Supporting Information

Donutlike RuCu Nanoalloy with Ultrahigh Mass Activity for Efficient and Robust Oxygen Evolution in Acid Solution

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1. Experimental Section

Chemicals

Ruthenium acetylacetonate (Ru(acac)₃, 97%), Ruthenium(IV) oxide (RuO₂, 99.9%), Copper acetylacetonate (Cu(acac)₂, 97%), Oleylamine (oAm, 80-90%), and Borane dimethylamine complex (DMAB, 96%) were purchased from Aladdin. Toluene (TOL). Ethanol and Methylcyclohexane were purchased from Sinopharm Chemical Reagent Co., Ltd. Nafion® 117 solution (~5%) was purchased from Sigma-Aldrich. Agon (Ar, 99.999%) was supplied by Airgas, Inc. All these chemicals and gases were used without further purification.

Synthesis of Ru and Donutlike RuCu Nanomaterials

Typically, 73.9 mg Ru(acac)₃ and 48.6 mg Cu(acac)₂ were dissolved in a mixed solution of 22 mL oAm and 50 mL toluene under magnetic stirring at room temperature for 10 min. Subsequently, 180 mg DMAB was added with continuously stirring for 20 min. The resulting suspension was transferred to a Teflon-lined stainless-steel autoclave and heated at 190 \degree for 12 h. Finally, the products were precipitated by centrifugation and washed three times with ethanol. Ru monometallic nanomaterials were prepared according to the above procedure but only using Ru(acac)₃ as raw materials.

2. Materials Characterizations

Morphology and Structure Characterizations

Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy-energy dispersive spectroscopy (STEM-EDS) were performed on a JEOL JEM-2100F microscope at an acceleration voltage of 200 kV. X-ray diffraction (XRD) patterns were measured with a PANalytical X'Pert PRO X-ray diffractometer operating a Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å) in a 2 θ range from 20 ° to 60 °. The Ru *M*-edge, Cu *L*-edge and O *K*-edge XANES spectra were obtained at the BL12B station of National

Synchrotron Radiation Laboratory in the total electron yield mode under a vacuum better than 5×10^{-6} Pa. The beam from the bending magnet was monochromatized utilizing a varied line-spacing plane grating and refocused by a toroidal mirror. The ICP-MS instrument used was a PlasmaQuad 3 (VG Elemental Ltd, Winsford, Cheshire, UK). X-ray photoelectron spectra (XPS) were acquired on an ESCALAB MKII with Al K α as the excitation source. The binding energies obtained in the XPS spectral analysis were corrected for specimen charging by referencing C 1s to 284.8 eV.

Electrochemical Measurements

Electrochemical measurements were performed by using a CH Instruments CHI760D electrochemical workstation with a standard three-electrode electrochemical cell, where the prepared electrodes immersed in a sulfuric acid electrolyte solution (0.5 M), graphite and Ag/AgCl (saturated KCl) act as the counter and reference electrode, respectively. The linear sweep voltammetry (LSV) curves were measured at a rate of 10 mV s⁻¹ after dozens of cyclic voltammetric scans until stable. Tafel slopes were calculation from the polarization curves at the current density from 1~10 mA cm⁻². Mass activity (MA) values were calculated by the formula described later. The amperometric i-t curve was held at initial current of 10 mA cm⁻² for 20 h. The electrochemical double layer capacitance (Cdl) was measured at a range of 0.8~0.9V vs. RHE at rate ranging from 20 to 100 mV s⁻¹ with interval 20 mV increment. The electrochemical impedance spectroscopy (EIS) was measured at 1.55 V vs. RHE, and the perturbation signal was 5 mV with the frequency ranging from 0.01 Hz to 100 kHz. All the electrolyses were conducted at room temperature, and no IR correction was applied in all measurements.

Electrode Preparation

The pre-prepared electrocatalysts were dispersed in appropriate amount of cyclohexane (~75 mL), and then the cleaned carbon fibers (CF) were dropped with the above solution (~0.5 mL). The treated CF was heated to 300 $^{\circ}$ C for 2 h in the Ar atmosphere at a heating rate of 5 $^{\circ}$ C/min to remove organic surfactants.^{1, 2} The CF has an area of 1

cm², corresponding to the catalyst loading about 0.0135 mg/cm², which were calculated according to the Ru mass. As a reference, the commercial RuO₂ electrode preparation method was as follows. 2.5 mg of RuO₂ powder was dispersed in 1 mL of 3:1 (v/v) DI-water/ethanol mix solvent with 40 μ l Nafion solution, and then the mixture was sonicated in an ultrasonic water bath for about 1 h. After that, 5 μ L of the dispersion was transferred onto the glassy carbon disk with a diameter of 3 mm, leading to the catalyst loading about 0.176 mg/cm². Finally, the as-prepared electrode was dried at room temperature. The glassy carbon electrode was polished with different polishing S2 powder (1.0 and 0.3 μ m alpha alumina, 50 nm gamma alumina, orderly) and thoroughly cleaned with deionized water and acetone before loaded.

