Electronic Supplementary Information

Designing an efficient bifunctional electrocatalyst heterostructure †

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I. HETEROSTRUCTURE GEOMETRIES AND ELECTRONIC BAND STRUCTURES

Oxygen and hydrogen evolutions have been studied for N, P-doped graphene-MoX₂ (or MoXY, where X, Y = S, Se) heterostructures (Fig. S1). Electronic bandstructures have been shown along with the heterostructures. Nitrogen and phosphorus doping in the graphene layer of the heterostructures shift the dirac cone downwards indicating the n-type doping. Also, the heteroatom doping opens the dirac cone. Variation is observed in the bands of MoXY in the heterostructure as well and a decrease in the gap is obtained. The band gap values and the optimized interlayer distances are shown in Fig. S1.



Figure S1. Graphical representation (top and side views) of the optimized heterostructure geometries: (a) NC-MoS₂, (b) NC-MoSe₂, (c) NC-MoSSe, (d) PC-MoS₂, (e) PC-MoSe₂ and (f) PC-MoSSe along with their electronic band structures. N, P, C, Mo, S and Se are represented by blue, light-green, red, dark-green, orange and purple balls.

System	PBE (eV)	HSE (eV)
PC	0.12	0.29
MoSSe	1.54	1.98
PC-MoSSe	0.46	1.20
NC-MoSSe	0.20	0.61

TABLE S1. Calculated band gaps of PC, MoSSe, PC-MoSSe and NC-MoSSe heterostructure using PBE and HSE functionals.

For all these systems, the band gap values have increased using HSE functional in comparison to those calculated using PBE. We also observe that band gaps have increased nearly 2-3 times for small band gap materials PC, PC-MoSSe and NC-MoSSe excluding the large band gap material MoSSe.

II. CALCULATION OF GIBBS ENERGY

OER involves the transfer of 4e⁻s during the whole process with the intermediate steps as:

$$H_2O + * \to OH^* + H^+ + e^- \tag{1}$$

$$OH^* \to O^* + H^+ + e^- \tag{2}$$

$$H_2O + O^* \to OOH^* + H^+ + e^-$$
 (3)

$$OOH^* \to * + O_2 + H^+ + e^- \tag{4}$$

where * indicates an active site on the surface of catalyst or heterostructure. O *, OH * and OOH * represent the adsorbed intermediates on the surface.

Good catalysts have lower free energies i.e small energy barriers while the reaction goes from reactants to the products. The free energy is defined as

$$\Delta G = \Delta E + ZPE - T\Delta S + KTln_{a_{H^+}} - eU \tag{5}$$

where ZPE is the zero point energy correction, T is the temperature, ΔS is the change in entropy, K is Boltzmann constant, a_{H^+} is the activity of protons, U is the potential at the electrode and e is the charge transferred. The additional term $\text{KTln}_{a_{H^+}}$ - eU is added to accomodate the effect of pH of electrolyte and external electrode potential. At standard conditions, pH = 0 and T= 298.15 K and therefore, the term $\operatorname{KTln}_{a_{H^+}}$ turns out to be zero. The value of ZPE - T ΔS is not measured and hence, assumed to be zero. So, the gibbs energy for each intermediate step is calculated as

$$\Delta G_1 = \Delta G_{OH^*} - eU \tag{6}$$

$$\Delta G_2 = \Delta G_{O^*} - \Delta G_{OH^*} - eU \tag{7}$$

$$\Delta G_3 = \Delta G_{OOH^*} - \Delta G_{O^*} - eU \tag{8}$$

$$\Delta G_4 = \Delta G_{O_2} - \Delta G_{OOH^*} - eU \tag{9}$$

where ΔG_{OH^*} , ΔG_{O^*} and ΔG_{OOH^*} are equal to ΔE_{OH^*} , ΔE_{O^*} and ΔE_{OOH^*} , respectively. ΔG_{O_2} has the experimental value of 4.92 eV, the required potential for the overall OER process. Each step involves the equal charge transfer and therefore, the potential of each step is 1.23 eV ideally at U = 0V. The other electrocatalytic reaction, HER involves two intermediate steps such that

$$H^+ + e^- + * = H^* \tag{10}$$

The first step is the adsorption of hydrogen atom on the heterostructure surface and the second step describes the desorption of H_2 gas from the surface and it can happen in two ways:

$$2H^* \to H_2 + 2^{'*'}$$
 or $H^+ + e^- \to H_2 + '*'$ (11)

Here, gibbs energy is defined as

$$\Delta G_{H^*} = \Delta E_{H^*} + 0.24eV \tag{12}$$

where 0.24 eV is the zero point energy correction term.

