## Electronic Supplementary Information (ESI) for:

# Hollow carbon shells enhanced by confined ruthenium for costefficient and superior catalysts in alkaline hydrogen evolution reaction

Zhikun Peng,<sup>a</sup> Haiyang Wang,<sup>a</sup> Leilei Zhou,<sup>a</sup> Yibo Wang,<sup>a</sup> Jie Gao,<sup>b</sup> Guoji Liu,<sup>a</sup> Simon A. T. Redfern,<sup>c</sup> Xiaolei Feng,<sup>c</sup> Siyu Lu,<sup>\*,a</sup> Baojun Li,<sup>\*,a</sup> and Zhongyi Liu<sup>\*,a</sup>

<sup>a</sup> College of Chemistry and Molecular Engineering, School of Chemical Engineering and Energy, Henan Key Laboratory of Green Catalytic Hydrogenation, Zhengzhou University, 100 Science Road, Zhengzhou 450001, P.R. China

<sup>b</sup> Integrated Analytical Laboratories, 273 Franklin Road #10, Randolph, New Jersey 07869, United States

<sup>c</sup> Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, United Kingdom

\* Corresponding authors. E-mail: sylu2013@zzu.edu.cn, lbjfcl@zzu.edu.cn, and liuzhongyi@zzu.edu.cn.

## Synthesis of SiO<sub>2</sub> nanospheres (NSs)

Typically, 9 mL of ammonium hydroxide (28–30 wt%) was dispersed in 16 mL of ethanol (99.5%) and 25 mL of deionized water. An aqueous mixture of 4.5 mL of tetraethyl orthosilicate (TEOS, 99.0%) with 45.5 mL of ethanol (99.5%) was added to the above solution. Then the resulting mixture was stirred for 20 hat room temperature. The suspended white colloidal particles were centrifuged and washed with water (2 times), acetone (1 time), and ethanol (1 time), respectively.

## Synthesis of modified-SiO<sub>2</sub> templates

Specifically, 0.6 g of SiO<sub>2</sub> NSs were dispersed in 40 mL of anhydrous toluene by sonication for 10 min, then 3 mL of APTES was added and continued sonication for 30 min. The mixture was refluxed for 20 h to obtain APTES modified SiO<sub>2</sub> NSs. The products were centrifuged and washed with toluene for 1 time and ethanol for 3 times, respectively, and dried in vacuum drying oven at 60 °C for 3 h.



**Fig. S1** TEM images of (a, b) SiO<sub>2</sub>@RF, (c, d) SiO<sub>2</sub>@C (calcinated products of a and b), (e-h) HCSs (chemical corrosion results of c and d).



**Fig. S2** (a, b) SEM images of samples after hydrothermal treatment with unmodified  $SiO_2$ , (c, d)  $SiO_2@RuO_2$  NPs coated with a thinner layer of RF, (e, f) calcinated products of c and d in Ar atmosphere.



Fig. S3 XRD patterns of the corresponding precursors.



**Fig. S4** (a, b) HRTEM images of HCRNs and (c) its corresponding particle size distribution histograms with Gaussian analysis fittings of Ru NPs.



**Fig. S5** XPS survey spectra of (a) the carbon-based hollow architectures, (b) the samples before and after before and after HF etching.



**Fig. S6** (a)TG/DSC curve s of RF up to 850 °C in Ar atmosphere, (b) XRD patterns of Ru/C mixtures calcined at 850 °C in Ar atmosphere. The mixtures were prepared according to the mass ratio calculated based on the results of TG and ICP analysis, RuN/C (4.8 wt% Ru), RuL/C (23.5 wt% Ru).

Sample	$S_{\rm BET}$ (m <sup>2</sup> g <sup>-1</sup> )	$S_{\text{Micropore}}(\text{m}^2 \text{g}^{-1})$	$V_{\text{Pore}}(\text{cm}^3\text{g}^{-1})$	$V_{ m Micropore} ( m cm^3 g^{-1})$	D <sub>Pore</sub> (nm)	Ru (wt%) <sup>a</sup>	Dispersion (%) <sup>b</sup>
HCSs	1092	369 (33%)	0.99	0.16 (16%)	3.6	0	0
HCRNs	961	288 (30%)	0.78	0.13 (17%)	3.3	4.8	18.9
HCRLs	316	73 (23%)	0.23	0.03 (14%)	2.9	23.5	19.9
Pt/C	n.m. <sup>c</sup>	n.m.	n.m.	n.m.	n.m.	n.m.	31.6

Table S1. The texture property of the samples.

