## **Supporting Information**

# Delineating the Multifunctional Performance of Janus WSSe with Nonmetals in Water Splitting and Hydrogen Fuel Cell Applications via First-Principles Calculations

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#### 1. Cohesive Energy Calculation

The stability of the Janus WSSe and the NM doped structures are investigated using the cohesive energy  $(E_{coh})$  calculation. The  $E_{coh}$  is calculated as,

$$E_{coh} = \frac{E_{JW} - (N_W E_W + N_S E_S + N_{Se} E_{Se} + N_{NM} E_{NM})}{N}$$

Where,  $E_{JW}$  is the ground state energy of the pristine and NM-doped Janus WSSe depending on the system being calculated,  $E_W$ ,  $E_S$ ,  $E_{Se}$ , and  $E_{NM}$  are the energies of the W, S, Se and NM atom found from the stable structure, and  $N_W$ ,  $N_S$ ,  $N_{Se}$ , and  $N_{NM}$  are the number of individual atom present in the structure.

#### 2. Elementary Steps of HER, OER and ORR Process.

The computational hydrogen electrode (CHE) model as proposed by Nørskov et al., is employed to study the electrochemical performance of the structure. According to the model, the electron proton pair under standard condition (pH = 0, T = 298.15, P = 1 bar) can be used as a reference to evaluate the Gibbs free energy of hydrogen adsorption on the catalyst surface.

$$H^+_{(aq)} + e^- \rightleftharpoons \frac{1}{2}H_2$$

#### 2.1 Hydrogen Evolution Reaction

In an acidic electrolyte medium, HER process is a two-step process. The first step is the adsorption of hydrogen on the catalytic surface, known as the Volmer reaction, which can be represented as,

Volmer reaction: 
$$H^+ + e^- \rightarrow H^*$$

The second and final part of the reaction can proceed through two possible pathways: the Volmer–Tafel mechanism and the Volmer–Heyrovsky mechanism.

Volmer – Tafel:  
Volmer – Heyrovsky:  

$$H^* + H^+ \to H_2$$
  
 $H^* + H^+ + e^- \to H_2$ 

Where \* denotes the active site of the catalytic surface. The hydrogen molecule in its adsorbed state (H\*) being the key species for the evaluating the HER performance.

#### 2.2 Oxygen Evolution Reaction

Similarly, in an acidic medium, the OER proceeds through a four-electron  $(4e^{-})$  pathway, as given by:

$$H_2 0 + * \longrightarrow 0H^* + H^+ + e^-$$
$$0H^* \longrightarrow 0^* + H^+ + e^-$$
$$H_2 0 + 0^* \longrightarrow 00H^* + H^+ + e^-$$
$$00H^* \longrightarrow 0_2 + H^+ + e^-$$

Where \* denotes the active site of the catalytic surface.

#### 2.3 Oxygen Reduction Reaction

The ORR is the reverse reaction of the OER, represented as:

$$O_2 + 2H_2 \rightleftharpoons 2H_2O$$

Then the ORR pathway will be:

$$O_2 + * + H^+ + e^- \rightarrow OOH^*$$
$$OOH^* + H^+ + e^- \rightarrow O^* + H_2O (H_2O_2)$$
$$O^* + H^+ + e^- \rightarrow OH^*$$
$$OH^* + H^+ + e^- \rightarrow O_2 + H_2O$$

As mentioned, the reaction can proceed via a two-electron  $(2e^{-})$  pathway, producing H<sub>2</sub>O<sub>2</sub> as a by-product, which is unstable and subsequently reduced to H<sub>2</sub>O.

#### **3.** Gibbs Free Energy Change ( $\Delta G$ )

The Gibbs free energy change ( $\Delta G$ ) of the reaction pathways are calculated using the relation:

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S + \Delta G_U + \Delta G_{pH}$$

Where  $\Delta E$  is the adsorption energy of the intermediates,  $\Delta ZPE$  and  $T\Delta S$  are the change in zeropoint energy and entropy at 298.15 K.  $\Delta G_U = -neU$  is the free energy contribution by the electron transfer due to applied potential U.  $\Delta G_{pH} = k_B T \times \ln 10 \times pH$  is the contribution from the proton ( $H^+$ ) exchange.