S. No	. Surface	Total Energy	\mathbf{E}_{ads} (eV)	Bond length (Å)
1	$NC-MoS_2$	-497.3592532	-	-
2	$NC-MoS_2+O$ (C-site)	-501.9498895	3.49	C-O = 1.32
3	$NC-MoS_2+OH$ (C-site)	-507.1060869	1.73	C-O = 1.46
				O-H = 0.97
4	$NC-MoS_2+OOH$ (C-site)	-510.8589164	6.06	C-O1 = 2.48
				O1-O2 = 1.40
				O2-H = 0.98
5	$NC-MoS_2+O$ (S-site)	-502.9853002	2.46	S-O = 1.47
6	$NC-MoS_2+OH$ (S-site)	-505.8626275	2.97	S-O = 1.84
				O-H = 0.98
7	$NC-MoS_2+OOH$ (S-site)	-510.4975933	6.43	S-O1 = 1.48
				O1-O2 = 2.44
				O2-H = 0.98
8	$NC-MoSe_2$	-482.9289815	-	
9	$NC-MoSe_2+O$ (C-site)	-487.6528226	3.36	C-O = 1.32
10	$NC-MoSe_2+OH$ (C-site)	-492.8041454	1.60	C-O = 1.46
				O-H = 0.97
11	$NC-MoSe_2+OOH$ (C-site)	-496.5358509	5.96	C-O1 = 2.38
				O1-O2 = 1.41
				O2-H = 0.98
12	$NC-MoSe_2+O$ (Se-site)	-487.6694233	3.34	Se-O = 1.67
13	$NC-MoSe_2+OH$ (Se-site)	-491.4434240	2.96	Se-O = 2.04
				O-H = 0.98
14	$NC-MoSe_2+OOH$ (Se-site)	-496.1131508	6.38	Se-O1 = 2.80
				O1-O2 = 1.38
				O2-H = 0.99
15	NC-MoSSe	-490.1315454	-	
16	NC-MoSSe+O (C-site)	-494.8032546	3.41	C-O = 1.32
17	NC-MoSSe+OH (C-site)	-499.9424112	1.67	C-O = 1.46
				O-H = 0.97
18	NC-MoSSe+OOH (C-site)	-504.1225267	5.57	C-O1 = 1.47
				O1-O2 = 1.50
				O2-H = 0.97
19	NC-MoSSe+O (Se-site)	-494.7806215	3.43	Se-O = 1.67
20	NC-MoSSe+OH (Se-site)	-498.8360754	2.77	Se-O = 2.13

TABLE S2: Total energy, adsorption energy (E_{ads}) and bond lengths of the adsorbates (O, OH and OOH) on the surfaces of different heterostructures for OER process

