Transition Metal-Embedded Nb2S2C as a High-Performance Bifunctional Electrocatalyst for OER and ORR: Insights from DFT Simulations

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SUPPLYMENTARY INFORMATION

SI.1. Thermodynamics mechanism of OER and ORR:

Prioritizing the adsorption energy followed by the Gibbs free energy is the first step in determining the surplus potential for OER. Using the relation provided below, the adsorption free energies were calculated. The equilibrium potential energy (eV) of the intermediate species OH*, O*, and OOH* is determined to be 0.37, 0.07, and 0.44 eV in relation to H_2O and H_2 (at U = 0 and pH = 0) by the adsorption free energies equation $\Delta Gi = \Delta E_{ads}i + \Delta ZPEi - T\Delta Si$, where $\Delta E_{ads}i$ is the species' adsorption energy while $\Delta ZPEi - T\Delta Si$ is the zero-point energy correction term alongside entropic term.

$$\Delta E_{OH} = E(OH^*) - E(*) - [E(H_2O) - \frac{1}{2}E(H_2)] \quad (1)$$

$$\Delta E_{O} = E(O^*) - E(*) - [E(H_2O) - E(H_2)] \quad (2)$$

$$\Delta E_{OOH} = E(OOH^*) - E(*) - [2E(H_2O) - \frac{3}{2}E(H_2)] \quad (3)$$

It is feasible to write the alteration in Gibbs free energy for stages as

$$\Delta G_1 = \Delta G_{OH} - eU + \Delta G_{H+}(pH) \quad (4)$$

$$\Delta G_2 = \Delta G_O - \Delta G_{OH} - eU + \Delta G_{H+}(pH) \quad (5)$$

$$\Delta G_3 = \Delta G_{OOH} - \Delta G_O - eU + \Delta G_{H+}(pH) \quad (6)$$

$$\Delta G_4 = 4.92[eV] - \Delta G_{OOH} - eU + \Delta G_{H+}(pH) \quad (7)$$

where U represents the potential measured against a conventional hydrogen electrode (NHE) under standard circumstances (T = 298.15 K, pH = 0, P = 1 bar).

One of the most important markers for evaluating OER activity is the excess potential [ηOER (eV)], which is contingent on how firmly the intermediate elements of OER cling to the catalyst surface. The following formulae can be used to determine the theoretical over potential η_{OER}:

$$\eta_{OER} = Max\frac{[\Delta G_1,\ \Delta G_2,\ \Delta G_3,\ \Delta G_4]}{e} - 1.23\ V \quad (8)$$

A difference of 3.2 eV between GOOH and GOH is expected, according to the "scaling relationship". A lower bond for excess potential is also provided by it, since $\eta \geq (3.2/2) - 1.23 = 0.37$ eV. The free energies of GOOH and GOH, however, are stated to deviate from the "scaling relationship" by, $\eta < 0.37$ eV and to be substitutionally away from the 3.2 eV difference [4].

Despite being merely a thermodynamic variable, the over potential derived in equation 8 has been found to scale harmoniously with legitimate over potentials, which are impacted by current density and the concentration of active sites themselves.

The OER process, which manoeuvre by the 4-electron transfer pathway shown, can be thought of as the reciprocal of the ORR process:

$$* + O_2(g) + H^+ + e^- \rightarrow OOH^* \quad (9)$$

$$OOH^* + H^+ + e^- \rightarrow O^* + H_2O \quad (10)$$

$$O^* + + H^+ + e^- \rightarrow + OH^* \quad (11)$$

$$OH^* + H^+ + e^- \rightarrow H_2O(l) + * \quad (12)$$

Free energy changes associated with each of the four basic ORR phases can be computed as follows:

$$\Delta G_a = -\Delta G_4 \quad (13)$$

$$\Delta G_b = -\Delta G_3 \quad (14)$$

$$\Delta G_c = -\Delta G_2 \quad (15)$$

$$\Delta G_d = -\Delta G_1 \quad (16)$$

Thus, that being said, the following equation determines the overpotential, of ORR activity:

$$\eta_{ORR} = Max\frac{[\Delta G_a,\ \Delta G_b,\ \Delta G_c,\ \Delta G_d]}{e} + 1.23\ V \quad (17)$$

In this scenario, the equilibrium potential is represented by the value 1.23. Theoretical η_{OER} and η_{ORR} are affected by the adsorption energies but are independent of pH. This section will emphasis on the performance of Nb_2S_2C and doped versions of it in the further portion of the water splitting, which is called OER and ORR, in order to give a thorough knowledge of the water splitting mechanism.

Table S1: Measured bond lengths (d) of OH, O, and OOH on pristine Nb_2S_2C, respectively.

