# Electronic Supplementary Information

# Ultrafine Ru Nanoclusters over CB[6]/rGO for Efficient Hydrogen Evolution in Broad pH Range

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# Experimental:

**Chemicals**: Ruthenium Acetylacetonate (Ru(acac)$_3$), urea and graphite powder were purchased from Alfa Aesar. Commercial 20 wt% Pt/C was purchased from Premetek. Sulfuric Acid, potassium permanganate, potassium persulfate, phosphorus(V) oxide, hydrogen peroxide 30% aqueous solution, concentrated hydrochloric acid, glyoxal, formic acid, ammonium hydroxide solution, glycerol and isopropanol were available from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All chemicals were used without further purification. All solutions were prepared with ultrapure water with resistivity of 18.2 MΩ·cm.

**Material synthesis:** Cucurbit[6]urils was synthesized according to the literature.[1] GO was synthesized by chemical oxidation exfoliation of graphite powers using a modified Hummers method.[2] Ru-CB[6]/rGO were prepared by a simple hydrothermal method. GO suspension (50 mg GO) and 25 mg CB[6] were mixed in 40 mL deionized water under a ultrasonication of 4 h. After dissolving the 40 mg Ru(acac)$_3$ in 10 mL isopropanol, we added it to the mixed GO and CB [6] solution and ultrasonicate the mixture for another 4 h. After the adjustment of the pH of the mixture by ammonium hydroxide solution to 3, the solution was transferred into a 100 mL Teflon-lined stainless-steel autoclave and maintained at 150 °C for 18 hours. The autoclave was cooled down naturally after the reaction. The products were collected via centrifugation, washing process with deionized water and ethanol and vacuum drying. The loading content of Ru in Ru-CB[6]/rGO is 5.58% measured by inductively coupled plasma–atomic emission spectrometry (ICP-AES). Ru-rGO and Ru-CB[6] were prepared by similar procedures.

**Characterization:** Scanning Electron Microscope (SEM) images were obtained using a JSM6700-F FESEM. Transmission Electron Microscope (TEM) analyses were carried out using a Tecnai F20 FETEM operated at 200 kV. The X-ray powder diffraction (XRD) measurements were carried out using a Rigaku Dmax 2500 diffractometer equipped with a Cu $K\alpha$ radiation source over the 2θ range of 5-85° with a scan speed of 1°/min. The X-ray photoelectron spectroscopy (XPS) patterns were carried out on ESCALAB 250Xi. Inductively coupled plasma−atomic emission spectrometry (ICP-AES) measurements were carried out on Ultima2. Fourier transform infrared (FT-IR) spectroscopy was performed by Lambda900. Raman measurements were carried out using a Labram HR800 Evolution.

**Electrochemical measurement:** The electrochemical measurements were carried out by a standard three electrode glass cell connected to an electrochemical workstation (Zahner, Germany). The commercial glass carbon electrode (GCE) with the diameter of 5 mm was used as the working electrode. The current densities were normalized by the geometric surface area of the GCE. To prepare the working electrode, different amount of catalysts was dispersed in 2 ml solvent (1.94 ml isopropyl alcohol and 0.06 ml Nafion). A GCE was cleaned by sonication in distilled water for 3 min after pre-polished and the catalyst ink was pipetted onto electrode surface. The catalyst loading was 20 μg/cm$^2$ for metal Ru. The working electrodes were obtained after the solvent was dried naturally. A graphite rod and an Ag/AgCl (saturated KCl) electrode were used as the counter electrode and reference electrode, respectively. The 0.5 M $H_2SO_4$, 1 M KOH and 1 M PBS aqueous solution were used as electrolytes. After dozens of CV scans in the range of 0.2~1.2 V vs. RHE, the polarization data were collected using linear sweep at a scan rate of 10 mV/s. All polarization curves were corrected for ohmic-drop compensation with 90% ohmic resistance obtained by the workstation.

The exchange current density ($j_0$) was obtained from the Tafel equation $\eta = a + b\log j$, where $\eta$ is the overpotential, a is the Tafel constant, b is the Tafel slope, j is the current density and $j_0$ is obtained when $\eta$ is assumed to be zero. The $C_{dl}$ of the test electrocatalysts were obtained from double layer charging curves in a non-faradic potential range of 0.80 V to 1.0 V vs. RHE, which was recorded by CV at various scan rates of 2, 4, 6, 8, and 10 mV/s. The halves of the difference between the positive and negative current densities at 1/2 of the scanning range were further plotted vs. scan rates, where the fitted slopes could be correlated to $C_{dl}$. The Nyquist plots were performed with frequencies ranging from 100 kHz to 100 mHz at an overpotential of 100 mV. For the durability tests, the as prepared electrocatalysts and Pt/C were measured at the applied current density of -10 mA/cm$^2$ in 0.5 M $H_2SO_4$.