				O-H = 0.98
21	NC-MoSSe+OOH (Se-site)	-503.44044848	6.25	Se-O1 = 2.72
				O1-O2 = 1.40
				$\mathrm{O2}\text{-}\mathrm{H}=0.98$
22	$PC-MoS_2$	-492.0752065	-	
23	$PC-MoS_2+O$ (P-site)	-499.8203324	0.34	P-O = 1.49
24	$PC-MoS_2+OH$ (P-site)	-503.8507770	-0.29	P-O = 1.63
				O-H = 0.97
25	$PC-MoS_2+OOH$ (P-site)	-507.7059427	3.93	P-O1 = 1.65
				O1-O2 = 1.51
				$\mathrm{O2}\text{-}\mathrm{H}=0.97$
26	$PC-MoS_2+O$ (S-site)	-497.7040850	2.45	S-O = 1.48
27	$PC-MoS_2+OH$ (S-site)	-500.6604777	2.89	S-O = 1.73
				O-H = 0.98
28	$PC-MoS_2+OOH$ (S-site)	-505.1641880	6.48	S-O1 = 1.47
				O1-O2 = 2.59
				O2-H = 0.98
29	$PC-MoSe_2$	-477.7253136	-	
30	$PC-MoSe_2+O$ (P-site)	-485.4551930	0.35	P-O = 1.49
31	$PC-MoSe_2+OH$ (P-site)	-489.48480792	-0.27	P-O = 1.63
				O-H = 0.97
32	PC-MoSe ₂ +OOH (P-site)	-493.4057556	3.88	P-O1 = 1.65
				O1-O2 = 1.90
				O2-H = 0.98
33	$PC-MoSe_2+O$ (Se-site)	-482.4920902	3.32	Se-O = 1.67
34	$PC-MoSe_2+OH$ (Se-site)	-486.2396290	2.96	Se-O = 2.06
				O-H = 0.98
35	PC-MoSe ₂ +OOH (Se-site)	-490.8320584	6.46	Se-O1 = 3.02
				O1-O2 = 1.38
				O2-H = 0.98
36	PC-MoSSe	-484.8884494	-	
37	PC-MoSSe+O (P-site)	-492.5806871	0.39	P-O = 1.49
38	PC-MoSSe+OH (P-site)	-496.5891408	-0.22	P-O = 1.63
				O-H = 0.97
39	PC-MoSSe+OOH (P-site)	-499.9080922	4.54	P-O1 = 1.49
				O1-O2 = 2.58
				$\mathrm{O2}\text{-}\mathrm{H}=0.98$
40	PC-MoSSe+O (Se-site)	-489.5258722	3.45	Se-O = 1.67

41	PC-MoSSe+OH (Se-site)	-493.5420253	2.82	Se-O = 2.10
				O-H = 0.98
42	PC-MoSSe+OOH (Se-site)	-498.10849112	6.34	Se-O1 = 3.08
				O1-O2 = 1.39
				O2-H = 0.98

TABLE S3: Total energy, adsorption energy (E_{ads}) and bond lengths of the H-atom on the surfaces of different heterostructures for HER process

S. No.	Surface	Total Energy	\mathbf{E}_{ads} (eV)	Bond length (Å)
1	$NC-MoS_2+H$ (C-site)	-500.2354964	0.52	C-H = 1.12
2	$NC-MoS_2+H$ (S-site)	-499.2725837	1.48	S-H = 1.36
3	$NC-MoSe_2+H$ (C-site)	-485.9150890	0.41	C-H = 1.12
4	$NC-MoSe_2+H$ (Se-site)	-484.2212202	2.10	Se-H = 1.57
5	NC-MoSSe+H (C-site)	-493.0411061	0.48	C-H = 1.12
6	NC-MoSSe+H (Se-site)	-491.4126379	2.11	Se-H = 1.61
7	$PC-MoS_2+H$ (P-site)	-495.8081594	-0.34	P-H = 1.44
8	$PC-MoS_2+H$ (S-site)	-494.0575265	1.41	S-H = 1.36
9	$PC-MoSe_2+H$ (P-site)	-481.4986046	-0.38	P-H = 1.44
10	$PC-MoSe_2+H$ (Se-site)	-479.2521600	1.86	Se-H = 1.54
11	PC-MoSSe+H (P-site)	-488.6237665	-0.34	P-H = 1.44
12	PC-MoSSe+H (Se-site)	-486.3402500	1.94	Se-H = 1.60



Figure S2. The calculated gibbs free energy diagrams for OER on (a) Graphene and (b) MoS_2 at equilibrium potential of 1.23 eV.



Figure S3. (a) Differential charge density (top and side views) for NC-MoSSe heterostructure.(b), (c), (d) Side views of charge density difference for the adsorbed OER intermediates (OH*, O* and OOH*) and (e) HER intermediate (H*). Yellow and blue colors represent the charge accumulation and depletion regions, respectively with values in $e/Å^3$.

III. STABILTY

Dynamical Stabilty

The structural stability of C-MoS₂, C-MoSe₂ and C-MoSSe heterostructures is studied via phonon dispersion calculations. The phonon frequencies are obtained for these heterostructures using $2 \times 2 \times 1$ k-mesh using Phonopy[1]. The calculation of forces has been done using the finite displacement method with a displacement of 0.03 Å in supercell structures. Fig. S4 shows the phonon DOS plots of the heterostructures to be perfectly stable due to the absence of imaginary or negative modes.



