

## Supporting information

### Seeds-assisted synthesis of *fcc* Ru-Cu bimetallic nanostructures and their catalytic properties for hydrogen evolution reaction

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#### Experiments

**Materials:** Polyvinylpyrrolidone (PVP K30, average molecular weight: 58000), Cupric (II) acetylacetonate ( $\text{Cu}(\text{acac})_2$ ), benzyl alcohol (BP), formaldehyde and Ruthenium (III) acetylacetonate ( $\text{Ru}(\text{acac})_3$ ) are purchased from Macklin Ltd Co. All the chemical reagents are analytical grade and used without further purification in the experiments of this study.

**Synthesis of Cu nanocrystals:** 0.2 mmol of  $\text{Cu}(\text{acac})_2$ , 1.2 g of PVP and 30 ml of BP were mixed and stirred for 0.5 h, then 3 ml of formaldehyde was added. Stirred overnight, then placed in an oven at 190 °C for 12 h to produce Cu. After being cooled down to room temperature, the resulting Cu NCs were collected by centrifugation at 10000rpm for 10 min, washed three times with acetone/ethanol (3:1 in volume), and then placed in a vacuum oven and dried at 80 °C.

**Synthesis of Ru nanocrystals:** Using the same synthetic method of synthetic Cu NCs, only 0.2 mmol of  $\text{Ru}(\text{acac})_3$  was used instead of  $\text{Cu}(\text{acac})_2$ .

**Synthesis of  $\text{Cu}_{0.5}\text{-Ru}_{0.5}$  /  $\text{Cu}_{0.25}\text{-Ru}_{0.75}$  /  $\text{Cu}_{0.16}\text{-Ru}_{0.84}$  nanocrystals:** 0.2/0.067/0.04 mmol of  $\text{Cu}(\text{acac})_2$ , 1.2 g of PVP and 30 ml of BP were mixed and stirred for 0.5 h, then 0.2 mmol of  $\text{Ru}(\text{acac})_3$  and 3 ml of formaldehyde was added. Stirred overnight, then placed in an oven at 190 °C for 12 h. After being cooled down to room temperature, the resulting Cu-Ru NCs were collected by centrifugation at 10000rpm for 10 min, washed three times with acetone/ethanol (3:1 in volume), and then placed in a vacuum oven and dried at 80 °C.

**Control experiment of  $\text{Cu}_{0.5}\text{-Ru}_{0.5}$  nanocrystals:** The experiment by heating  $\text{Cu}(\text{acac})_2$  and  $\text{Ru}(\text{acac})_3$  at 190 °C for 1-2 hours is carried out and testifies that Cu nanoparticles form firstly. As shown in the Fig.S2, for the sample 1h, the three peaks at 43.3, 50.5 and 74.1° correspond to the diffraction peaks of the (111), (200) and (220) diffractions of face-centered cubic (*fcc*) phase Cu (JCPDS # 85-1326). For the sample 2h, in addition to the above three Cu peaks, we found a broadened peak at 40.3~42.3° due to the presence of Ru in the sample. In order to judge the type of elements in the sample, we dropped the sample

on the molybdenum grid for TEM testing. The TEM image and EDX show (Fig. S3) that the sample 1h are composed of Cu nanoparticles with a size of 10~20nm, and there is almost no presence of Ru. When the hydrothermal time is prolonged to 2h, the sample particle size becomes larger as shown by the TEM image, and EDX indicates that the Ru element content is increased obviously. Hence, we conceive that the Cu seeds formed firstly in the benzylalcohol system.

**Characterization:** To analyze the phases and composition of the sample, X-ray diffraction (XRD) is conducted by using a Rint-2000V/PC diffractometer (Rigaku, Japan) with standard Cu/K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). The morphology is characterized on a ZEISS SUPRA® 55 scanning electron microscope (SEM). Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) study are carried out in Tecnai G2 F30, which is equipped with an EDS detector (Oxford X-Max 20). X-ray photoelectron spectroscopy (XPS) is performed using PHI-5000 VersaprobeII (Ulvac-Phi, Japan).

**Electrochemical measurements:** The LSV measurement is carried out with an electrochemical workstation CHI760E. A glassy carbon electrode loaded with the samples, an Ag/AgCl electrode and a Pt plate are used as a working, a reference and a counter electrode respectively, which creates a traditional three-electrodes system. And the  $0.5 \text{ mol}\cdot\text{L}^{-1} \text{ H}_2\text{SO}_4$  solution is used as electrolyte to transform electric charges. To avoid the Pt dissolved in the acidic solution and loaded on the working electrode, affecting the HER activity of the working electrode, we used a device as shown in Fig. S7 which using a proton exchange membrane to separate the cathode and anode reaction zones.

