## Supplementary Information

Bifunctional Electrocatalyst for Oxygen Reduction and Oxygen Evolution: Theoretical Study on 2D Metallic WO<sub>2</sub>-supported Single Atom (Fe, Co, Ni) Catalysts

Yuli Ma<sup>a</sup>, Fangming Jin<sup>a</sup>, and Yun Hang Hu<sup>b,\*</sup>

<sup>a</sup>School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China.

<sup>b</sup>Department of Materials Science and Engineering, Michigan Technological University,

Houghton, Michigan 49931, USA.

\*Corresponding authors. E-mails: <u>yunhangh@mtu.edu</u>



Fig. S1. The calculated total energy of different materials under the cut-off energy in the range of

300~700 eV.



Fig. S2. The calculated binding energies of Fe/2D WO<sub>2</sub> with Fe atom ratios in the range from 1/72 to 1/6.



**Fig. S3**. Electron density of states (DOS): (a) 2D WO<sub>2</sub>, (b) Fe/2D WO<sub>2</sub>, (c) Co/2D WO<sub>2</sub>, and (d) Ni/2D WO<sub>2</sub> (The fermi level was set as zero).



**Fig. S4**. d band center calculations: (a) 2D WO<sub>2</sub>, (b) Fe/2D WO<sub>2</sub>, (c) Co/2D WO<sub>2</sub>, and (d) Ni/2D WO<sub>2</sub> (The black line is d band PDOS, and the red line is a multiplication of PDOS by energy.).

## d band center calculation:

The surface d-band center  $(E_d)$  was computed as the first moment of the projected d-band density of states about the Fermi level  $(E_F)$  and is expressed as<sup>1</sup>

$$E_d = \frac{\int \rho E dE}{\int \rho dE}$$
(S1)

where  $\rho$  represents the density of states and E is the energy (eV) of the states.

| E (eV)               | *H      | *OH     | *ООН    | *0      | H <sub>2</sub> O | O <sub>2</sub> |
|----------------------|---------|---------|---------|---------|------------------|----------------|
| 2D WO <sub>2</sub>   | -333.24 | -338.05 | -343.27 | -332.57 | -344.68          | -339.23        |
| Fe/2DWO <sub>2</sub> | -345.06 | -352.86 | -357.30 | -348.01 | -357.43          | -353.04        |
| Co/2DWO <sub>2</sub> | -343.98 | -351.67 | -356.13 | -346.22 | -356.27          | -351.64        |
| Ni/2DWO <sub>2</sub> | -342.77 | -350.10 | -354.66 | -344.32 | -354.90          | -350.35        |

Table S1. Total energies of various intermediates on different catalysts.

Table S2. Zero point energy (ZPE) corrections of various intermediates on different catalysts.

| E <sub>ZPE</sub> (eV) | *Н   | *OH  | *OOH | *0   |
|-----------------------|------|------|------|------|
| WO <sub>2</sub>       | 0.37 | 0.30 | 0.40 | 0.06 |
| Fe/WO <sub>2</sub>    | 0.15 | 0.34 | 0.44 | 0.08 |
| Co/WO <sub>2</sub>    | 0.16 | 0.35 | 0.43 | 0.06 |
| Ni/WO <sub>2</sub>    | 0.17 | 0.33 | 0.44 | 0.06 |

**Table S3**. Total energies (E), and entropic contributions (TS) to the free energies of various species.<sup>2</sup>

| Species | *OH   | *OOH   | *0   | H <sub>2</sub> O | H <sub>2</sub> |
|---------|-------|--------|------|------------------|----------------|
| Е       | -7.09 | -12.75 | -    | -14.22           | -6.76          |
| TS      | 0.07  | 0.16   | 0.05 | 0.67             | 0.41           |

| Catalysts            | $\Delta G_{*\mathrm{OH}}/\mathrm{eV}$ | $\Delta G_{*0}/\mathrm{eV}$ | $\Delta G_{*OOH}$ |
|----------------------|---------------------------------------|-----------------------------|-------------------|
| 2DWO <sub>2</sub>    | 3.632                                 | 5.354                       | 5.787             |
| Fe/2DWO <sub>2</sub> | 0.716                                 | 1.790                       | 3.647             |
| Co/2DWO <sub>2</sub> | 0.723                                 | 2.372                       | 3.617             |
| Ni/2DWO <sub>2</sub> | 0.945                                 | 3.031                       | 3.859             |