#### **3.1 Free Energy Changes in Reaction Steps**

For OER process, the free energy changes during the pathway can be calculated as,

$$\Delta G_1 = G(OH^*) + G(H^+ + e^-) - G(H_2O) - G(*)$$
  

$$\Delta G_2 = G(O^*) + G(H^+ + e^-) - G(OH^*)$$
  

$$\Delta G_3 = G(OOH^*) + G(H^+ + e^-) - G(H_2O) - G(O^*)$$
  

$$\Delta G_4 = G(O_2) + G(*) + G(H^+ + e^-) - G(OOH^*)$$

Since DFT provides a poor description of the high-spin energy of the O<sub>2</sub> molecule, the free energy is adopted from the gas phase, expressed as,

$$G(O_2)_g + G(H_2)_g - G(H_2O)_l = 4.92 \ eV$$

The free energy of  $H_2O$  in the liquid phase is challenging to determine directly; therefore, the vapor phase at equilibrium pressure is used as a reference. Since ORR is the reverse process of OER, hence the free energy changes are calculated as,

$$\Delta G_4 = -\Delta G_a$$
$$\Delta G_3 = -\Delta G_b$$
$$\Delta G_2 = -\Delta G_c$$
$$\Delta G_1 = -\Delta G_d$$

#### 4. Overpotential $(\eta)$

Overpotential refers to the additional potential needed beyond the thermodynamic equilibrium potential to drive an electrochemical reaction at a given rate. The theoretical overpotential for the HER process is calculated from the  $\Delta G$  as,

$$\eta_{HER} = \frac{|\Delta \mathbf{G}_{H^*}|}{e} \ V$$

Theoretical potential for the OER process is calculated from the highest free energy change  $(\Delta G)$  of the four-electron pathway.

$$\eta_{OER} = \frac{max[\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4]}{e} V$$

Similarly for the ORR process,

$$\eta_{ORR} = \frac{max[\Delta G_a, \Delta G_b, \Delta G_c, \Delta G_d]}{e} V$$

Theoretical exchange current  $(i_0)$  for the HER process is also evaluated using the Nørskov's assumption as,

$$i_0 = -\frac{ek_0}{1 + \exp\left(\frac{|\Delta G_{H^*}|}{k_B T}\right)} Acm^{-2}$$

where  $k_0$  is the rate constant which is taken as 1.

### 5. Transition states (TS)

To find the energy barrier for the formation of intermediates OH\*, O\*, and OOH\*, CI-NEB is used for four pathways as given below.

1<sup>st</sup> pathway: OH\* formation

$$H_2O(R1) \xrightarrow{TS1} OH^*(I1)$$

2<sup>nd</sup> pathway: O\* formation

$$OH^*(R2) \xrightarrow{TS2} O^*(I2)$$

3<sup>rd</sup> pathway: OOH\* formation

$$O^*(R3) \xrightarrow{TS3} OOH^*(I3)$$

4<sup>th</sup> pathway: O2 evolution

$$OOH^*(R4) \xrightarrow{TS4} O^*(I4)$$

Since, OER and ORR are reversible processes, the observed TS will be equivalent for the ORR process with negative reaction energy ( $\Delta E$ )

Figure S1. Electron localization function plot of pristine and NM doped Janus WSSe.











Figure S2. Optimized structure of NM doped Janus WSSe











Figure S3. AIMD plot of NM doped Janus WSSe



Figure S4. Band structure plot of NM doped Janus WSSe















Figure S6. Optimized structures of H\* adsorbed pristine and NM doped Janus WSSe



Figure S7. Optimized structures of OH\*, O\*, and OOH\* adsorbed pristine and NM doped Janus WSSe







Figure S8. Reaction energy plots for OER and ORR process of pristine and NM doped Janus WSSe



![](_page_17_Figure_1.jpeg)

![](_page_18_Figure_0.jpeg)

h) PSe@JW

Figure S9. The reaction energy plot for the formation of intermediates in the a) NS@JW and b) NSe@JW systems

![](_page_18_Figure_3.jpeg)

Figure S10. The CI-NEB plot for the transition states observed for the a) NS@JW and b) NSe@JW systems

![](_page_19_Figure_0.jpeg)

Figure 11. P band center ( $\epsilon_p$ ) and p orbital projection of NM doped JW systems

![](_page_19_Figure_2.jpeg)

c) NS@JW

d) NSe@JW

![](_page_20_Figure_0.jpeg)

Figure S12. Crystal Orbital Hamiltonian Population (COHP) analysis plot of intermediates adsorbed NM doped Janus WSSe

![](_page_20_Figure_2.jpeg)

![](_page_21_Figure_0.jpeg)

![](_page_21_Figure_1.jpeg)

![](_page_21_Figure_2.jpeg)

![](_page_21_Figure_3.jpeg)

![](_page_22_Figure_0.jpeg)

![](_page_23_Figure_0.jpeg)

![](_page_23_Figure_1.jpeg)

![](_page_24_Figure_0.jpeg)

f) PSe@JW

System	dw-nm (Å)	Q (e)	E <sub>coh</sub> (eV)	Magnetic moment (µ <sub>B</sub> )	Eg(eV)
CS@JW	2.03	-0.90	-5.84	0	0.78
CSe@JW	2.02	-0.91	-5.88	0	0.73
NS@JW	2.01	-1.06	-5.80	0.97	0.11
NSe@JW	2.01	-1.08	-5.84	0.98	0.12
OS@JW	2.08	-0.99	-5.84	0	1.69
OSe@JW	2.08	-0.99	-5.88	0	1.71
PS@JW	2.39	-0.41	-5.74	0.98	0.02
PSe@JW	2.43	-0.49	-5.78	0	0.01