**Electrode preparation of working:** The sample (2 mg) was dispersed in a mixed solution of  $50 \mu\text{l}$  Nafion (5 wt%),  $150 \mu\text{l}$  absolute ethanol, and  $50 \mu\text{l}$  ultrapure water, and then sonicated for 30 min. Then  $10 \mu\text{l}$  of the drop was placed on a glassy carbon electrode ( $0.196 \text{ cm}^2$ ).

**ICP:** 1.1mg sample of  $\text{Cu}_x\text{-Ru}_{1-x}$  nanocrystals and  $200 \mu\text{l}$  of NaClO (effective chlorine content: 5%) were mixed and stirred for 10 min, then add ultrapure water to dilute to 300ml.

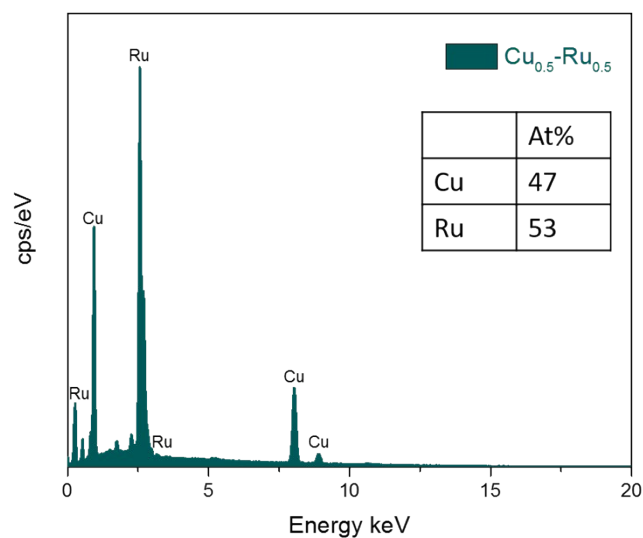


Fig.S1 EDS pattern of the Cu<sub>0.5</sub>-Ru<sub>0.5</sub> NCs.

