

## Supporting Information

### Self-supporting Ru<sup>3+</sup> doped copper phosphate with Pt/C-like hydrogen evolution reaction activity

Meiting Wang,<sup>a,#</sup> Juan Jian,<sup>a,#</sup> Zhuo Wang,<sup>a</sup> Xiangxin Xue,<sup>a</sup> Ping Nie<sup>a,\*</sup> and Limin Chang<sup>a,\*</sup>

<sup>a</sup> Key Laboratory of Preparation and Applications of Environmental Friendly Material of the Ministry of Education, College of Chemistry, Jilin Normal University, Changchun 130103, P. R. China

\* Corresponding authors' E-mails: xdnieping2009@sina.com; changlimin2139@163.com

Authors marked “#” made the same contribution to this work.

## **1. Material and Experimental Instruments**

### **1.1 Materials used in the experiment**

Pt/C (20 wt%) was obtained from Macklin Ltd. (Shanghai, China). RuO<sub>2</sub>, RuCl<sub>3</sub>·3H<sub>2</sub>O, KOH, Na<sub>2</sub>HPO<sub>4</sub>·12H<sub>2</sub>O, H<sub>8</sub>N<sub>2</sub>O<sub>8</sub>S<sub>2</sub> were purchased from Beijing Chemical Reagents Company (Beijing, China). Copper foam (CF) was provided by the Hao Ke Technology Co. Ltd. (Beijing, China). Apart from the CF, all the drugs mentioned above are analytically pure and no further processing required.

### **1.2 Experimental Section**

#### **1.2.1 Preparation of the CF**

CF was washed with deionized water and anhydrous ethanol three times, and each time ultrasonic treatment for 3 minutes. Finally, the CF was vacuum dried at 60 °C for subsequent use.

#### **1.2.2 Instruments used for basic phase characterizations**

X-ray diffraction (XRD) experiment was tested on a Rigaku D-Max 2550 diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX) images were obtained on a JEOL-6700 scanning electron microscope. Transmission electron microscope (TEM), high resolution TEM (HRTEM) images were obtained with microscopy of Philips-FEI Tecnai G2S-Twin, equipped with a field emission gun operating at 200 kV. X-ray photoelectron spectra (XPS) analysis was performed on a VG Scienta R3000 spectrometer with Al K $\alpha$  (1486.6 eV) as the X-ray source. Contact angle (CA) experiment was analyzed by the machine of Dataphysics OCA20 at room temperature.

#### **1.2.3 Electrochemical measurements**

The electrochemical measurements were conducted using the three-electrode system with the electrochemical workstation (CHI 760e). The as-prepared electrodes were directly used as the work electrodes; meanwhile, graphite rod and Hg/HgO electrode were served as counter

and reference electrodes, respectively. 1.0 M KOH solution was used as electrolyte for OER and HER devices. The seawater is the mixture of 1.0 M KOH and 0.5 M NaCl.

Potentials were normalized versus the standard hydrogen electrode (RHE) according to formula below:

$$E_{(\text{RHE})} = E_{(\text{Hg}/\text{HgO})} + 0.098 \text{ V} + 0.591 \text{ pH} \quad (1)$$

Here, " $E_{(\text{Hg}/\text{HgO})}$ " is the potential we directly measured during the experiment. For that we applied the 1.0 M KOH throughout the OER test,  $\text{pH} = 14$ .

Polarization curves were performed via sweeping potentials at a scan rate of  $2.0 \text{ mV s}^{-1}$ . Corresponding stabilities were examined through current-time curves at the constant potentials.

The Tafel slope can be plotted by the gained linear sweep voltammetry (LSV) curves, which is obtained from the follow equation:

$$\eta = a + b \log j \quad (2)$$

Where, " $\eta$ " refers to the overpotential; " $j$ " is the current density; " $a$ " relates to the  $j_0$  (exchange current density) and can be reflected by the intercept; " $b$ " is the Tafel slope we need to acquire.

The electrochemical active surface area (ECSA) is calculated by the formula below:

$$\text{ECSA} = A * C_{\text{dl}} / C_s \quad (3)$$

Herein, " $A$ " refers to the area of the working electrode, we set the electrode area to  $0.25 \text{ cm}^2$  throughout the electrocatalytic testing; " $C_s$ " relates to the electrolyte and  $C_s$  is  $0.04 \text{ mF cm}^{-2}$ , " $C_{\text{dl}}$ " is the abbreviation of double layer capacitance and calculated from a series of CV curves that tested within the non-Faraday potential range ( $0.9254\text{-}1.0254 \text{ V vs. RHE}$ ), scan rate changed from  $10$  to  $100 \text{ mV s}^{-1}$ , increased with  $10 \text{ mV s}^{-1}$  each time.

