Supporting Information

Ru-doped CoS$_{1.097}$ nanoparticles for improved electrocatalytic hydrogen evolution reaction

Jun Zhang,*,[1] Xin Pang, [1] Jiabing Luo,[1] Xingzhao Wang,[1] Shutao Wang,[2] and Yan Zhou*, [1]

1.School of Materials Science and Engineering, China University of Petroleum (East China), Qingdao 266580, China.

2. College of Chemistry and Chemical Engineering, China University of Petroleum (East China), Qingdao 266580, China.

Experimental section

1. Chemicals and materials

Cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O), thioacetamide (CH$_3$CSNH$_2$, TAA), ethanol and methanol were purchased from Sinopharm Group Chemical Reagents Co. Ltd. RuCl$_3$·xH$_2$O was purchased from Tianjin Komiou Chemical Reagent Development Center. 2-Methylimidazole (2-MIM) was purchased from Aladdin. Carbon fiber paper was purchased from Shanghai Hesen Electric Co. Ltd. Nafion (5 wt %) was purchased from Alfa Aesar (China) Chemical Co. Ltd. All chemicals are used directly without further purification.

2. Catalyst synthesis

2.1 Synthesis of ZIF-67

The synthesis of ZIF-67 was referred to the previous literature[1]. Firstly, 1.46 g of cobalt nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O) and 3.28 g of 2-methylimidazole (2-MIM) were dissolved in 100 mL methanol solution, respectively. After rapid mixing and stirring for 10 minutes, the solution was kept at room temperature for 24 hours. The purple product was centrifuged three times with

methanol to remove impurities. The product was then dried overnight in a vacuum oven at 60 ℃.

2.2 Synthesis of Ru-ZIF-67

The obtained ZIF-67 was dispersed in 12 mL ethanol solution, and then a certain amount of RuCl$_3$ · xH$_2$O was mixed with ZIF-67 in ethanol solution. Heat in an oil bath at 80 ℃ for 12 hours. By changing the molar ratio of ZIF-67 and RuCl$_3$ · xH$_2$O, catalysts with different doping amounts were prepared(The total molar weight of all metal cations in the catalyst is 1mmol). The input amounts of the two substances are shown in Table S1. The black product was separated by centrifugation, washed three times with ethanol, and dried overnight in a vacuum drying oven at 60 ℃. The products were named Ru-ZIF-4, Ru-ZIF-6 and Ru-ZIF-8 respectively.

Table S1. The raw materials used in the synthesis of Ru-ZIF-67.

Sample	ZIF-67(mmol)	ZIF-67(g)	RuCl$_3$ · xH$_2$O(mmol)	RuCl$_3$ · xH$_2$O(g)
Ru-ZIF-4	0.9615	0.2798	0.0385	0.0080
Ru-ZIF-6	0.9434	0.2746	0.0566	0.0117
Ru-ZIF-8	0.9259	0.2695	0.0741	0.0154

2.3 Synthesis of CoS$_x$ and Ru-CoS$_{1.097}$

Ru-CoS$_{1.097}$ was prepared by one-step hydrothermal sulfuration method. Typically, 87.31 mg of Ru-ZIF-67 with different doping amounts obtained by the above steps was weighed, and then 112.69mg (1.5 mmol) of thioacetamide (CH$_3$CSNH$_2$) was taken. The two were mixed in 40 mL ethanol solution and subjected to ultrasonic treatment for 20 minutes. The mixture was then transferred to a Teflon-lined stainless steel autoclave (50 mL) and kept at 200 ℃ for 12 h. After natural cooling to room temperature, the black product was separated by centrifugation and washed with ethanol, and then dried overnight in a vacuum oven at 60 ℃. Finally, Ru-CoS$_{1.097}$ with different doping amounts was obtained, named Ru-CoS$_{1.097}$-4, Ru-CoS$_{1.097}$-6 and Ru-CoS$_{1.097}$-8, respectively. The preparation of CoS$_x$ is the same as the above method, except for replacing Ru-ZIF-67 with ZIF-67.

3.Characterizations

X-ray powder diffraction (XRD) was performed using a Philips X 'Pert diffractometer with Cu Kα radiation. Hitachi S-480 was used to obtain scanning electron microscope (SEM) images. JEM-

2100UHR was used to obtain test transmission electron microscope (TEM), high resolution transmission electron microscope (HRTEM) and selected area electron diffraction (SAED) images. X-ray photoelectron spectroscopy (XPS) was obtained using an ESCALAB 250 analyzer. Agilent 730ES is used to obtain inductively coupled plasma (ICP) data.