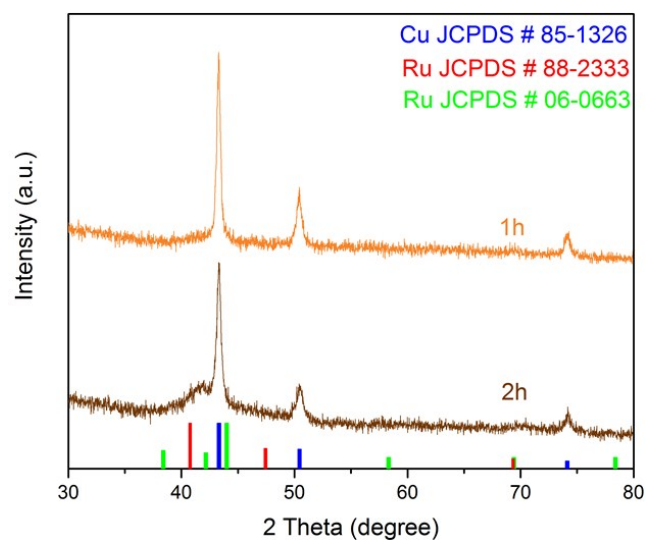


Fig.S2 XRD pattern of the sample 1h and 2h

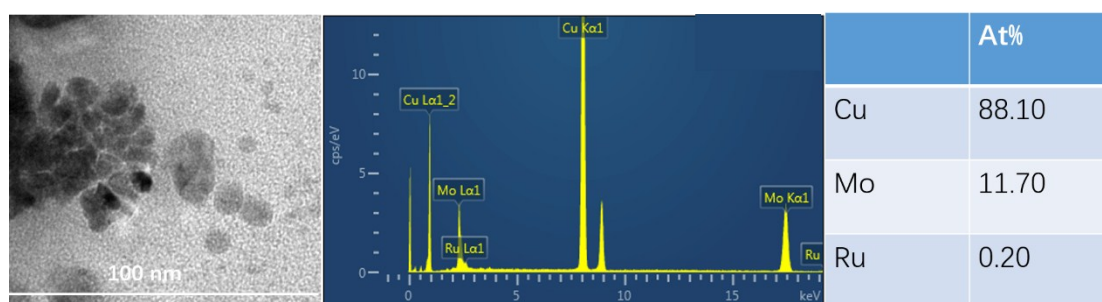


Fig.S3 TEM image and EDX of the sample 1h

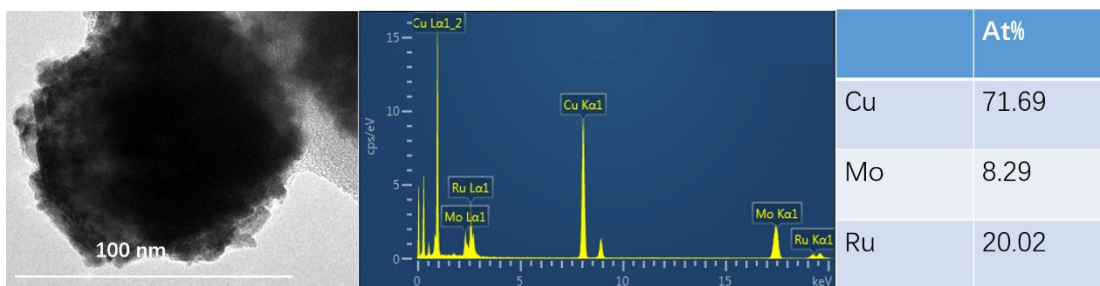


Fig.S4 TEM image and EDX of the sample 1h

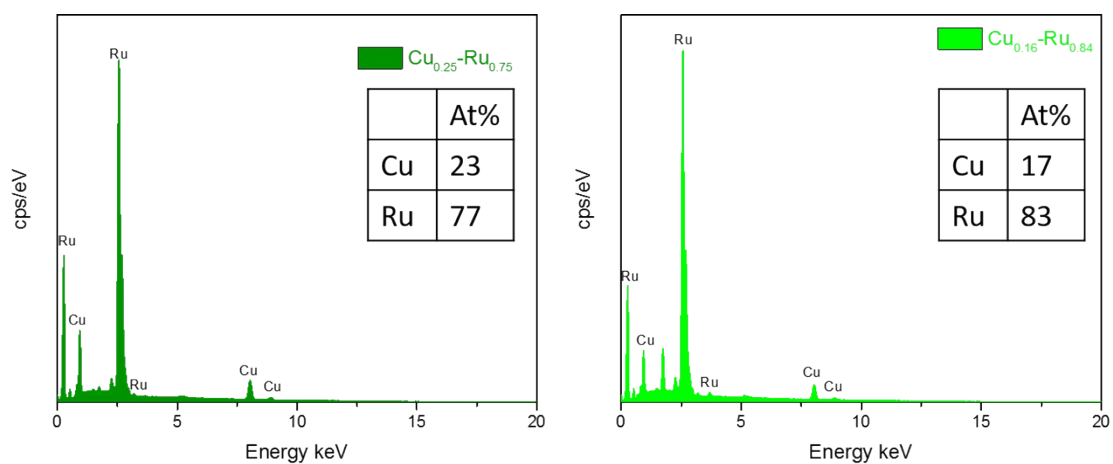
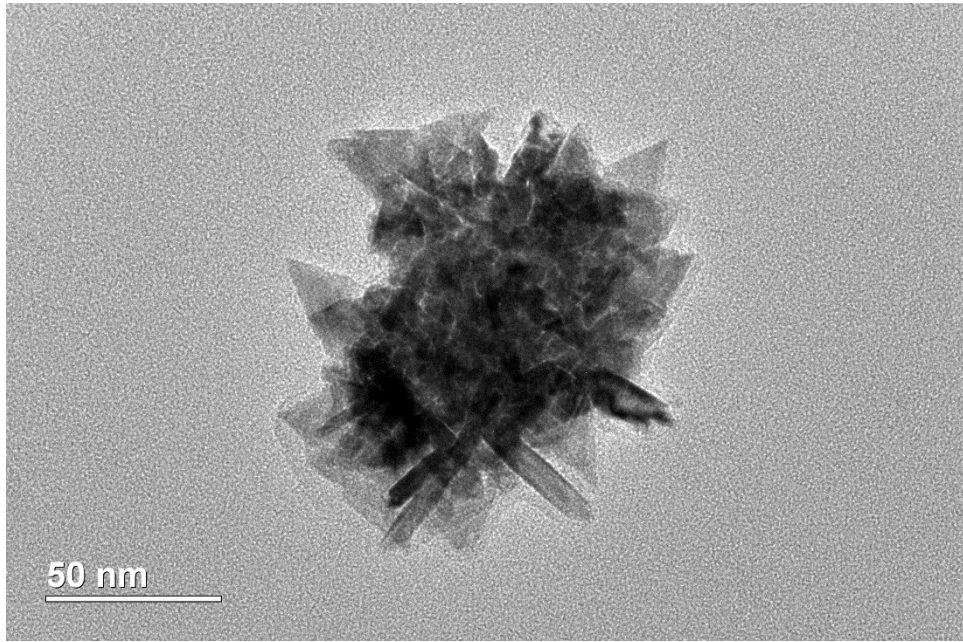


Fig. S5 EDS pattern of  $\text{Cu}_{0.25}\text{-Ru}_{0.75}$  NCs and  $\text{Cu}_{0.16}\text{-Ru}_{0.84}$  NCs.