Faraday efficiency (FE) of Ru-Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>/CF for HER can be calculated by the ratio of the amount of H<sub>2</sub> collected by drainage method and the theoretical H<sub>2</sub>. Take HER for example, the actual amount H<sub>2</sub> production (labeled as  $n_{\text{H-experimental}}$ ) can be calculated using the equation of  $n_{\text{H-experimental}} = V / V_m$ , where  $V$  is the volume of H<sub>2</sub> collected from the chronoamperometry testing;  $V_m$  is molar volume of ideal gas, and  $V_m = 22.4 \text{ L mol}^{-1}$ . For the theoretical H<sub>2</sub> (marked as  $n_{\text{H-theoretical}}$ ) accumulated during the HER. According the HER equation of  $\text{H}_2\text{O} \rightarrow 1/2\text{O}_2 + \text{H}_2 + 2\text{e}^-$ , where, the electrolytic efficiency ( $\eta$ ) can be measured by the equation of  $\eta = z * n * F / Q$ . Here, “ $n$ ” is the mole of H<sub>2</sub> generated during the HER, and can be marked as  $n_{\text{H-theoretical}}$ ; “ $z$ ” is the number of transferred electrons generated per mole of H<sub>2</sub> during the HER, herein,  $z = 2$ ; “ $F$ ” is the Faraday constant,  $F = 96485 \text{ C mol}^{-1}$ ; “ $Q$ ” refers to the actual quantity of electric charge, and can be calculated by the flume of  $Q = \Sigma i * t$ . In the chronoamperometry experiment, the  $Q$  can be directly calculated. To evaluate the FE of a catalyst for HER, we assume that 100 % current efficiency occurs during the whole reaction. Hence,  $1 = 2 * F * n_{\text{H-theoretical}} / Q$ , therefore,  $n_{\text{H-theoretical}} = Q / (2 * F)$ .<sup>[1]</sup>

## 2. Theory calculation section

The density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP),<sup>[1,2]</sup> with the generalized gradient approximation (GGA) Perdew-Burke-Ernzerhof (PBE) functional<sup>[3]</sup> to describe electron exchange and correlation. The projector-augmented plane wave (PAW)<sup>[4,5]</sup> potentials were used to describe the core-valence electron interaction and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 450 eV. Partial occupancies of the Kohn-Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than  $10^{-5}$  eV. A geometry optimization was considered convergent when the force change was smaller than  $0.02 \text{ eV/\AA}$ .

A k-points sampling of  $2 \times 2 \times 1$  with Monkhorst-Pack<sup>[6]</sup> scheme was used in all calculations and all calculations were considered the spin polarization effect.

The (111) plane of  $\text{Cu}_3(\text{PO}_4)_2$  ( $3 \times 2 \times 1$ ) supercell and was generated for adsorption calculation, and the model of  $\text{Ru-Cu}_3(\text{PO}_4)_2$  represent a Ru-doped  $\text{Cu}_3(\text{PO}_4)_2$  (111) surface.

The adsorption energy  $\Delta E$  for  $A = \text{OH}, \text{O},$  and  $\text{OOH}$  groups on the surfaces of substrates was defined as:

$$\Delta E = E_{*A} - (E_* + E_A) \quad (4)$$

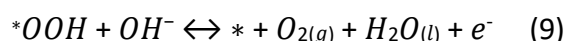
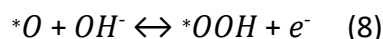
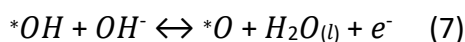
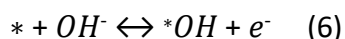
where  $*A$  and  $*$  denote the adsorption of  $A$  groups on active sites and the bare substrates, while  $E_A$  denotes the energy of  $A$  groups.