<sup>a</sup> Determined by ICP results; <sup>b</sup> Determined by H<sub>2</sub> chemisorption; <sup>c</sup> n.m. means not measured.

		Loading			Tafal plats	
Catalyst	Electrode	amount	Electrolyte	η <sub>10</sub> (mV)	(mV doct)	Ref.
		(mg cm <sup>-2</sup> )			(mv dec -)	
Ni <sub>43</sub> Ru <sub>57</sub>	SCE	0.28	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	41	~31	[1]
Hollow Cu <sub>2-x</sub> S@Ru NPs	Ag/AgCl	0.230	1 М КОН	82	48	[2]
Ru/C <sub>3</sub> N <sub>4</sub> /C	Ag/AgCl	0.204	0.1 M KOH	79	~65	[3]
CoP NAs/CC	SCE	N/A	1 M KOH	80	60	[4]
CoWZnRu	Ag/AgCl	N/A	1 M KOH	197	114	[5]
Cu/Ni/NiZn-Ru	Ag/AgCl	N/A	1 M KOH	~60	119	[6]
RuO <sub>2</sub> /Co <sub>3</sub> O <sub>4</sub>	Ag/AgCl	0.285	1 M KOH	89	91	[7]
[PW <sub>11</sub> CoO <sub>39</sub> ] <sup>5-</sup> @Ru- rGO	Ag/AgCl	N/A	2 M KOH	509	59.76	[8]
Ru–MoO <sub>2</sub> nanocomposites	Ag/AgCl	0.285	1 M KOH	29	31	[9]
Ru powder	SCE	0.285	1 M KOH	84	79	[9]
Ru/CP	N/A	N/A	1 M KOH	35	50	[10]
5.0% F-Ru@PNC-800	Ag/AgCl	0.159	0.1 M KOH	30	28.5	[11]
PtNi/CNFs	SCE	N/A	1 M KOH	82	34	[12]
Pt/CNFs	SCE	N/A	1 M KOH	118	44	[12]
Pt-Co(OH) <sub>2</sub> /CC	SCE	1.95	1 M KOH	32	70	[13]
Co NPs@C	Hg/HgO	0.33	1 M KOH	153	106	[14]
Mo <sub>2</sub> C/CNT	RHE	0.420	1 M KOH	93	58	[15]
Pd/Cu-Pt	Ag/AgCl	0.04	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	22.8	25	[16]
$Mo_1N_1C_2$	$Hg/Hg_2Cl_2$	0.408	0.1 M KOH	132	90	[17]
CoNi@NC	Ag/AgCl	1.6	$0.1 \ M \ H_2 SO_4$	142	104	[18]
Pt <sub>3</sub> Ni <sub>2</sub> NWs-S/C	SCE	0.30	1 M KOH	50	NA	[19]
Ru/NC	Hg/HgO	0.013	1 M KOH	21	~31	[20]
HCRNs	SCE	0.418	1 M KOH	32	50	This work
HCRLs	SCE	0.418	1 M KOH	18	47	This work

 Table S2. The data of metal-based electrocatalysts for HER reported recently.

## Preparation of RuN/C and RuL/C mixuters

RuN/C and RuL/C mixtures were prepared according to the TG and ICP results, the preparation ratio of RF/RuO<sub>2</sub> were calculated (RuO<sub>2</sub> were obtained from hydrothermal of RuCl<sub>3</sub>, RF were prepared according to the preparation part) according to the following equations:

$$\frac{m(RuO2) * 75.9\%}{m(RuO2) * 75.9\% + m(RF) * 77.9\%} = 4.8\%$$
(1)  
$$\frac{m(RuO2) * 75.9\% + m(RF) * 77.9\%}{m(RuO2) * 75.9\% + m(RF) * 77.9\%} = 23.5\%$$
(2)



**Fig. S7** (a) HER polarization curves of HCRLs with different Ru loadings; (b) HER polarization curves and (c) durability test of the samples at higher overpotential.

Fig. S7a shows that the catalytic performance of HCRLs has not been greatly improved by increasing the Ru loading from 23.5 to 28.5 wt% ( $\eta_{10}$  from 18 to 16 mV). When decrease the Ru loading to 19.1 wt%, the  $\eta_{10}$  increased to 22 mV. Considering the Ru loading, cost, and specific activity (TOF), we think the lower Ru loading around 23.5 wt% is more effective and commercial for HER.