4.Electrochemical measurements

Electrochemical tests were performed in 1.0 M KOH electrolyte using a three-electrode system in the CHI 660 electrochemical workstation (Shanghai, China). Before the electrochemical test, nitrogen is injected into the electrolyte for 30 minutes to remove oxygen. The graphite rod and Ag/AgCl (saturated KCl) electrode were used as counter electrode and reference electrode, respectively. The preparation method of the working electrode is as follows: 5mg catalyst sample is dispersed into a mixed solution containing 500μL ethanol and 25μL Nafion to form a uniform slurry, which is subjected to ultrasonic treatment for 1h. Then 100μL of the mixed solution was added dropwise to the pretreated carbon paper with a loading concentration of 1 mg cm^{-2}. The area of carbon paper immersed in electrolyte is 1cm^2. After 20 cyclic voltammetry (CV) tests, linear sweep voltammetry (LSV) without and with *iR* compensation was performed at a scan rate of 10 mV S^{-1}. The Tafel plots is obtained by polarization curve. In the non-faradic region, CV measurements were performed at different scan rates (10, 20, 30, 40, 50, 60, 70, and 80 mV S^{-1}), and the above CV results were used to estimate the double-layer capacitance (Cdl). The compensation resistance is obtained from the EIS results. The EIS test was performed at a DC potential of 10 mA cm^{-2} (-1.226 V vs RHE) in the LSV curve. The test frequency range is 10^5 ~ 0.01 Hz.
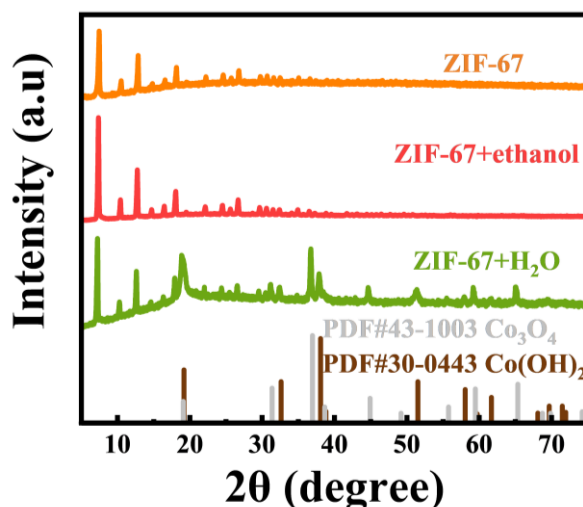

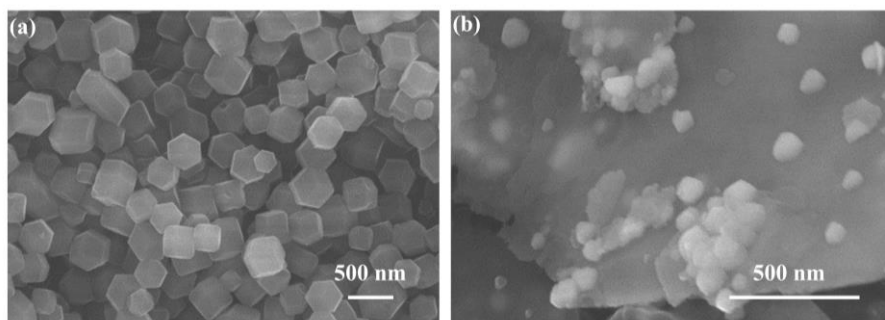**Fig. S1.** XRD patterns of ZIF-67, ZIF-67+ethanol and ZIF-67+H$_2$O.