Tab. S1 ICP of  $\text{Cu}_x\text{-Ru}_{1-x}$  NPs.

Sample	Ru (mg/L)	Cu: Ru (At)
$\text{Cu}_{0.5}\text{-Ru}_{0.5}$	<b>2.291</b>	<b>48.6:51.4</b>
$\text{Cu}_{0.25}\text{-Ru}_{0.75}$	<b>2.949</b>	<b>27.7:72.3</b>
$\text{Cu}_{0.16}\text{-Ru}_{0.84}$	<b>3.281</b>	<b>15.6:84.4</b>



**Fig. S6** TEM image of the  $\text{Cu}_{0.16}\text{-Ru}_{0.84}$  NCs



**Fig. S7** Electrocatalytic HER device

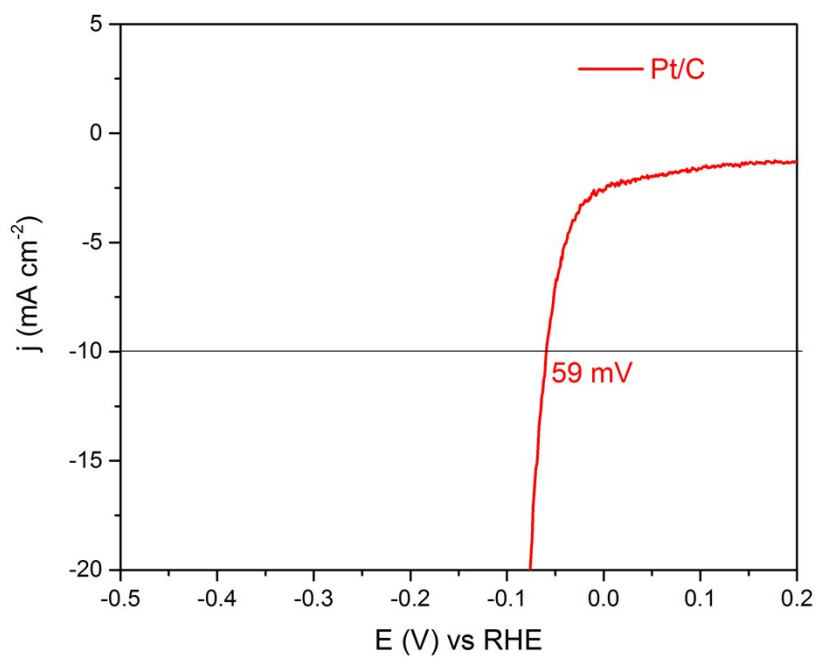


Fig. S8 Linear volt-ampere scanning curve at a scanning rate of 1 mV/s of Pt/C.

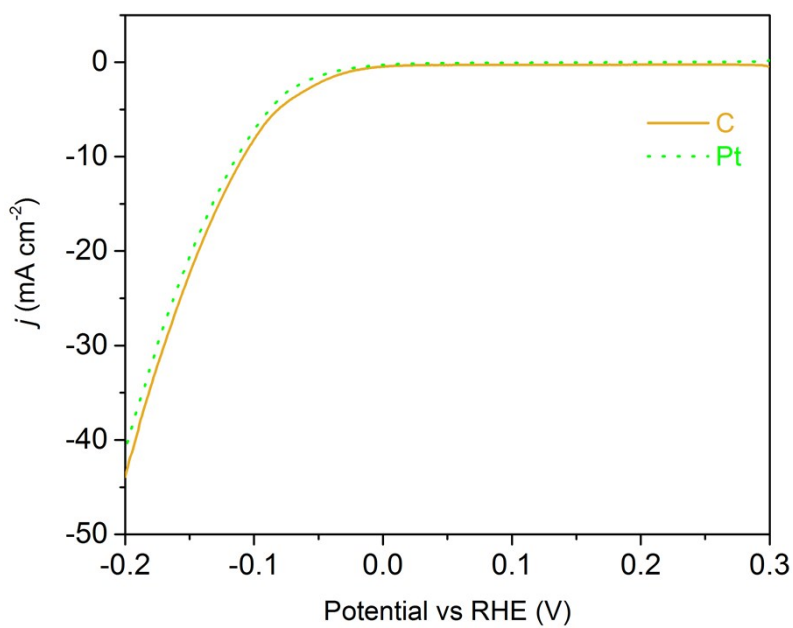


Fig. S9 The LSV comparison chart of the counter electrode is Pt and graphite.