The potentials reported in this study were all *i*R-corrected and converted to the RHE using the equation $E_{RHE} = E_{Ag/AgCl} + 0.197\ V + 0.059 \times pH$.

## Supplementary Figure

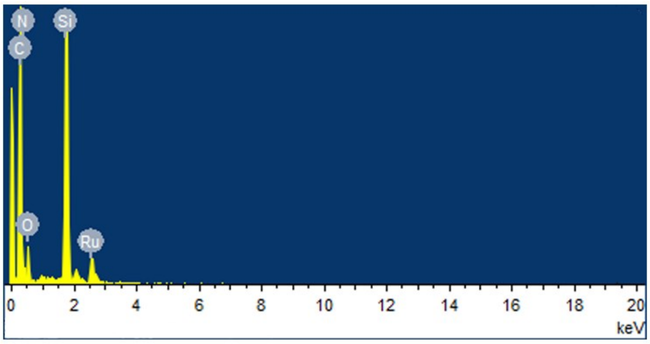


**Fig. S1** EDX spectrum of Ru-CB[6]/rGO showing the presence of Ru signal and N signal (from CB[6]).

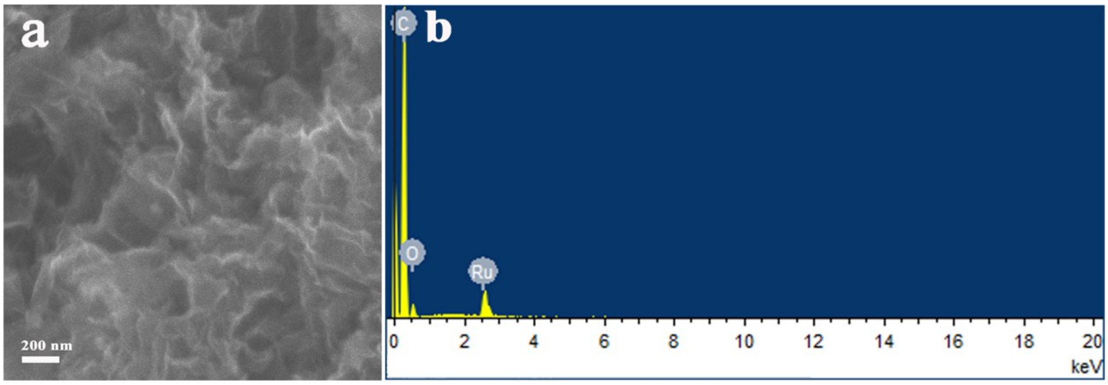