Table S4. Adsorption free energy values of oxygenated intermediates on different catalysts.



**Fig. S5** Optimized three possible structures with oxygen vacancies on the surface of Fe/2D WO<sub>2</sub>. (The red, gray, and gold balls represent O, W, and Fe atom, respectively.)

The oxygen vacancy formation energy  $E_{vac}$  can been calculated by<sup>3</sup>

$$E_{vac} = E_{cellvac} + \frac{1}{2E_{0_2}} - E_{cell}$$
(S2)

where  $E_{cellvac}$  and  $E_{cell}$  are the total energies of the optimized supercells with and without an O vacancy, and  $E_{0_2}$  is the total energy for the ground state of an optimized oxygen molecule in the gas phase. A positive value for  $E_{vac}$  indicates that energy is needed to create O vacancy. The oxygen vacancy formation energies of three possible structures (Fig. S5) are 4.26, 5.42, and 5.86 eV. The

large formation energy reveals that the introduction of single atoms is thermodynamically difficult to generate oxygen vacancies.



**Fig. S6** Optimized structure of (a)2D WO<sub>2</sub> and (b) 2D WO<sub>2</sub> with oxygen vacancy (2D WO<sub>2</sub>-Ov); Adsorption structures for\*OH of (c) 2D WO<sub>2</sub>-Ov-1 (active sites are oxygen vacancies) and (d) 2D WO<sub>2</sub>-Ov-2 (active sites are not oxygen vacancies), where red, gray, and white balls represent oxygen, tungsten, and hydrogen atoms, respectively; Free energy diagrams for OER of (e) 2D WO<sub>2</sub>-Ov-1 and (f) 2D WO<sub>2</sub>-Ov-2.

The 2D WO<sub>2</sub> model with oxygen vacancy on the surface (denoted as 2D WO<sub>2</sub>-Ov) was built for OER simulation. The bond angle of W-O-W, which is 92.4361° in WO<sub>2</sub>, changes to 79.7617° after introducing oxygen vacancies, indicating that the distances between atoms around the oxygen vacancies are shortened to achieve energy balance (Fig.S6a~b). For the oxygen-defective model, both the vacant and adjacent W sites were considered as the possible active sites and denoted as 2D WO<sub>2</sub>-Ov-1 and 2D WO<sub>2</sub>-Ov-2, respectively. The optimized structural configurations with \*OH were presented in Fig. S6c~d. When oxygen vacancies are used as active sites to adsorb \*OH, two processes occur simultaneously during the energy relaxation process. One is the adsorption of \*OH on the surface, which is an exothermic process. Another is the endothermic process of filling the surface oxygen vacancies with oxygen in \*OH to expand the distance between surrounding atoms, leading to an increase of the W-O-W bond angle. The calculated  $\Delta G_{*OH}$  for 2D WO<sub>2</sub>-Ov-1 is too large to proceed the OER process (Fig.S6e). In contrast, when oxygen vacancies are not used as active sites, a smaller overpotential (1.4 V) can be obtained (Fig.S6f). Therefore, the OER process is easier to take place on the surface of 2D WO<sub>2</sub>-Ov than the stoichiometric ones (with an overpotential of 2.4 V) when adjacent W sites are considered as the possible active sites. However, the overpotential of 2D WO<sub>2</sub>-Ov-2 was still larger than those of single metal atom (Fe, Co, Ni) doped models.

Reference:

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