The free energy change  $\Delta G$  of the reaction was calculated as the difference between the free energies of the initial and final states, as showed below:

$$\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S \quad (5)$$

Here,  $\Delta E$  is the energy change between the reactant and product obtained from DFT calculations;  $\Delta \text{ZPE}$  is the change in the zero-point energy;  $T$  and  $\Delta S$  denote the temperature and the change of entropy, respectively. Herein,  $T = 300 \text{ K}$  was considered.

The electrochemical model of the oxygen evolution reaction (OER) in alkaline media could be divided into four one-electron reactions:



Where the  $*$  denotes the substrates. The adsorption energies of intermediates ( $*\text{OH}^-$ ,  $*\text{O}$ , and  $*\text{OOH}^-$  groups) on substrates were calculated by the following equations:

$$\Delta E_{*O} = E_{(sub/O)} - E_{(sub)} - [E_{(H_2O)} - E_{(H_2)}] \quad (10)$$

$$\Delta E_{*OH} = E_{(sub/OH)} - E_{(sub)} - [E_{(H_2O)} - E_{(H_2)}/2] \quad (11)$$

$$\Delta E_{*OOH} = E_{(sub/OOH)} - E_{(sub)} - [2 \times E_{(H_2O)} - 3 \times E_{(H_2)}/2] \quad (12)$$

Wherein,  $E_{(sub/H_2O)}$ ,  $E_{(sub/OH)}$ ,  $E_{(sub/O)}$  and  $E_{(sub/OOH)}$  denoted the total energies of H<sub>2</sub>O, OH, O, and OOH groups on substrates.  $E_{(sub)}$ ,  $E_{(H_2O)}$  and  $E_{(H_2)}$  were the energies of the bare substrate, water, and hydrogen gas, respectively.

The Gibbs free energy changes of Equations (6-9) could be estimated by:

$$\Delta G_1 = \Delta G_{*OH} \quad (13)$$

$$\Delta G_2 = \Delta G_{*O} - \Delta G_{*OH} \quad (14)$$

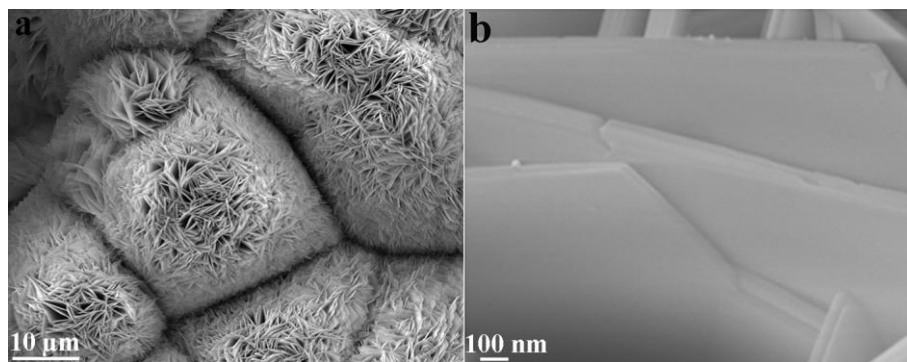
$$\Delta G_3 = \Delta G_{*OOH} - \Delta G_{*O} \quad (15)$$

$$\Delta G_4 = 4.92 \text{ eV} - \Delta G_{*OOH} \quad (16)$$

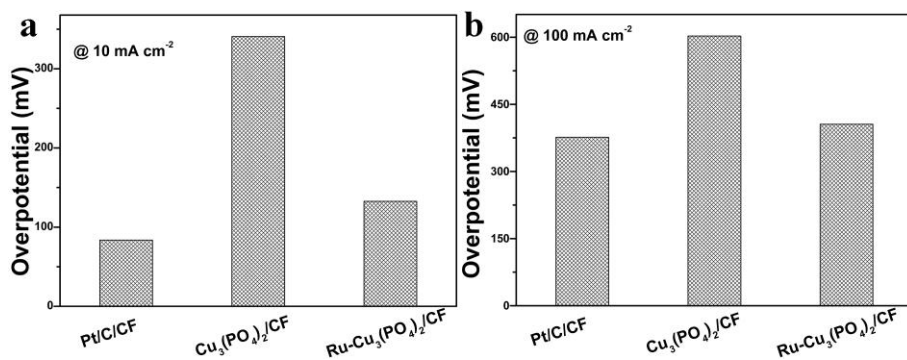
Where, the sum of  $\Delta G_{13-16}$  was fixed to the negative of the experimental Gibbs free energy of the formation of two water molecules.

