

Electronic Supplementary Material for:

## Vacancy-mediated transition metal as efficient electrocatalyst for water splitting

Yingju Yang, Jing Liu\*, Bo Xiong

State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong  
University of Science and Technology, Wuhan 430074, China

### Corresponding Author:

\* Tel: +86 27 87545526; fax: +86 27 87545526;

E-mail address: [liujing27@mail.hust.edu.cn](mailto:liujing27@mail.hust.edu.cn).

**Content includes:** Computational methods and two figures.

**Fig. S1** Structural model of CuS(001) surface: (a) Top view. (b) Side view.

**Fig. S2** The most stable structures of TM atoms adsorption on the CuS(001) surface.

**Fig. S3** Total density of states of the M@CuS surface.

**Fig. S4** Density of states of transition metal single atoms on M@CuS catalysts: (a) Co@CuS; (b) Cr@CuS; (c) Cu@CuS; (d) Fe@CuS; (e) Mn@CuS; (f) Ni@CuS; (g) Sc@CuS; (h) Ti@CuS; (i) V@CuS; and (j) Zn@CuS.

## 1. Gibbs free energy of HER

The overall hydrogen evolution reaction under the standard condition is described as following:



The overall HER pathway involves the initial state  $\text{H}^+(\text{aq}) + \text{e}^-$ , intermediate  $\text{H}^*$ , and final product  $\text{H}_2(\text{g})$ . According to the computational hydrogen electrode model,<sup>1</sup> the chemical potential of  $\text{H}^+ + \text{e}^-$  pair is equal to one half of the chemical potential of hydrogen molecule. Thus, the Gibbs free energy change ( $\Delta G_{\text{H}^*}$ ) of atomic H adsorption on the catalyst surface is the key descriptor to evaluate the HER activity of electrocatalysts:<sup>2</sup>

$$\Delta G_{\text{H}^*} = \Delta E_{\text{H}} + \Delta E_{\text{ZPE}} - T\Delta S_{\text{H}} \quad (1)$$

where  $\Delta E_{\text{H}}$  is the adsorption energy of atomic hydrogen.  $\Delta E_{\text{ZPE}}$  is the zero-point energy difference between the adsorbed-state and gas-phase hydrogen.  $\Delta S_{\text{H}}$  is the entropy contribution of atomic hydrogen adsorption.

The strong or weak adsorption of intermediate is unfavorable for the HER performance, which leads to a typical volcano curve. Based on the Norskov's assumption,<sup>3</sup> the theoretical exchange current ( $i_0$ ) was calculated to establish the volcano curve of HER. If the proton transfer is exothermic ( $\Delta G_{\text{H}^*} \leq 0$ ), the exchange current at pH = 0 is defined as:

$$i_0 = -ek_0 \frac{1}{1 + \exp(-\Delta G_{\text{H}^*}/k_{\text{B}}T)} \quad (2)$$

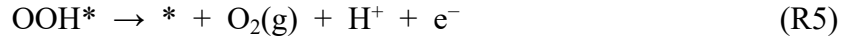
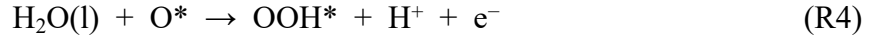
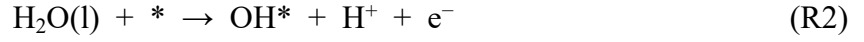
If the proton transfer is endothermic ( $\Delta G_{\text{H}^*} > 0$ ), the exchange current is given by

$$i_0 = -ek_0 \frac{1}{1 + \exp(\Delta G_{\text{H}^*}/k_{\text{B}}T)} \quad (3)$$

where  $k_{\text{B}}$  and  $k_0$  are the Boltzmann constant and rate constant, respectively.