3. Calculation Methods

Mass Activity Calculation

Mass activity (MA, A g⁻¹) values were calculated from the electrocatalyst loading *m* and the measured current density *j* (mA cm⁻²) near at $\eta = 270$ mV:

MA = j/m

DOS Calculation

The first-principles density functional theory (DFT) calculations were performed using a plane wave basis set with the projector augmented plane-wave (PAW) method.^{3, 4} The exchange-correlation interaction was described within the generalized gradient approximation (GGA) in the form of PW91.⁵ The energy cutoff was set to 400 eV, and the atomic positions were allowed to relax until the energy and force were less than 10⁻⁴ eV and 10⁻² eV/Å, respectively. The crystal of RuCu alloy exists in a face-centered cubic structure. Its cell constant is a=3.6589 Å. We used the (111) surface to mimic the active surface of the RuCu alloy. The slab model of RuCu was simulated by periodically repeating the RuCu layers along the [111] direction of the unit cell. Each slab model consists of four RuCu planes and is separated by a vacuum region of 15 Å. A H₂O molecule was adsorbed on the surface Ru site. A Monkhorst-Pack 11 × 11 × 1 k-point grid was used to sample the Brillouin zone. A non-spin polarized calculation was performed in this work. The Gibbs free energy can be calculated by the following formula:

 $\Delta G = \Delta E + \Delta Z P E - T \Delta S$

 $\Delta E = E_{(A+S)} - E_A - E_S$

 $\Delta ZPE = 1/2h\nu$

where, ΔE is the binding energy, ΔZPE the zero point energy, ΔS the entropy change at 273 K, and $E_{(A+S)}$, E_A , and E_S are the total energy of the catalyst model with adsorbed molecule, the adsorbed molecule, and the catalyst model, respectively. The entropy and zero point energy were obtained by frequency calculation at 300 K.

4. Supplementary Figures



Figure S1. Schematic of the fabricated strategy of RuCu nanoalloys.



Figure S2. The complete XPS spectra of RuCu catalysts at different reaction times.



Figure S3. HRTEM images of RuCu catalysts at different reaction times.

Reaction time	Ru 3p (Atomic %)	Cu 2p (Atomic %)
1 hour	0	100
5 hour	37.2	62.8
8 hour	50.5	49.5
12 hour	51.4	48.6

Table S1. The element atomic percentage variation according to XPS results.

	Element	Wt%	At%
⁸ . (Cu K	47.90	59.39
· I	Ru K	52.10	40.61

Figure S4. EDS pattern of RuCu nanoalloys.



Figure S5. TEM and HRTEM pattern of RuCu nanoalloys after 10000 cycles.



Figure S6. Cu L-edge XANES curves of Cu powders and RuCu nanoalloys.



Figure S7. (a) Ru 3p and (b) O 1s XPS spectra of RuCu catalysts before and after OER.



Figure S8. Cyclic voltammograms (CV) are taken in a potential window without

faradaic processes.

Table S2. The dissolved metal masses for RuCu catalysts.

Operating conditions	Ru µg	Cu µg
Before i-t	5.629	3.559
1h after i-t	0.030	0.201
20h after i-t	bld*	0.0021

bld*-blew limit of detection

Electrocatalysts	Electrolyte	Mass activity (A g ⁻¹) (Ru/Ir)	η (mV at 10mA cm ⁻²)	Ref.
Donutlike RuCu	0.5 M H ₂ SO ₄	~800	270	This
nanoparticles				work
hollow Pt/NiO/RuO2	0.1 M HClO ₄	~714	235	6
Nanovoid-incorporated Ir ₃ Cu aerogel	0.1 M HClO ₄	~400	298	7
IrNiCu double-layered nanoframes	0.1 M HClO ₄	~500	300	8
Pd core–Ru nanobranches	0.1 M HClO ₄	~25	225	9
Au core–Ru nanobranches	0.1 M HClO ₄	~25	220	10
Co-IrCu octahedral nanocages	0.1 M HClO ₄	~640	300	11
IrCoNi porous hollow nanocrystals	0.5 M H ₂ SO ₄	~1000	309	12
Ir-Ni thin layer nanoparticles	0.05 M H ₂ SO ₄	~498	280	13
IrTe nanotubes	0.1 M HClO ₄	~392	290	14
r-RuO ₂ nanoparticles	0.1M HClO ₄	~18	250	15

Table S3. Comparisons of the mass activities compared to previously reported

catalysts.

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