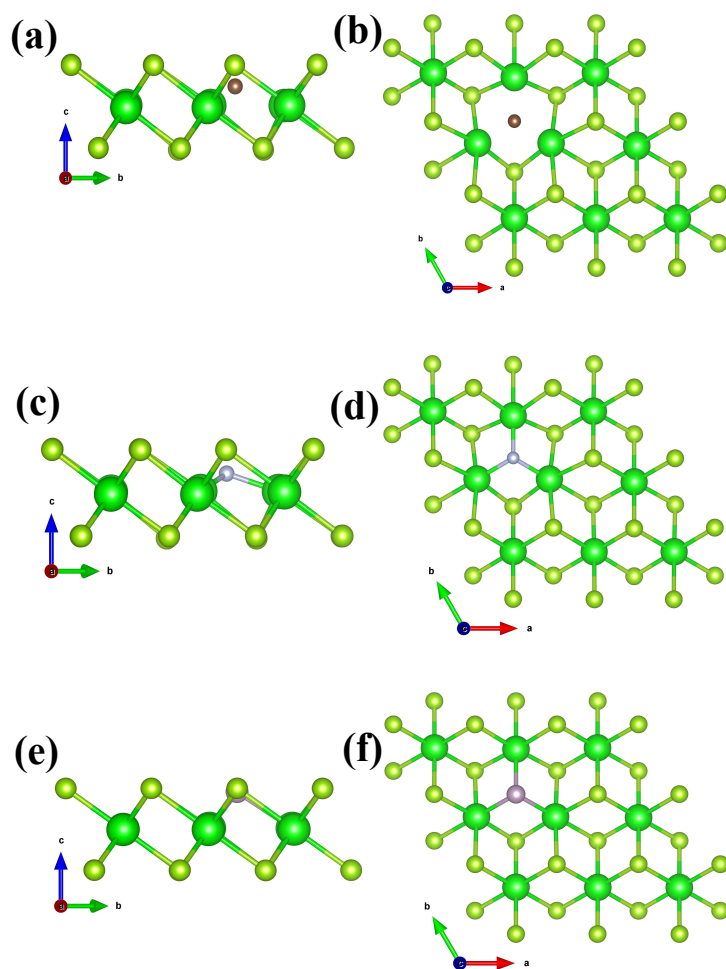


Figure 2: Side and top views of doped ZrTe_2 structure: (a), (b) for C doped (C - brown color atom); (c), (d) for N doped (N - light blue color atom); and (e), (f) for P doped (P - purple color atom).

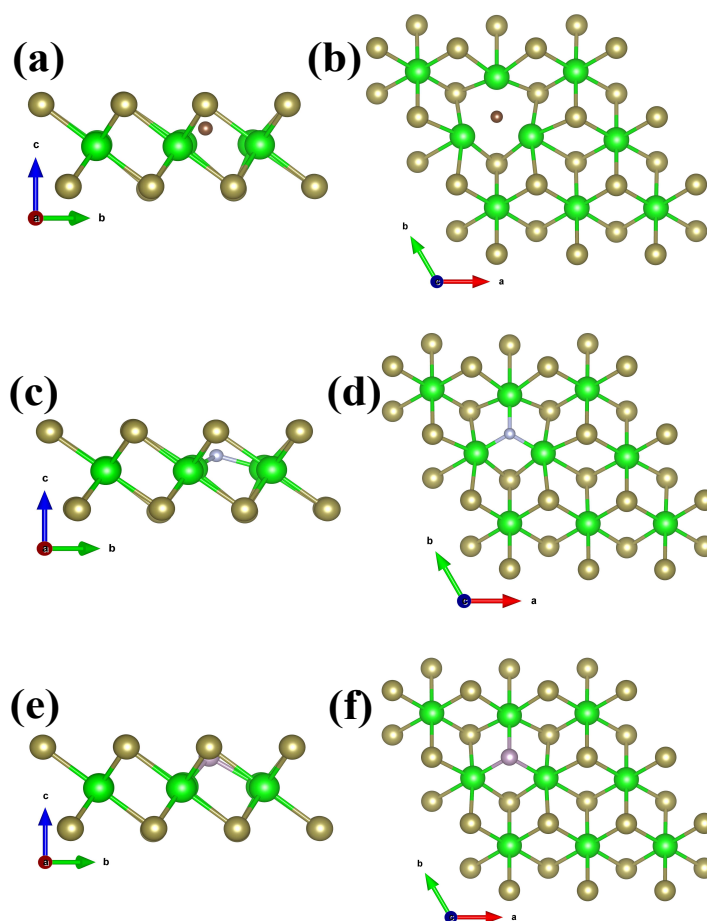


Figure 3: Illustrated the density of states of 'd' orbital of Zr atoms with the d-band center for functionalized cases; (a) ZrS_2 (b) ZrSe_2 and (c) ZrTe_2 . The black dashed line shows the d-band center and gray dotted line represents the Fermi level.