## 2. Gibbs free energy of OER

In an acidic environment of water electrolysis cell, OER is controlled by the following four elementary steps (Fig. 1):



where \* denotes active site of electrocatalysts. (l) and (g) represent liquid and gaseous phases, respectively. OH\*, O\*, and OOH\* are the intermediates of OER. The Gibbs free energy change ( $\Delta G$ ) of each reaction step is given by

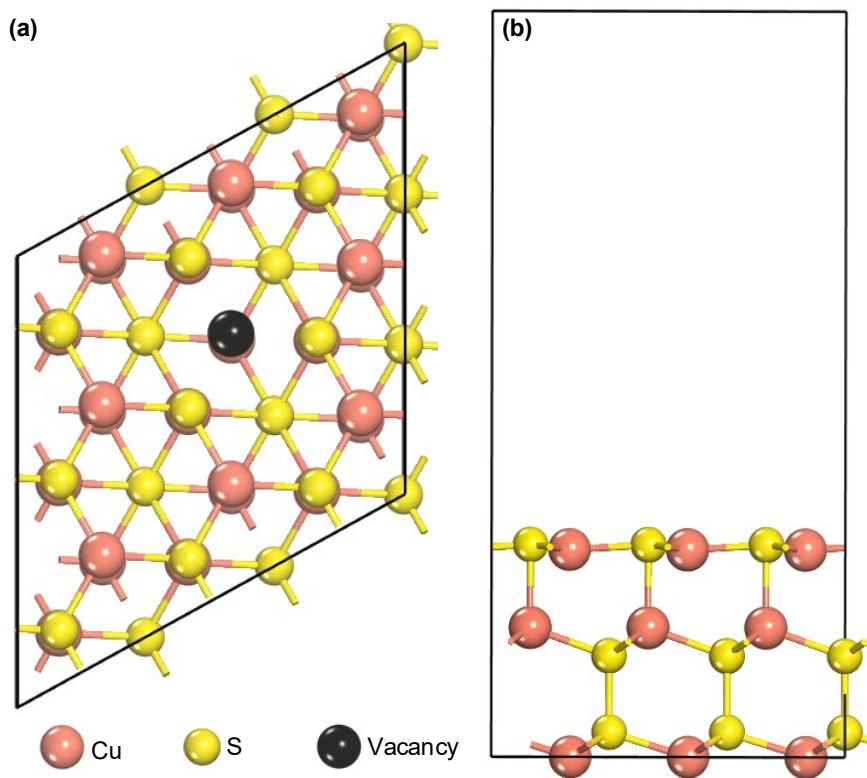
$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S - eU_{\text{SHE}} + k_{\text{B}}T\ln 10 \times \text{pH} \quad (4)$$

where  $U_{\text{SHE}}$  and  $e$  are the standard hydrogen electrode (SHE) potential and charge transferred, respectively. The last term ( $k_{\text{B}}T\ln 10 \times \text{pH}$ ) is the corrected Gibbs free energy of  $\text{H}^+$  ions. Based on the  $\Delta G$  of reactions (R2)-(R5), the OER overpotential ( $\eta$ ) can be determined by the Gibbs free energy change ( $\Delta G_{\text{PLS}}$ ) of the potential limiting step:

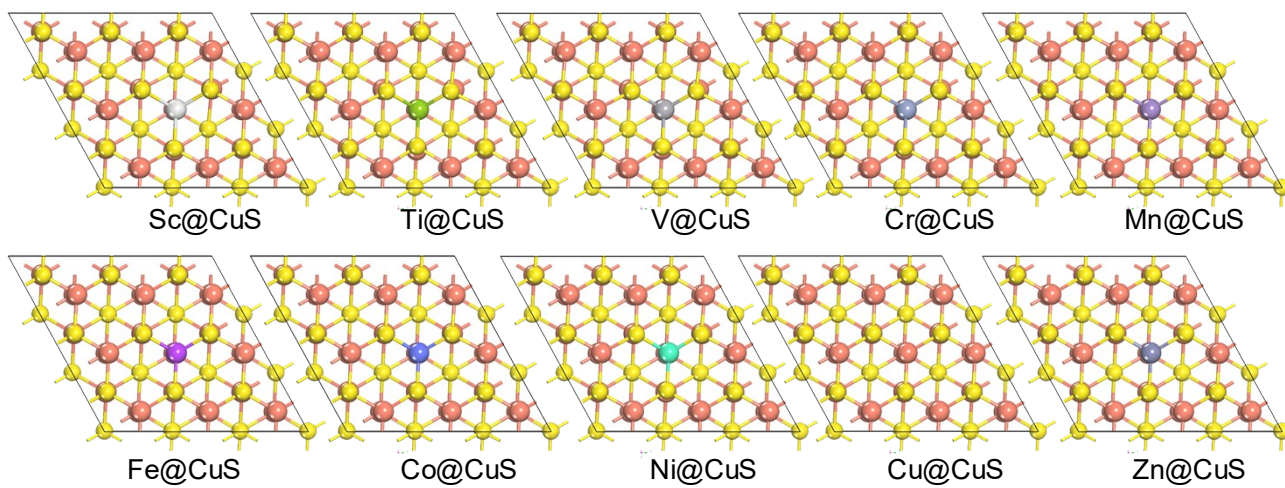
$$\Delta G_{\text{PLS}} = \max(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4) \quad (5)$$