**Fig. S8** (a-d) CV curves measured within the range of 0.175 to 0.275 V vs. RHE with scan rate from 15 to 40 mV s<sup>-1</sup>, (e) current density ( $\Delta$ j at 0.271 V vs. RHE) versus scan rates plots for the samples; (f) normalization of special activity taking into account of their electrochemical active surface areas (ECSA) at an overpotential of 100 mV.

Catalyst	$C_{dl} (mF cm^{-2})$	$C_{DL}$ (mF)	ECSA (cm <sup>2</sup> )	$J_{\eta=100\;mV}\left(mA\right)$	RF
HCRNs750	74.8	14.7	368	6.2	1878
HCRNs850	73.7	14.4	360	6.5	1837
HCRLs750	46.5	9.1	228	7.1	1163
HCRLs850	42.8	8.4	210	7.9	1071

 $C_{DL} = C_{dl} * 0.196 \text{ cm}^2$ ; ECSA =  $C_{DL}/C_s$ ;  $C_s = 0.04 \text{ mF cm}^2$ ,  $J_{\eta}=100 \text{ mV}$  represents the current obtained at overpotential of 100 mV; RF = ECSA/0.196 cm<sup>2</sup>.<sup>[21]</sup>

The ECSA of samples was tentatively evaluated using a simple cyclic voltammetry (CV) method.<sup>[22, 23]</sup> The relative surface area of the samples are estimated because the double layer capacitance (C<sub>dl</sub>) is considered to be linearly proportional to the ECSA with similar composition and structure.<sup>[2, 21, 24]</sup> Fig. S8a-d show that the CV curves are tested at a potential between 0.175 to 0.275 V (vs. RHE) and the current densities are plotted according to the different scan rates (Fig. S8e). The specific capacitance of samples is calculated by plotting the  $\Delta j$  at E = 0.271 V (vs. RHE) against the scan rates. As illustrated in Fig. 7e, the C<sub>dl</sub> of HCRNs750, HCRNs850, HCRLs750, and HCRNs850 are 74.8, 73.7, 46.5, and 42.8 mF cm<sup>-2</sup>, respectively. The higher capacitance for HCRNs is probably because the specific surface area of HCRNs (961 m<sup>2</sup> g<sup>-1</sup>) is much higher than that of HCRLs (316 m<sup>2</sup> g<sup>-1</sup>).To better understand the intrinsic activity of those catalysts, the current densities for the HER polarization curves is normalized according to the ECSA at a overpotential of 100 mV. As shown in Fig. S8f, these catalysts also follow the same trend of the catalytic performance.

### Active sites measurements:

The dispersion of metal-based catalysts measured by chemisorption has proven to be an ideal method for qualifying their corresponding active sites.<sup>[25, 26]</sup> In this approach, the number of active sites (n) can be qualified based on the dispersion (Table S1) with the following equation:

$$n = \frac{m_{cat} \times W_{cat} \times dispersion}{M_{metal}}$$
(3)

Here,  $m_{cat}$ ,  $W_{metal}$  and  $M_{metal}$  are the catalyst loading on the electrode, the metal loading on the catalyst, and molar mass of metal, respectively. The dispersion of Ru was determined by  $H_2$  chemisorption.

## **Calculation of the turnover frequency (TOF)**

The TOF (s<sup>-1</sup>) can be calculated with the following equation:<sup>[27]</sup>

$$TOF = \frac{I}{2Fn} \tag{4}$$

where I is the current (A) during linear sweep measurement, F is the Faraday constant (C mol<sup>-1</sup>), n is the number of active sites (mol). The factor 1/2 is based on the consideration that two electrons are required to form one hydrogen molecule.



Fig. S9 (a) HER polarization curves, and (b) Tafel plots of the samples in 0.5 M H<sub>2</sub>SO<sub>4</sub>.



**Fig. S10** TEM images of (a, b) HCRLs and (c and d) HCRNs after 5000 cyclic voltammetry (CV) cycles from -0.08 to 0.12 V (vs. RHE).



Fig. S11 XPS spectra of the samples before and after 5000 CV cycles (from -0.08 to 0.12 V vs. RHE).



Fig. S12 Nyquist curves for the HCSs in 1 M KOH solution. Inserts are the related equivalent circuits.