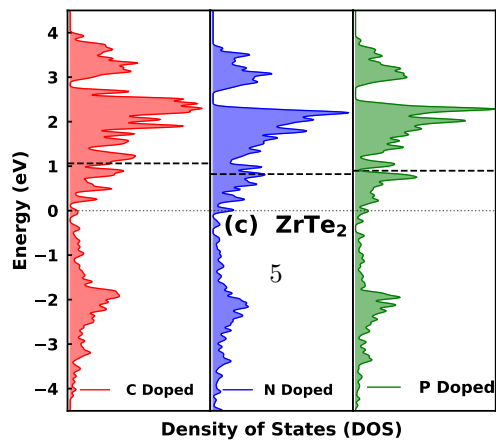
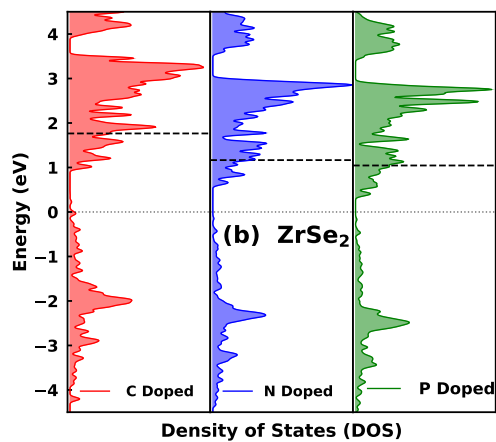
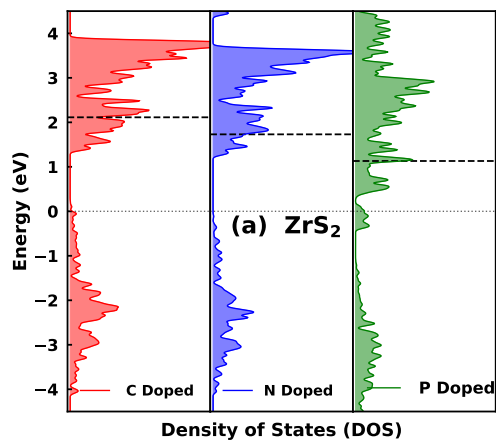


Table 1: Calculated lattice constants (a), bond length (D) of Zr and X, distance (d) between the Zr and dopant (d) for pristine and functionalized (C, N, and P doped) ZrX_2 monolayers.

| Parameters | ZrS ₂ | | | | ZrSe ₂ | | | | ZrTe ₂ | | | |
|-------------|------------------|-------|-------|-------|-------------------|-------|-------|-------|-------------------|-------|-------|-------|
| | Pristine | C | N | P | Pristine | C | N | P | Pristine | C | N | P |
| a (Å) | 11.04 | 11.04 | 11.04 | 11.04 | 11.38 | 11.38 | 11.38 | 11.38 | 11.90 | 11.90 | 11.90 | 11.90 |
| D (Å) | 2.55 | 2.58 | 2.57 | 2.53 | 2.70 | 2.72 | 2.70 | 2.69 | 2.92 | 2.92 | 2.91 | 2.91 |
| d (Å) | | 2.21 | 2.22 | 2.62 | | 2.18 | 2.21 | 2.64 | | 2.17 | 2.20 | 2.63 |
| ϕ (eV) | 3.60 | 3.59 | 3.65 | 3.68 | 3.46 | 3.46 | 3.46 | 3.51 | 4.13 | 4.08 | 4.09 | 4.13 |

Table 2: Adsorption energies and free energies of H* adsorbed on pristine and functionalized layered ZrX₂ structures along with the optimized surface-adsorbate distances.

| System | Adsorption Site | E_H [eV] | ΔG_H [eV] | $d_{surface-H}$ (in Å) |
|----------------------------|--------------------|------------|-------------------|------------------------|
| Pristine ZrS ₂ | Top on S atom | +0.734 | +0.974 | 1.36 |
| C doped | Top on dopant atom | -1.89 | -1.65 | 1.11 |
| N doped | Top on dopant atom | -1.63 | -1.39 | 1.03 |
| P doped | Top on dopant atom | -1.14 | -0.90 | 1.41 |
| Pristine ZrSe ₂ | Top on Se atom | +0.871 | +1.111 | 1.48 |
| C doped | Top on dopant atom | -1.70 | -1.46 | 1.11 |
| N doped | Top on dopant atom | -0.962 | -0.722 | 1.03 |
| P doped | Top on dopant atom | -0.749 | -0.50 | 1.41 |
| Pristine ZrTe ₂ | Top on Te atom | +0.964 | +1.204 | 1.68 |
| C doped | Top on dopant atom | -0.980 | -0.740 | 1.11 |
| N doped | Top on dopant atom | -0.178 | +0.06 | 1.03 |
| P doped | Top on dopant atom | -0.113 | +0.126 | 1.42 |