Additionally, the Gibbs free energy of (H<sup>+</sup> + e<sup>-</sup>) in solution was estimated as half the energy of the H<sub>2</sub> molecule in the standard condition.

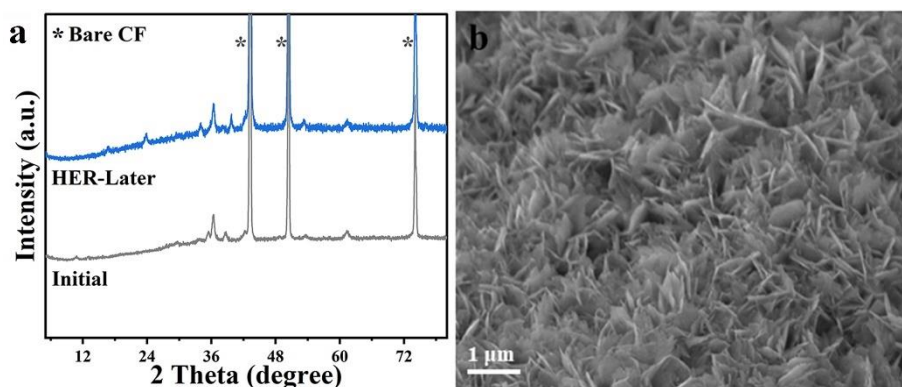
### 3. Supplementary Figures and Tables



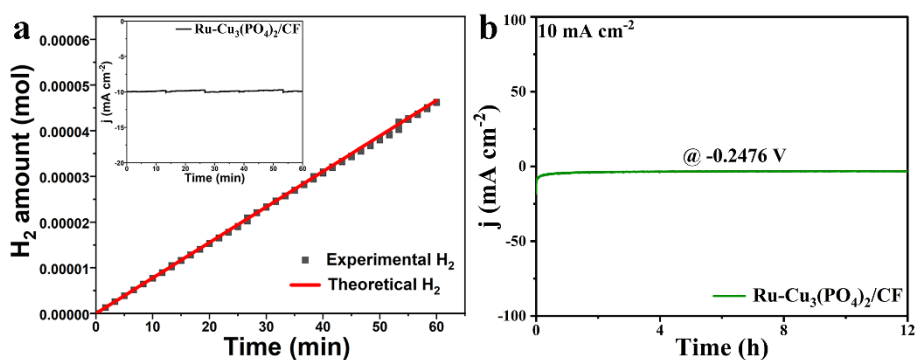
**Fig. S1.** The SEM images of Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>/CF.



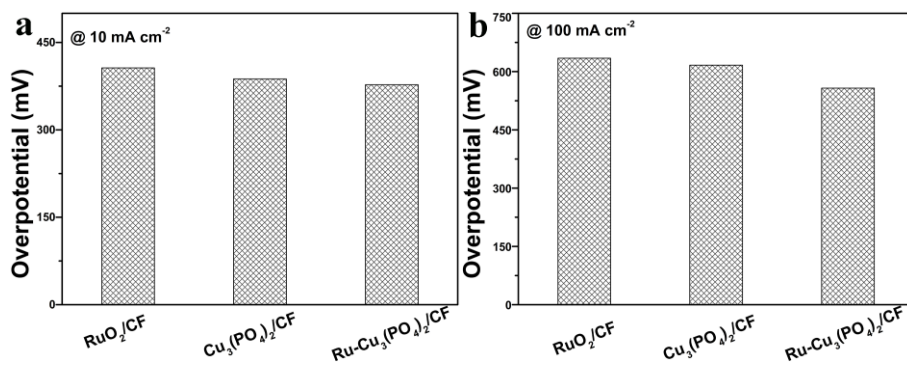
**Fig. S2.** Bar graphs between potential and current density at (a) 10 and (b) 100 mA cm<sup>-2</sup> of Pt/C/CF, Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>/CF and Ru-Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>/CF during the HER process.