Sample	$\mathrm{R}_{\mathrm{s}}\left(\Omega ight)^{\mathrm{a}}$	CPE2-T	CPE2-P	$R_{ct} (\Omega)^b$
HCSs	7.8	0.001	0.710	68.4
HCRNs750	6.3	0.008	0.932	15.0
HCRNs850	6.3	0.010	0.911	14.0
HCRLs750	7.1	0.010	0.884	10.6
HCRLs850	6.5	0.007	0.774	4.8

Table S4. The fitting results of electrochemical element parameters for various samples.<sup>[1]</sup>

<sup>a</sup> represents the resistance of the electrolyte and intrinsic resistance of the active materials coated on the electrode; <sup>b</sup> stands for the electron or charge transfer resistance, which determines the interfacial electron transfer kinetics of each catalyst.

## **Computational details**

All spin-polarized DFT calculations are performed with PBE exchange correlation<sup>[28]</sup> in the Gaussian and plane waves (GPW) formalism<sup>[29]</sup> as implemented in the CP2K code<sup>[30]</sup>. DZVP

Molopt local basis sets in combination with Geodcker-Teter-Hutter (GTH) pseudopotentials were used, and the plane wave density cutoff was set to be 400 Ry<sup>[31, 32]</sup>. For the H, C, Ru, and Pt, 1, 4, 16, and 18 electrons were taken into account, respectively. Calculations were performed in a periodic cubic simulation box of  $32 \times 32 \times 32$  Å<sup>3</sup>, large enough to neglect the interaction between the nanoclusters in periodic images. The free energy calculation methods is similar to the literature.<sup>[23]</sup>The reaction paths for H<sub>2</sub>O dissociation were calculated by using the climbing image nudged elastic band (CI-NEB) method, and the convergence criterion of maximum force on the band was fixed at  $2 \times 10^{-3}$  Ha per Bohr.

In these calculations, a graphitic cage containing 500 carbon atoms ( $C_{500}$ ) was used as the ideal hollow carbon model (Fig. S13a). The hollow Ru layer model was simulated by using two shells of Ru clusters containing 134 Ru atoms (Ru<sub>134</sub>), moreover, the layer model has the symmetry with an icosahedron (symmetry of Ih, as shown in Fig. S13c). For Ru NPs model, since the literature reported that the Ru<sub>8</sub> clusters have very high stability,<sup>[33]</sup> we have put 4 such Ru<sub>8</sub> clusters (Fig. S13b) in one graphitic cage. Meanwhile, the defects in different models were also considered because of a large amount of defects existed in the carbon shells for HCRNs and HCRLs (Fig. 3b). Specifically, 12 uniformly distributed holes are introduced to HCRLs model and 4 holes are introduced to the HCRNs model, respectively.



**Fig. S13** (a) Graphitic carbon cage model of  $C_{500}$ , (b) cluster model of  $Ru_8$  for Ru NPs, (c) hollow Ru layer model of  $Ru_{134}$ , the dark and light yellow ball refers to the outer side and inside Ru shell.



**Fig. S14** Current-time curve of samples before and after the addition of SCN<sup>-</sup> ions. The measurements are in 1 M KOH solution.



Fig. S15 The initial state (H<sub>2</sub>O), the transition state (TS) and the final state (H + OH) for (a)  $C_{500}Ru_{134}$ , (b)  $C_{500}Ru_{8}$ , (c)  $Ru_{147}$ , (d)  $Pt_{147}$  cluster model.



Fig. S16 H\* adsorbed on (a) bridge site of  $Pt_{147}$  cluster model and (b) hollow site of  $Ru_{147}$  cluster model.

Model	C <sub>500</sub>	C496Ru32	C488Ru134	C500Ru8	C500Ru134	Ru <sub>147</sub>	Pt <sub>147</sub>
$\Delta G_{\mathrm{H}^{*}}\left(\mathrm{eV}\right)$	1.32	-0.31	-0.13	0.78	1.23	-0.18	-0.14
Energy barrier (eV)	2.96	0.04	1.29	2.70	2.83	0.70	0.84

**Table S5.** Calculated free energies  $\Delta G_{H^*}$  of various models.

**Table S6.** Total number of transferred electrons from Ru metal to graphene based on Bader charge analysis.

Model	$C_{496}Ru_{32}$	$C_{488}Ru_{134}$	$C_{500}Ru_{32}$	$C_{500}Ru_{134}$
Transferredelectrons (e <sup>-</sup> )	0.48	1.26	0.03	0.26

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