Figure S4. Phonon density of states for (a) C-MoS₂, (b) C-MoSe₂ and (c) C-MoSSe heterostructures.

Mechanical Stability

The mechanical stability of the heterostructures is studied via calculating elastic constants. The finite difference method[2], as implemented in VASP is used to calculate the elastic constants of the heterostructures. Elastic constant is defined as $C_{ijkl} = d\sigma_{ij}/d\epsilon_{kl}$, where σ_{ij} and ϵ_{kl} are the stress and strain tensors, respectively. VASP calculates these elastic constants in the form of ionic and electronic components, $C_{ijkl} = C_{ijkl}^{(ion)} + C_{ijkl}^{(elec)}$. Here, we report the total elastic constants for 2D systems. The following Born criteria for mechanical stability of hexagonal systems[3] must be satisfied:

 $C_{11} > \!\! C_{12}, \, C_{12} > \!\! 0, \, C_{22} > \!\! 0, \, C_{66} > \!\! 0, \, C_{11} \! = \!\! C_{22}, \, C_{11}C_{22} \text{ - } C_{12}^2 > \!\! 0$

TABLE S4. Calculated elastic constants of C-MoS₂, C-MoSe₂ and C-MoSSe heterostructures.

Heterostructure	C_{11} (N/m)	C_{12} (N/m)	$C_{66}~(N/m) = (C_{11}\text{-}C_{12})/2$	$\nu = \mathbf{C}_{12}/\mathbf{C}_{11}$
$\overline{\text{C-MoS}_2}$	401.16	66.29	167.43	0.16
$C-MoSe_2$	446.09	112.48	166.80	0.25
C-MoSSe	338.66	99.90	119.38	0.29

Li et al.[4] reported Poisson' ratio for C-MoS2, $\nu = 0.17$, which is close to the calculated value. The above mentioned conditions for mechanical stability are satisfied by all the three heterostructures. Also, the Poisson's ratio is well below 0.5 for the heterostructures. Therefore, the above systems are mechanically stable.

Thermodynamical Stabilty

Adhesive energies for the heterostructures are determined to test their thermodynamic stability. Adhesive energy is calculated as $E_{adh} = E_{C-MoXY} - E_C - E_{MoXY}$, where X, Y = S, Se

TABLE S5. Adhesive energies of C-MoS₂, C-MoSe₂ and C-MoSSe heterostructures.

Heterostructure	\mathbf{E}_{adh} (eV)
$C-MoS_2$	-7.64
$C-MoSe_2$	-9.88
C-MoSSe	-8.93

Adhesive energy for C-MoS₂ is in excellent agreement with the value reported by Fu et al.[5] for stable configurations of C-MoS₂. As the calculated adhesive energies are negative for all the three heterostructures, so the construction of the above three systems is favorable and they are thermodynamically stable. Thermodynamical stability of the heterostructures has also been verified using the convex hull based phase diagrams as shown below:



Figure S5. Computed convex hull for (a) C-MoS₂, (b) C-MoSe₂ and (c) C-MoSSe heterostructures. Green solid circles represent stable materials and red triangles represent unstable phases.

These phase diagrams are computed using Pymatgen modules - pymatgen.analysis.phase_ which defines tools to generate and analyze phase diagrams and pymatgen.ext.matproj module which uses classes to interface with the Materials Project REST API v2[6–8]. Materials with E_H (energy above hull) close to zero are completely stable and the ones approaching 0.5 eV/atom are said to be metastable materials while materials with E_H values above 0.5 eV/atom are unstable. The ternary convex hull for C-MoS₂ and C-MoSe₂ give negative formation energies of -0.537 eV/atom and -0.492 eV/atom, respectively. The negative energies indicate the thermodynamical stability of the systems. Also, the energies above hull for C-MoS₂ and C-MoSe₂ are +0.062 eV/atom and 0 eV/atom suggesting the heterostructures are stable. We obtained a quaternary convex hull for C-MoSSe heterostructure with formation energy of -0.513 eV/atom and its energy above hull is 0 eV/atom. Therefore, C-MoSSe is also thermodynamically stable.

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