Table 3: Adsorption (E_A ; $A = O^*$, OH^* , and OOH^*), free energies (ΔG_A) of O^* , OH^* , and OOH^* and difference of free energy (ΔG_1 and ΔG_2) of intermediates on functionalized layered ZrS_2 structure. ($\Delta G_1 = \Delta G_O^* - \Delta G_{OH}^*$ and $\Delta G_2 = \Delta G_{OOH}^* - \Delta G_O^*$)

| System | Adsorbate | Free energy (ΔG_H) [eV] | ΔG_1 and ΔG_2 [eV] |
|------------------|-----------|-----------------------------------|------------------------------------|
| Pristine ZrS_2 | O^* | -0.351 | $\Delta G_1 = 0.461$ |
| | OH^* | -0.812 | $\Delta G_2 = 0.448$ |
| | OOH^* | +0.097 | |
| C Doped ZrS_2 | O^* | -3.871 | $\Delta G_1 = -0.778$ |
| | OH^* | -3.093 | $\Delta G_2 = 1.835$ |
| | OOH^* | -2.036 | |
| N Doped ZrS_2 | O^* | -0.379 | $\Delta G_1 = -0.159$ |
| | OH^* | -0.220 | $\Delta G_2 = 1.835$ |
| | OOH^* | +0.096 | |
| P Doped ZrS_2 | O^* | -2.251 | $\Delta G_1 = 1.094$ |
| | OH^* | -3.345 | $\Delta G_2 = 0.681$ |
| | OOH^* | -1.57 | |

Table 4: Adsorption (E_A ; $A = O^*$, OH^* , and OOH^*), Free energies (ΔG_A) of O^* , OH^* , and OOH^* and difference of free energy (ΔG_1 and ΔG_2) of intermediates on functionalized layered $ZrSe_2$ structure. ($\Delta G_1 = \Delta G_O^* - \Delta G_{OH}^*$ and $\Delta G_2 = \Delta G_{OOH}^* - \Delta G_O^*$)

| System | Adsorbate | Free energy (ΔG_H) [eV] | ΔG_1 and ΔG_2 [eV] |
|-------------------|-----------|-----------------------------------|------------------------------------|
| Pristine $ZrSe_2$ | O^* | -0.130 | $\Delta G_1 = 1.016$ |
| | OH^* | -1.146 | $\Delta G_2 = 0.299$ |
| | OOH^* | +0.169 | |
| C Doped $ZrSe_2$ | O^* | -3.274 | $\Delta G_1 = 0.006$ |
| | OH^* | -3.280 | $\Delta G_2 = 0.642$ |
| | OOH^* | -2.632 | |
| N Doped $ZrSe_2$ | O^* | 0.375 | $\Delta G_1 = 0.284$ |
| | OH^* | +0.091 | $\Delta G_2 = -0.408$ |
| | OOH^* | -0.033 | |
| P Doped $ZrSe_2$ | O^* | -2.079 | $\Delta G_1 = 0.831$ |
| | OH^* | -2.910 | $\Delta G_2 = 0.990$ |
| | OOH^* | -1.089 | |

Table 5: Adsorption (E_A ; $A = \text{O}^*$, OH^* , and OOH^*), Free energies (ΔG_A) of O^* , OH^* , and OOH^* and difference of free energy (ΔG_1 and ΔG_2) of intermediates on functionalized layered ZrTe_2 structure. ($\Delta G_1 = \Delta G_{\text{O}^*}^* - \Delta G_{\text{OH}^*}^*$ and $\Delta G_2 = \Delta G_{\text{OOH}^*}^* - \Delta G_{\text{O}^*}^*$)

| System | Adsorbate | Free energy (ΔG_H) [eV] | ΔG_1 and ΔG_2 [eV] |
|--------------------------|----------------|-----------------------------------|------------------------------------|
| Pristine ZrTe_2 | O^* | -0.595 | $\Delta G_1 = 0.580$ |
| | OH^* | -1.175 | $\Delta G_2 = 0.856$ |
| | OOH^* | +0.261 | |
| C Doped ZrTe_2 | O^* | -2.190 | $\Delta G_1 = 0.208$ |
| | OH^* | -2.398 | $\Delta G_2 = 1.006$ |
| | OOH^* | -1.184 | |
| N Doped ZrTe_2 | O^* | -0.303 | $\Delta G_1 = 1.848$ |
| | OH^* | -2.151 | $\Delta G_2 = -0.293$ |
| | OOH^* | -0.596 | |
| P Doped ZrTe_2 | O^* | -1.954 | $\Delta G_1 = 0.305$ |
| | OH^* | -2.259 | $\Delta G_2 = 0.676$ |
| | OOH^* | -1.278 | |

Table 6: The values of d-band center (reference taken as the Fermi level at zero.) for 'd' orbital of Zr atoms in the non-metal (C, N and P) doped ZrS₂, ZrSe₂, and ZrTe₂ monolayers.

| Parameter | ZrS ₂ | | | ZrSe ₂ | | | ZrTe ₂ | | |
|---------------|------------------|----------|----------|-------------------|----------|----------|-------------------|----------|----------|
| | C | N | P | C | N | P | C | N | P |
| d-band center | 2.113 eV | 1.730 eV | 1.131 eV | 1.765 eV | 1.166 eV | 1.045 eV | 1.062 eV | 0.821 eV | 0.897 eV |