System	Bond length (Å)		
	S/Nb/C-O	O-O	O-H
S top in Nb_2S_2C+O	1.79	-	-
S top in Nb_2S_2C +OH	1.79	0.97	-
S top in Nb_2S_2C +OOH	2.00	1.43	0.98
C top in Nb_2S_2C +O	2.03	-	-
C top in Nb_2S_2C +OH	2.08	0.97	-
C top in Nb_2S_2C +OOH	2.09	1.45	0.97
Nb top in Nb_2S_2C +O	1.69	-	-
Nb top in Nb_2S_2C +OH	1.76	0.96	-
Nb top in Nb_2S_2C +OOH	1.85	1.43	0.97

Table S2: Measured bond lengths (d) of OH, O, and OOH on TM anchored Nb_2S_2C, respectively.			
System	**Bond length (Å)**		
	TM-O	**O-O**	**O-H**
Pt-Nb_2S_2C+O	1.79	-	-
Pt- Nb_2S_2C +OH	1.79		0.97
Pt- Nb_2S_2C +OOH	2.00	1.43	0.98
Cd- Nb_2S_2C +O	2.03	-	-
Cd- Nb_2S_2C +OH	2.08	-	0.97
Cd- Nb_2S_2C +OOH	2.09	1.45	0.97
Cu- Nb_2S_2C +O	1.69	-	-
Cu- Nb_2S_2C +OH	1.76	-	0.96
Cu- Nb_2S_2C +OOH	1.85	1.43	0.97
Rh- Nb_2S_2C +O	1.70	-	-
Rh- Nb_2S_2C+OH	1.90	-	0.97
Rh- Nb_2S_2C+OOH	1.89	1.42	0.98
Ir-Nb_2S_2C +O	1.75	-	-
Ir- Nb_2S_2C+OH	1.90	-	0.96
Ir- Nb_2S_2C+OOH	1.94	1.44	0.98

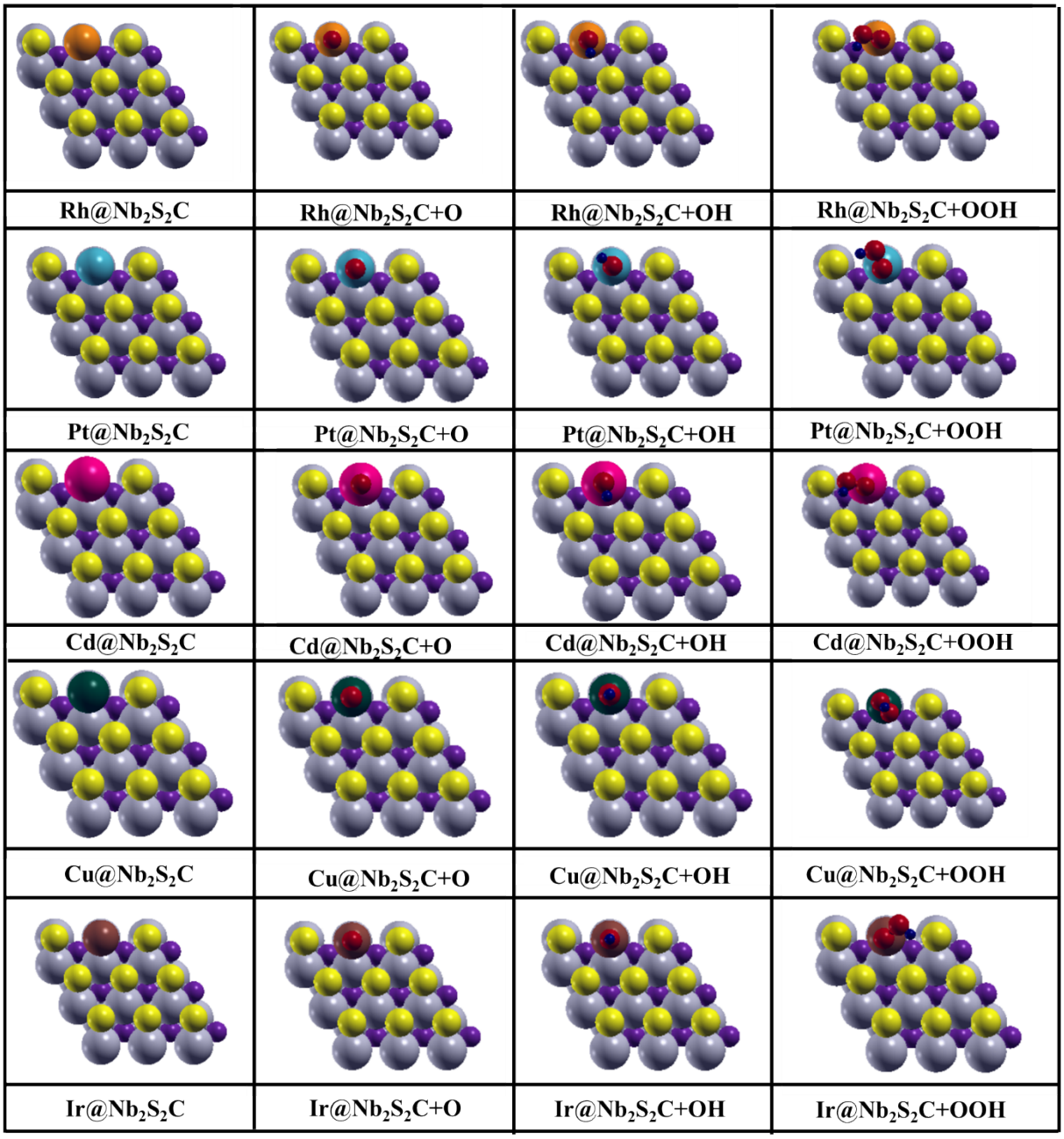

Fig.S1: Optimized structures of TM doped on Nb_2S_2C along with intermediate models: Grey Nb; Yellow S; Purple C; Red O; Navy blue H; Rh Orange; Pt Blue; Cd Pink; Cu Dark green; Ir Brown.