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Supporting Information

Controllable construction of ZIFs-derived Co_9S_8 hollow polyporous polyhedrons with Ru-doping for enhanced hydrogen evolution reaction

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Experimental

Reagents.

2-methylimidazole (2-MeIM, 98%), Co(NO₃)₂·6H₂O (99%), thioacetamide (TAA), ethyl alcohol, methyl alcohol, N, N-dimethylformamide (DMF), KOH (85%) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). RuCl₃(45-55 % Ru basis) was purchased from Macklin Biochemical Co., Ltd (Shanghai, China). Commercial Pt/C (20 wt%) and Nafion (5 wt%) were obtained from Sigma-Aldrich (Shanghai) Trading Co., Ltd. (Shanghai, China). Carbon papers (CP) were acquired from Toray Industries, Inc. (Tokyo, Japan). The water used in the experiment was ultrapure water with a resistivity of 18.25 MΩ·cm made by the laboratory.

Preparation of ZIF-67

The preparation of ZIF-67 has been reported in literature¹, with the specific procedure outlined as follows: Initially, 6 mmol of Co(NO₃)₂·6H₂O is dissolved in 50 mL of methanol, referred to as Solution 1. Subsequently, 40 mmol of 2-methylimidazole (2-MeIM) is dissolved in 50 mL of methanol, referred to as Solution 2. At room temperature, Solution 2 is rapidly added to Solution 1, stirred magnetically for 2 hours, and the resulting suspension is centrifuged at 6000 rpm for 5 minutes. Finally, the obtained precipitate is washed three times with methanol, dried in a vacuum oven, and the prepared ZIF-67 purple powder is collected.

Preparation of core-shell RuCo(OH)_x@ZIF-67 derivatives

According to the relevant literature, core-shell structured $RuCo(OH)_x@ZIF-67$ polyhedra were synthesized². Firstly, 100 mg of prepared ZIF-67 polyhedra were sonicated in 20 mL of ethanol, followed by the addition of 10 mL of a 2 mg mL⁻¹ RuCl₃ aqueous solution. Sonication continued for 40 minutes (sonication power: 150 W). The resulting suspension was then centrifuged at 6000 rpm for 5 minutes, washed three times with ethanol, and dried under vacuum at 60°C to obtain the deep purple core-shell structured Ru-Co MOF derivative.

The synthesis of yolk-shell structured CoRuS_x@ZIF-67 polyhedra

First, 80 mg of the core-shell RuCo(OH)_x@ZIF-67 were dispersed in 25 mL of ethanol by ultrasonication, denoted as solution 1. Then, 20 mg of TAA was dissolved in another 25 mL of ethanol, denoted as solution 2. Subsequently, solution 2 was poured into solution 1, and the mixture was refluxed and stirred at 80°C for 1 hour. The resulting solution was centrifuged at 6000 rpm for 5 minutes, washed three times with ethanol, dried in a vacuum oven at 60°C, and the product was collected.

Synthesis of Ru-Co₉S₈-T Hollow Polyporous Polyhedra and Their Comparative Samples

The obtained yolk-shell structured $CoRuS_x@ZIF-67$ polyhedra were annealed in Ar at a heating rate of 10 °C min⁻¹ and 500 °C for 2 h, resulting in Ru-Co₉S₈-500 hollow polyhedra (Ru-Co₉S₈-500 HPPs). Additionally, Ru-Co₉S₈-400 HPPs and Ru-Co₉S₈-600 HPPs electrocatalysts were prepared under different temperatures (400 and 600 °C) to explore the optimal morphology, catalytic activity, and treatment temperature of the electrocatalysts. To investigate the influence of Ru introduction on the catalytic activity and structure of the electrocatalyst, a comparative sample of Co₉S₈ hollow nanocages was also prepared. The preparation method was similar to that of Ru-Co₉S₈-500 HPPs, except that RuCl₃ was not added during the sonication process, i.e., Ru³⁺ was not introduced.

Electrochemical testing

5 mg of as-prepared electrocatalysts were dispersed in 1 mL mixture solution (980 μ L of DMF and 20 μ L of Nafion solution (5 wt%)), and was ultrasonicated for 10 min to form the uniform catalyst ink. 30 μ L of the well-dispersed catalysts ink was dropped onto a piece of carbon paper (CP) electrode (area of 0.5 ×0.5 cm²) and dried at 60 °C. The mass loading of the catalysts was 0.6 mg cm⁻². Electrochemical tests of all catalysts were performed by using a CHI 660E electrochemical workstation (CH Instruments, Inc., Shanghai) with the typical three-electrode system in 1.0 M KOH. The graphite rod, Hg/HgO electrode (salt bridge solution is 1.0 M KOH), and catalyst-loaded CP were respectively applied as the counter electrode, reference electrode, and working electrode. Unless otherwise noted, all of the measured potentials in our work were manually iR-corrected and calibrated to a reversible hydrogen electrode (RHE) through the Nernst equation as follows: E (vs. RHE) = E (vs. Hg/HgO) + 0.098 + 0.059 pH³.

