## **Supporting Information for:**

# Ti<sub>3</sub>C<sub>2</sub>O<sub>2</sub> Supported Single Atom, Trifunctional Catalyst for Electrochemical Reactions

Zhanzhao Fu, Chongyi Ling\*, Jinlan Wang\*

School of Physics, Southeast University, Nanjing, 211189, China Email: *lingchy@seu.edu.cn (C.L.), jlwang@seu.edu.cn (J.W.)* 

1. Calculation method of HER activity

$$H^+ + e^- + \stackrel{\Delta G_H}{\to} H^* \tag{1}$$

\* represents the active site and H\* represents the adsorbed intermediate. According to the computational hydrogen electrode model,<sup>s1</sup>  $\Delta G_{\rm H}$  can be calculated according to the following relationship:

$$\Delta G_H = \Delta E_H + \Delta E_{ZPE} - T \Delta S_H \tag{2}$$

 $\Delta E_{\rm H}$  is the adsorption energy of hydrogen calculated by DFT,  $\Delta E_{\rm ZPE}$  is the difference between the zero point energy of adsorbed hydrogen and gas phase hydrogen, T is the temperature (298.15 K), and  $\Delta S_{\rm H}$  is the change of entropy between the adsorption state and the gas phase. The entropy of the gas phase molecule is obtained by the NIST database, and the entropy and zero-point energy of the adsorbate can be obtained by calculating the vibration frequency where the entropy value is calculated by the following formula:<sup>s2</sup>

$$S(T) = \sum_{i=1}^{3N} \left[ -Rln \left( 1 - e^{-\frac{hv_i}{k_B T}} \right) + \frac{N_A hv_i e^{-\frac{hv_i}{k_B T}}}{T \frac{1 - e^{-hv_i/k_B T}}{1 - e^{-hv_i/k_B T}}} \right]$$
(3)

Where R stands for the ideal gas constant,  $k_B$  is Boltzmann constant, h is Planck constant,  $N_A$  is Avogadro constant,  $v_i$  represents the vibration of the normal mode, and N represents the number of adsorbed atoms.

#### 2. Calculation method of OER and ORR activity

At pH=0, the OER usually goes through the following four steps:

$$H_2 O(l) + * \rightarrow OH^* + H^+ + e^-$$
 (4)

$$OH^* \xrightarrow{\Delta G_2} O^* + H^+ + e^- \tag{5}$$

$$0^{*} + H_{2}O(l) \to OOH^{*} + H^{+} + e^{-}$$
(6)

$$00H^* \to *+ O_2(g) + H^+ + e^-$$
(7)

The change in free energy is calculated by the following formula:<sup>s3</sup>

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_U + \Delta G_{pH}$$
<sup>(8)</sup>

 $\Delta E$  refers to the energy obtained by DFT calculation;  $\Delta G_U = -eU$ , where U is the electrode potential, e is the number of transferred electrons;  $\Delta G_{pH} = k_B T ln 10 \times pH$ , in this work, pH = 0 was employed. A method developed by Nørskov et al was employed to calculate OER overpotentials, use the developed method of Nørskov et al:<sup>s4</sup>

$$\eta^{OER} = \frac{\max\left\{\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\right\}}{e} - 1.23 V$$

(9)

Since ORR is the reverse of OER, we also calculated the ORR overpotential ( $\eta^{ORR}$ ) for TMs@Ti<sub>3</sub>C<sub>2</sub>O<sub>2</sub>, which is defined as the difference between 1.23 V and the reaction energy of the minimum free energy change of the four mechanistic steps in this system:

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$$\eta^{ORR} = 1.23 V - \frac{\min\left\{\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\right\}}{e}$$

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(10)





**Figure S1**. The  $\Delta G_{\rm H}$  of primitive Ti<sub>3</sub>C<sub>2</sub>O<sub>2</sub> at different H coverage.



**Reaction Coordinate** 

Figure S2.  $\Delta G_{\rm H}$  of different TM<sub>1</sub>@Ti<sub>3</sub>C<sub>2</sub>O<sub>2</sub> at TM sites.



Figure S3. Free energy diagram for the OER over the TM sites of  $TM_1@Ti_3C_2O_2$  at an electrode potential of U = 0 V.



Figure S4. Free energy diagram for the OER (a) and ORR (b) of the primitive  $Ti_3C_2O_2$  at an electrode potential of U=0 V.



**Figure S5**. Calculated PDOS of the weight *d* band ( $D_F$ ) of the TM atoms in TM<sub>1</sub>@Ti<sub>3</sub>C<sub>2</sub>O<sub>2</sub>. The  $D_F$  is marked by the red dashed line, and the Fermi level is set as zero.



Figure S6. The DOS of  $Pd_1@Ti_3C_2O_2$ , and the Fermi level is set as zero.

#### 4. Tables:

**Table S1.** The number of electrons changed of O-site after the introduction of transition metals and the calculated OER/ORR overpotential of  $TM_1@Ti_3C_2O_2$  at non-TM site and the values of U were used.

| TM1@Ti3C2O2            | Fe    | Co    | Ni    | Cu    | Ru    | Rh    | Pd    | Ag    | Os    | Ir    | Pt    | Au    |
|------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| $\Delta N_{\rm e}$ (e) | 0.008 | 0.008 | 0.001 | 0.002 | 0.009 | 0.008 | 0.005 | 0.012 | 0.007 | 0.004 | 0.006 | 0.003 |
| NOER (V)               | 2.08  | 1.97  | 2.08  | 3.23  | 2.08  | 3.36  | 1.98  | 4.03  | 5.64  | 2.06  | 2.09  | 2.52  |
| Norr (V)               | 2.95  | 2.95  | 2.93  | 2.91  | 2.94  | 2.94  | 2.97  | 2.84  | 2.60  | 3.01  | 2.69  | 1.08  |
| U (eV)                 | 4.10  | 4.20  | 4.20  | 4.00  | 5.00  | 3.40  | 3.90  | 4.00  | 4.00  | 2.90  | 2.90  | 4.00  |

### References

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