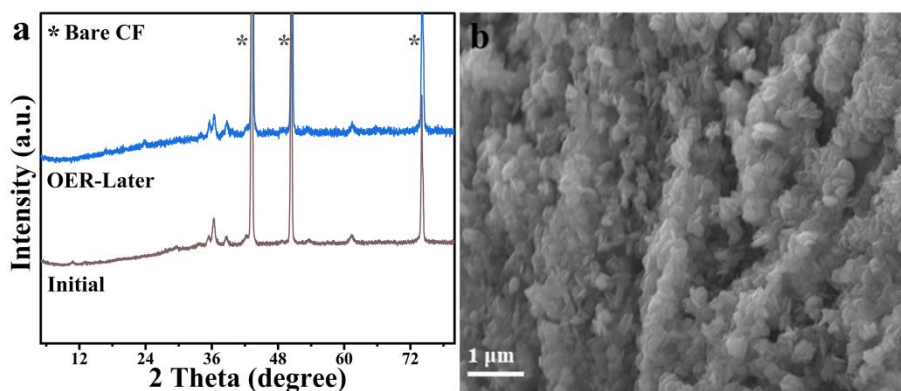
**Fig. S3.** The XRD and SEM image of Ru-Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>/CF that the HER test later.



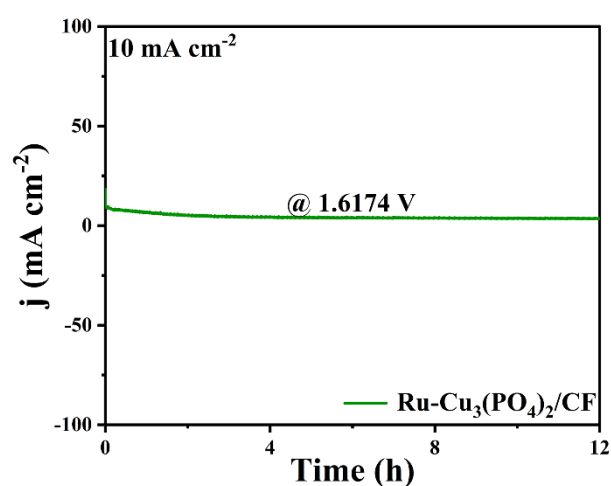
**Fig. S4.** (a) The Faraday efficiency curves of Ru-Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>/CF during the HER process, insert is the related *i*-*t* curves. (b) The *i*-*t* curves of Ru-Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>/CF operated in the seawater.



**Fig. S5.** Bar graphs between potential and current density at (a) 10 and (b) 100 mA cm<sup>-2</sup> of RuO<sub>2</sub>/CF, Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>/CF and Ru-Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>/CF during the OER course.

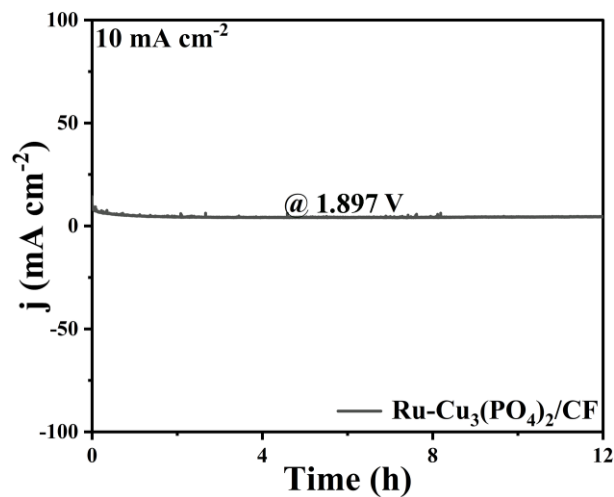


**Fig. S6.** The XRD and SEM image of the Ru-Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>/CF that the OER test later.