$$\eta = \Delta G_{\text{max}}/e - 1.23 \text{ V} \quad (6)$$

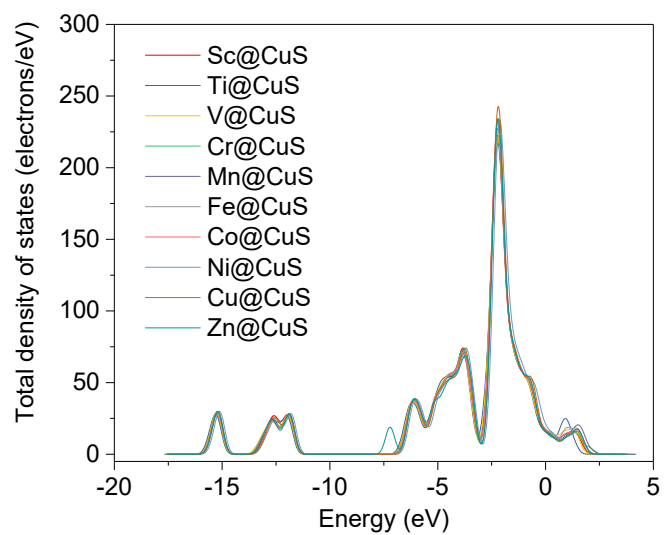
where  $\Delta G_1$ ,  $\Delta G_2$ ,  $\Delta G_3$ , and  $\Delta G_4$  are the Gibbs free energy changes of elementary steps (R2), (R3), (R4), and (R5), respectively. According to equation (6), the lower the overpotential, the better the OER performance of a given electrocatalyst.



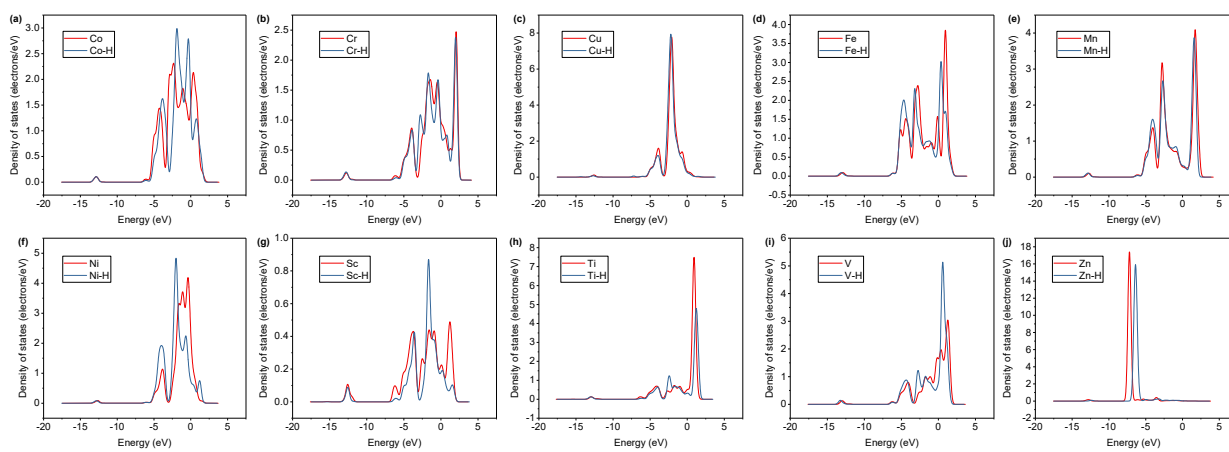
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## References

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