**Table S1.** The bond length between the W and NM ( $d_{W-NM}$ ), Bader charge (Q), cohesive energy ( $E_{coh}$ ), magnetic moment, and band gap ( $E_g$ ) of all the NM doped JW structure

**Table S2.** H\* adsorption distance ( $d_{NM-H*}$ ), adsorption energy ( $E_{ad}$ ), zero-point energy (ZPE), entropy contribution at T=298.15 K (TS), and Free energy change ( $\Delta G_{H*}$ ) for the Janus WSSe and NM doped Janus WSSe

System	dnm-н* (Å)	Ead (eV)	ZPE (eV)	TS (eV)	$\Delta \boldsymbol{G}_{H*}$ (eV)
S@JW	1.616	1.796	0.186	0.012	1.969
Se@JW	1.625	1.935	0.146	0.017	2.064
CS@JW	1.093	-1.010	0.277	0.006	-0.739
CSe@JW	1.097	-1.106	0.284	0.005	-0.827
NS@JW	1.025	-0.644	0.311	0.005	-0.338
NSe@JW	1.019	-0.658	0.311	0.004	-0.351
OS@JW	2.432	2.238	0.013	0.027	2.224
OSe@JW	2.289	3.501	0.015	0.090	3.425
PS@JW	1.413	-1.098	0.220	0.012	-0.890
PSe@JW	1.424	-1.042	0.224	0.010	-0.828

Systems	OER (eV)				ORR (eV)			
	$\Delta G_1$	$\Delta G_2$	$\Delta G_3$	$\Delta G_4$	$\Delta G_a$	$\Delta G_b$	$\Delta \boldsymbol{G_c}$	$\Delta G_d$
S@JW	2.56	3.32	-0.85	-0.11	0.11	0.85	-3.32	-2.56
Se@JW	2.52	2.14	0.39	-0.13	0.13	-0.39	-2.14	-2.52
CS@JW	-0.07	1.47	1.50	2.02	-2.02	-1.50	-1.47	0.07
CSe@JW	0.01	0.27	4.14	0.51	-0.51	-4.14	-0.27	0.01
NS@JW	1.09	1.10	1.42	1.31	-1.31	-1.42	-1.10	-1.09
NSe@JW	1.11	0.97	1.15	1.69	-1.69	-1.15	-0.97	-1.11
OS@JW	2.94	2.01	-0.07	0.04	-0.04	0.07	-2.01	-2.94
OSe@JW	2.79	2.32	-0.35	0.16	-0.16	0.35	-2.32	-2.79
PS@JW	-0.80	1.00	4.89	-0.17	0.17	-4.89	-1.00	0.80
PSe@JW	-0.75	0.81	4.04	0.83	-0.83	-4.04	-0.81	0.75

**Table S3.** The reaction energies of elementary step in OER and ORR for the pristine and NM doped Janus WSSe.

**Table S4**. The Free energy change ( $\Delta G$ ) for the adsorption of intermediates H\*, OH\*, O\* and OOH\* on Janus WSSe and NM doped Janus WSSe in the presence of water electrolyte.

System	$\Delta G_{H*}$ (eV)	$\Delta G_{OH*}$ (eV)	$\Delta G_{0*}$ (eV)	$\Delta G_{OOH*} \text{ (eV)}$
S@JW	1.932	2.697	2.390	4.708
Se@JW	2.037	2.284	3.025	4.683
CS@JW	-1.152	-0.383	1.715	2.671
CSe@JW	-1.325	-0.430	0.245	3.673
NS@JW	-0.570	0.883	2.247	3.465
NSe@JW	-0.574	0.975	2.193	4.069
OS@JW	2.259	2.297	4.813	4.509

OSe@JW	2.234	2.220	2.983	4.538
PS@JW	-0.894	-0.911	0.124	4.126
PSe@JW	-0.760	-0.733	0.192	4.263

**Table S5.** The relative energy observed for the reactants (R), transition states (TS), and intermediates (I) for NS@JW and NSe@JW systems

D - 41	<b>Relative energy (eV)</b>			
Patnway	NS@JW	NSe@JW		
R1	0	0		
TS1	1.47	1.27		
I1	1.18	1.19		
R2	0	0		
TS2	1.26	1.03		
12	1.16	0.99		
R3	0	0		
TS3	1.65	1.48		
I3	1.45	1.35		
R4	0	0		
TS4	1.37	1.59		
I4	1.23	1.51		