The electrocatalysts were activated and stabilized through continuous accelerated cyclic voltammetry (CV) before the linear sweep voltammetry (LSV) tests. Polarization

curves for HER acquired from LSV were recorded at a scan rate of 5 mV s⁻¹ from 0.1 V to -0.5 V vs. RHE. Tafel slope was calculated by the equation of $\eta = a + b \log j^4$. Here, *a* is a constant, *b* and *j* respectively represent the Tafel slope and current density. Double layer capacitance (*C*_{dl}) was determined by recording CV at different scan rates (10 - 200 mV·s⁻¹) in the range of 0.1 - 0.2 V vs. RHE to assess the electrochemical surface areas (ECSA) of the catalysts. Nyquist plots of the electrochemical impedance spectra (EIS) measurement were performed at an overpotential of 0.1 V along with the frequency range from 0.1 Hz to 100 KHz. Chronoamperometry (overpotential: 25 mV) was used for stability tests.

Methods and instruments for material characterization

The morphology and elemental composition of the electrocatalyst were characterized using transmission electron microscopy (TEM, Hitachi and Tecnai G2 F20 S-TWIN) and scanning electron microscopy (SEM) equipped with an energydispersive X-ray spectroscopy (EDX) system (OXFORD Instrument XMAX and Zeiss). The phase composition of the materials was analyzed using X-ray diffraction (XRD) with a D8 ADVANCE diffractometer (Bruker, Germany), with a scanning range of 5-90°20. Fourier-transform infrared spectroscopy (FTIR) spectra of the samples were recorded using a Vertex 70 spectrometer (Bruker, Germany) in the wavenumber range of 500-4000 cm⁻¹. The thermal properties of the yolk-shell structured CoRuS_x@ZIF-67 polyhedra were investigated using a thermal gravimetric analyzer (TGA, TA Instruments TGA500, USA). The electronic states of surface elements of the electrocatalyst were characterized using X-ray photoelectron spectroscopy (XPS, Thermo Fischer, ESCALAB 250Xi). The specific surface area and pore size distribution of the electrocatalyst were determined based on nitrogen adsorption-desorption isotherms measured at 77 K using the Brunauer-Emmett-Teller (BET) method, conducted on an Autosorb iQ station. The contents of elements in the catalysts were measured by inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo ICAP 6300).



Fig. S1 (A, B) SEM and (C, D) TEM images of ZIF-67.



Fig. S2 (A, B) SEM and (C, D) TEM images of core-shell structured $RuCo(OH)_x @ZIF-$

67.



Fig. S3 (A) SEM, (B) TEM, (C) HAADF-STEM, (D-G) EDX elemental mapping images of C, Co, S, Ru, and (H) EDX spectrum of yolk-shell structured CoRuS_x@ZIF-67.

Compared with the RuCo(OH)x@ZIF-67, the CoRuSx@ZIF-67 well maintains the regular dodecahedral morphology with a rougher surface decorated by many tiny nanoparticles after refluxing at 80 °C for 1 h, as exhibited in Fig. S3A. TEM image of CoRuSx@ZIF-67 in Fig. S3B demonstrates the formation of a yolk-shell structure accompanied by an irregular ZIF-67 yolk. This phenomenon is mainly caused by the fact that the edges of the ZIF-67 core possess more defects and provide more reactive sites for chemical etching⁵, thus the edges are preferentially etched and the inner ZIF-67 core has gradually become irregular as the reaction progresses⁶. The yolk-shell structure of CoRuSx@ZIF-67 also can be observed in a high-angle annular dark field (HAADF) image (Fig. S3C). According to the EDX elemental mapping images in Fig. S3D-G, the elements of C and Co are distributed in the yolk and shell regions, meanwhile, Ru and S elements are only can be observed in the outer shell. The corresponding EDX spectrum of CoRuSx@ZIF-67 also confirms the existence of C, Co, S, and Ru elements (Fig. S3H).



Fig. S4 (A) XRD patterns of pristine ZIF-67, core-shell structured $RuCo(OH)_x@ZIF-67$, and yolk-shell structured $CoRuS_x@ZIF-67$. (B) FT-IR spectra of pristine ZIF-67, core-shell structured $RuCo(OH)_x@ZIF-67$, yolk-shell structured $CoRuS_x@ZIF-67$, and $Ru-Co_9S_8-500$ HPPs.

As can be seen from the X-ray diffraction (XRD) patterns (Fig. S4A), the RuCo(OH)_x@ZIF-67 and CoRuS_x@ZIF-67 exhibit similar characteristic peaks compared to that of pristine ZIF-67 but with a much lower peak intensity, further indicating that ZIF-67 framework is partly etched during the reaction process. Besides, the Fourier transform infrared (FT-IR) spectra (Fig. S4B) display that the peaks of ZIF-67 powders, RuCo(OH)_x@ZIF-67 and CoRuS_x@ZIF-67 are mainly assigned to the 2-methylimidazole (2-MeIM) in ZIF-67. The peaks observed at 600-1500 cm⁻¹ are related to the stretching and bending modes of the imidazole ring, while the peaks at 1580 cm⁻¹ are related to the tensile mode of the C=N bond in 2-MeIM. The small peaks at 2930 and 3135 cm⁻¹ also correspond to the tensile mode of the C-H band of the aromatic ring and aliphatic chain in 2-MeIM. After the following annealing, the peaks of 2-MeIM completely disappeared, showing the successful phase transformation.