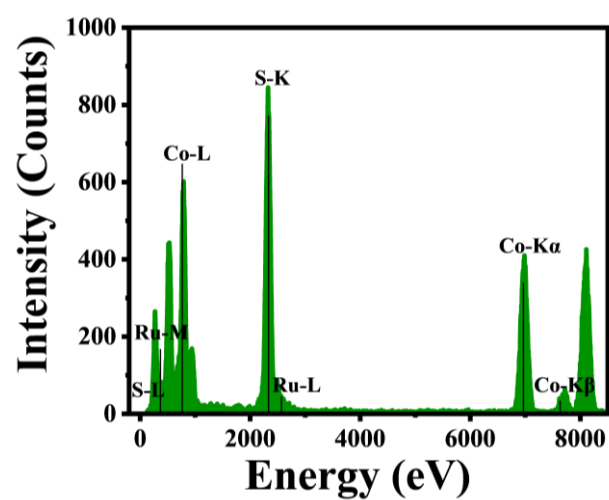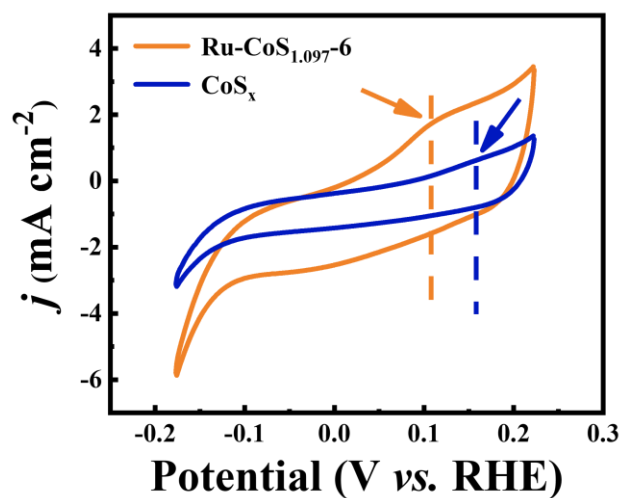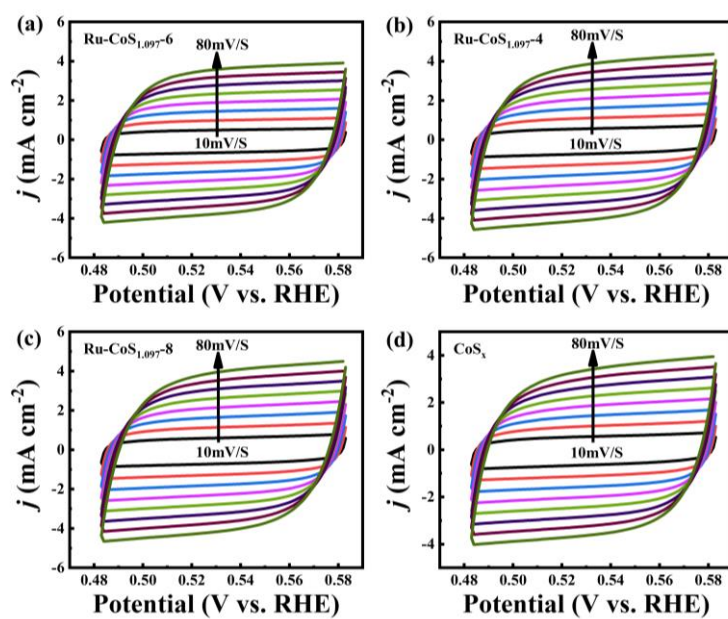**Fig. S2.** SEM images of (a) ZIF-67+ethanol, (b) ZIF-67+H_2O.

Fig. S3. EDX spectrum of Ru-CoS$_{1.097}$-6.

Table. S2. The Ru contents for Ru-CoS$_{1.097}$ catalysts quantified by ICP-OES.

| Obtained samples	Weight （%）
Ru-CoS$_{1.097}$-4	0.6733
Ru-CoS$_{1.097}$-6	1.4430
Ru-CoS$_{1.097}$-8	1.6369

Figure. S4. The Cyclic voltammograms recorded at E= -0.177 to 0.223 V vs RHE of Ru-CoS$_{1.097}$-6 and CoS$_x$.
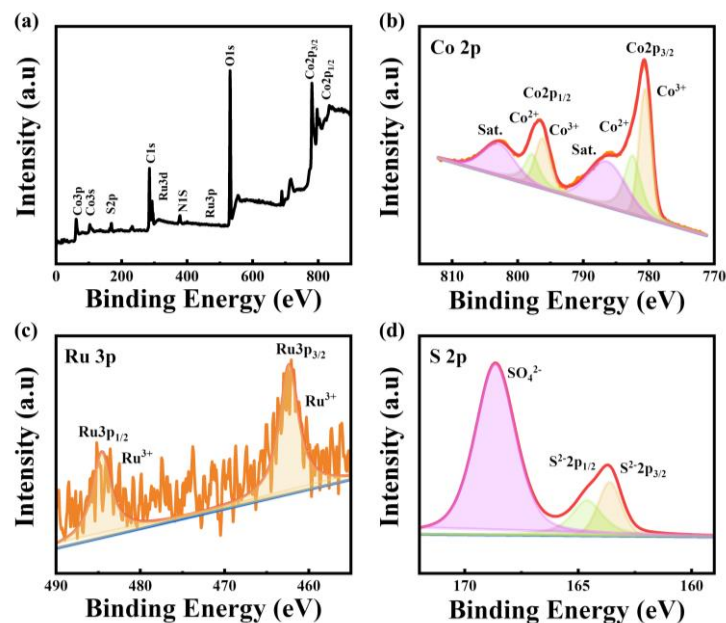