**Fig. S7.** The i-t curves of Ru-Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>/CF operated in the seawater.

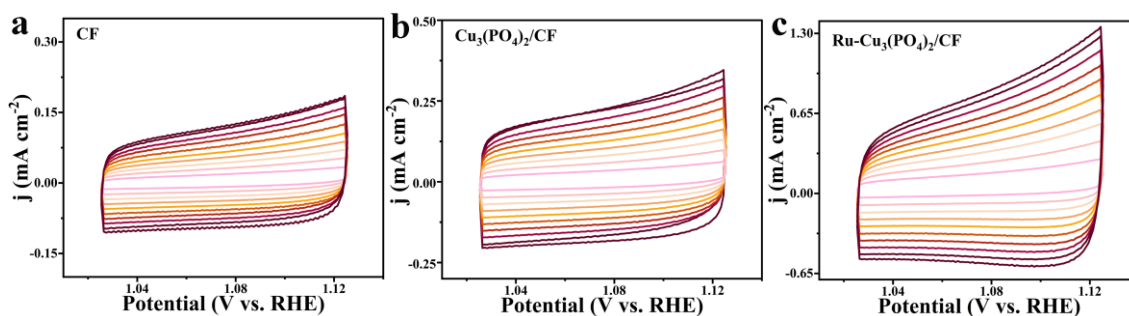




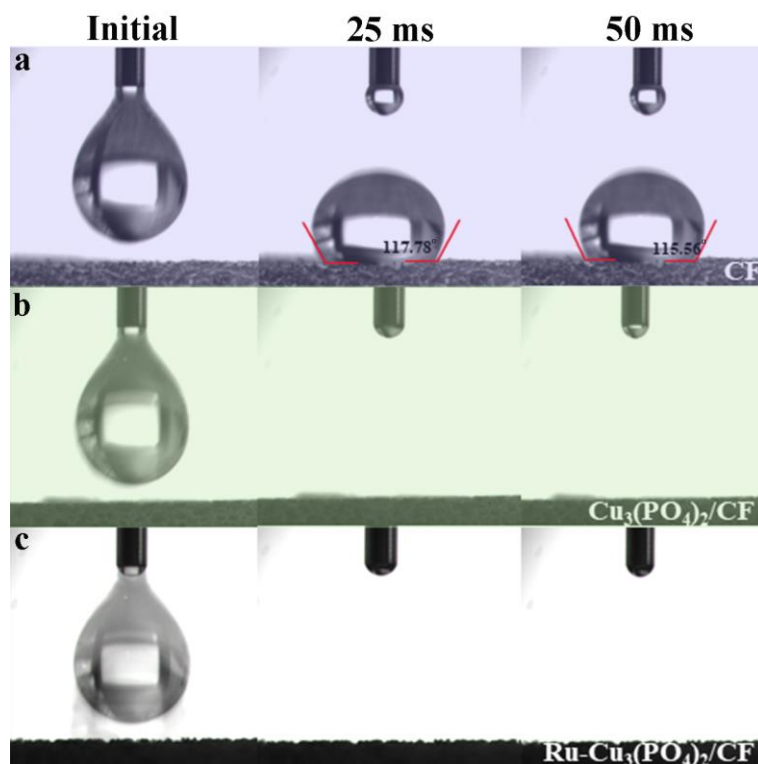
**Fig. S8.** The *i-t* curves of the Ru-Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>/CF measured in the seawater when the provided voltage is 1.897 V.

**Table S1.** *C*<sub>dl</sub>, ECSA and related data of bare CF, Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>/CF and Ru-Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>/CF.

Catalyst	<i>C</i> <sub>dl</sub> (mF cm <sup>-2</sup> )	<i>C</i> <sub>s</sub> (mF cm <sup>-2</sup> )	<i>A</i> (cm <sup>2</sup> )	ECSA (cm <sup>2</sup> )
Bare CF	1.17	0.04	0.25	7.31
Cu <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> /CF	2.21	0.04	0.25	13.81
Ru-Cu <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> /CF	7.18	0.04	0.25	44.88



**Fig. S9.** The CV curves at different scan rate of (a) Bare CF, (b) Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>/CF and (c) Ru-Cu<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>/CF.



**Fig. S10.** The water contact angle data of (a) bare CF, (b)  $\text{Cu}_3(\text{PO}_4)_2/\text{CF}$  and (c)  $\text{Ru-Cu}_3(\text{PO}_4)_2/\text{CF}$  when the time is 0, 25 and 50 ms, respectively.

#### 4. References

- [1] Jian, J.; Yuan, H. M.; Feng, S. H. et al. Sn-Ni<sub>3</sub>S<sub>2</sub> Ultrathin Nanosheets as Efficient Bifunctional Water-Splitting Catalysts with a Large Current Density and Low Overpotential, *ACS Appl. Mater. Inter.*, 2018, 10, 40568.
- [2] Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.*, 1996, 6, 15-50.
- [3] Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B*, 1996, 54, 11169-11186.
- [4] Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.*, 1996, 77, 3865-3868.

[5] Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B*, 1999, 59, 1758-1775.

[6] Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B*, 1994, 50, 17953-17979.

[7] Monkhorst, H.J.; Pack, J. D. On Special Points for Brillouin Zone Integrations, *Phys. Rev. B*, 1976, 13, 5188-5192.