Fig. S5 TGA curve of yolk-shell structured $CoRuS_x@ZIF-67$. The TGA curve of $CoRuS_x@ZIF-67$ was obtained in a temperature range of room temperature to 800 °C with a heating rate of 10 °C min⁻¹ under an N₂ atmosphere.



Fig. S6. N_2 adsorption-desorption isotherms and the corresponding pore size distribution curves (inset) of (A) Ru-Co₉S₈-400 HPPs, (B) Ru-Co₉S₈-500 HPPs, (C) Ru-Co₉S₈-600 HPPs.



Fig. S7 (A, B) SEM and (C, D) TEM images of Ru-Co₉S₈-400 HPPs.



Fig. S8 (A, B) SEM and (C, D) TEM images of Ru-Co₉S₈-600 HPPs.



Fig. S9 (A, B) SEM and (C, D) TEM images of Co_9S_8 HNCs.



Fig. S10 Survey XPS spectrum of Ru-Co₉S₈-500 HPPs.



Fig. S11 (A) Survey XPS spectrum of Ru-Co₉S₈-400 HPPs. High-resolution XPS spectra of Ru-Co₉S₈-400 HPPs: (B) C 1s, (C) Ru 3p, (D) Co 2p, and (E) S 2p.



Fig. S12 (A) Survey XPS spectrum of $Ru-Co_9S_8-600$ HPPs. High-resolution XPS spectra of $Ru-Co_9S_8-600$ HPPs: (B) C 1s, (C) Ru 3p, (D) Co 2p, and (E) S 2p.



Fig. S13 CVs for (A) Ru-Co₉S₈-400 HPPs, (B) Ru-Co₉S₈-500 HPPs, (C) Ru-Co₉S₈-600 HPPs, (D) CoRuS_x@ZIF-67 and (E) Co₉S₈ HNCs in 1.0 M KOH at different scan rates (10-200 mV S⁻¹). (F) The corresponding capacitive currents at 0.15 V vs. RHE as a function of scan rate for Ru-Co₉S₈-T HPPs, CoRuS_x@ZIF-67, and Co₉S₈ HNCs.



Fig. S14 (A) SEM, (B) TEM, (C) HAADF-STEM, (D-G) EDX elemental mapping images of C, Co, S, Ru, and (H) EDX spectrum of $Ru-Co_9S_8-500$ HPPs after the stability test.



Fig. S15 (A)Survey XPS spectrum and (B-E) high-resolution XPS spectra of Ru-Co₉S₈-500 HPPs after the stability test: C 1s (B), Ru 3p (C), Co 2p (D), and S 2p (E).

	Co content	Ru content	S content	Co : Ru (atomic
Samples	(%)	(%)	(%)	ratio)
Ru-Co ₉ S ₈ -400 HPPs	39.39	9.7	15.8	1:0.14
Ru-Co ₉ S ₈ -500 HPPs	37.9	9.2	15.2	1:0.14
Ru-Co ₉ S ₈ -600 HPPs	30.2	6.7	12.3	1:0.13
Co ₉ S ₈ HNCs	41.6	/	11.5	/

Table S1. The content of elements in the Ru-Co₉S₈-T HPPs and Co₉S₈ HNCs.

Table S2. Comparison of the HER activity for Ru-Co₉S₈-500 HPPs with other recently

Catalysts	$\eta_{\mathrm{j10}}(\mathrm{mV})$	Tafel siope (mV dec ⁻¹)	Ref.
Ru-Co ₉ S ₈ -500 HPPs	20	56	This work
Ru–SnO ₂	23	52.5	7
Ru-MoCoP	55	67	8
Ru@2D COF	42	46	9
Ru ₂ (M)-CoWO ₄ /CC	85	105	10
Ru-MnFeP/NF	35	69	11
MoO2@MoS2@Co9S8 nanorods	160	80	12
Co ₉ S ₈ @MoS ₂ /CNFs	190	110	13
Co3S4@FNC-Co3	140	103	14
NiCo-MOF rods	125	78	15
CoIr-MOF/NF	15	56.9	16
NiCo ₂ O ₄ @CoMoO ₄ /NF-7	121	77	17

reported catalysts in an alkaline medium.

Samples	$R_{ m s}\left(\Omega ight)$	$R_{\rm ct} 1 (\Omega)$	$R_{\rm ct}2~(\Omega)$
CoRuS _x @ZIF-67	2.96	15.7	42.81
Ru-Co ₉ S ₈ -400 HPPs	2.54	21.67	20.26
Ru-Co ₉ S ₈ -500 HPPs	3.39	1.09	6.53
Ru-Co ₉ S ₈ -600 HPPs	2.99	0.84	50.26
Co ₉ S ₈ HNCs	3.16	8.31	106.6

Table S3. R_s and R_{ct} values of the electrocatalysts were obtained by fitting Nyquist plots with equivalent circuits.

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