Fig. S5. CV in the region of 0.483 to 0.583 V vs. RHE of (a) Ru-CoS$_{1.097}$-6, (b) Ru-CoS$_{1.097}$-4, (c) Ru-CoS$_{1.097}$-8, and (d) CoS$_x$.
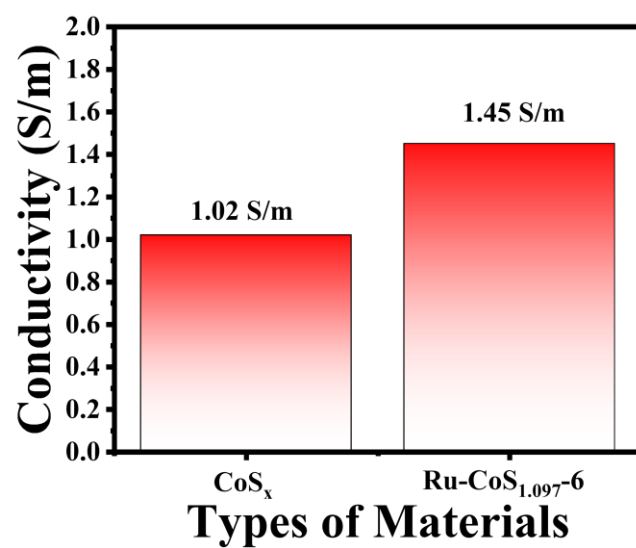
Figure S6. Conductivity diagram of CoS_x and $Ru-CoS_{1.097}-6$ tested with the 4-probe tester at the current range of 10 μA at three different positions.
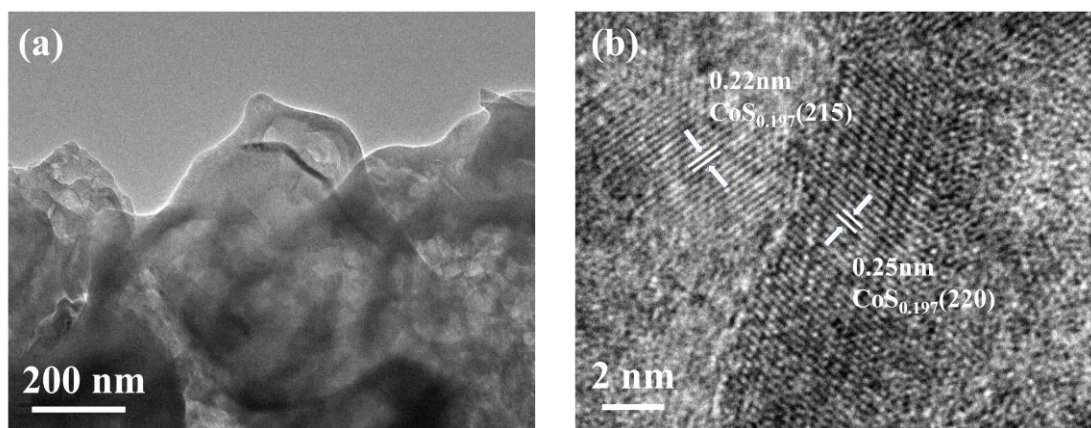
Fig. S7. The (a) TEM and (b) HRTEM image of $Ru-CoS_{1.097}-6$ after 5000 CVs.

Fig. S8. High resolution XPS spectrum of (a) full spectrum, (b) Co 2p, (c) Ru 3p and (d) S 2p in Ru-$CoS_{1.097}$-6 after 5000 CVs.

Table S3. Comparison of active retention rate of Ru-$CoS_{1.097}$ and recently reported electrocatalysts.

Catalysts	Current Density (j, mA cm^{-2})	Time (h)	electrolyte	Active retention rate (%)	Ref.
Ru-$CoS_{1.097}$	100	50	1.0 M KOH	98.84	This work
RuCoP	100	50	1.0 M KOH	20.00	2[2]
Ni-Co_3S_4 HNS/TM	10	24	1.0 M KOH	83.93	3[3]
Co_9S_8/CoNSC	10	30.6	1.0 M KOH	95.00	4[4]
Co_9S_8 HNSs	10	12	1.0 M KOH	84.07	5[5]
Co_3S_4 HNSs	10	12	1.0 M KOH	68.10	5[5]
CoS_2 HNSs	10	12	1.0 M KOH	68.00	5[5]
Sn-CoS_2	10	32	1.0 M KOH	97.73	6[6]

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