**Fig. S2** (a) SEM image and (b) EDX spectrum of Ru-rGO. Note the missing siginal from N compared to the Ru-CB[6]/rGO.

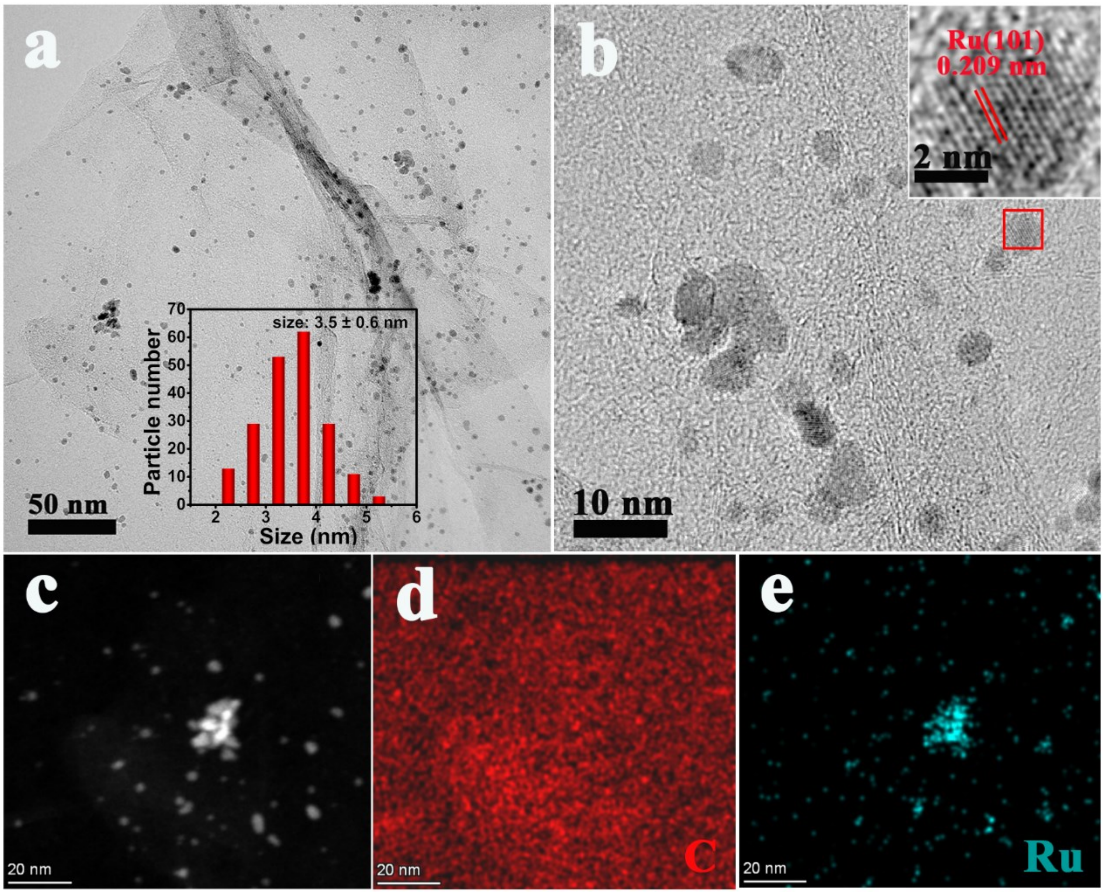


**Fig. S3** (a) TEM, (b) HRTEM, (c) STEM images, (e) EDX elemental mapping of C and Ru of Ru-rGO.

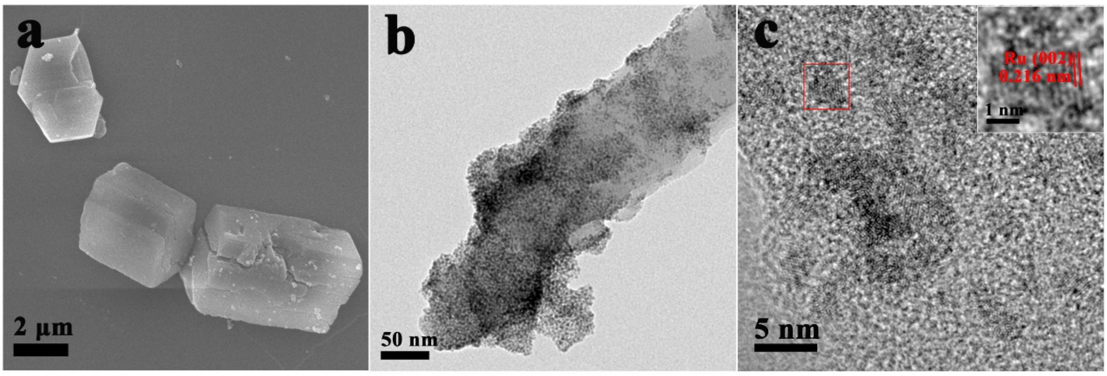


**Fig S4.** (a)SEM, (b) TEM, and (c) HRTEM images of Ru-CB[6].

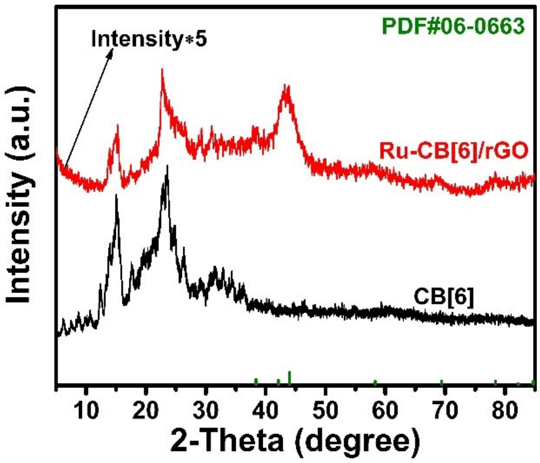


**Fig. S5** XRD patterns of Ru-CB[6]/rGO and CB[6].

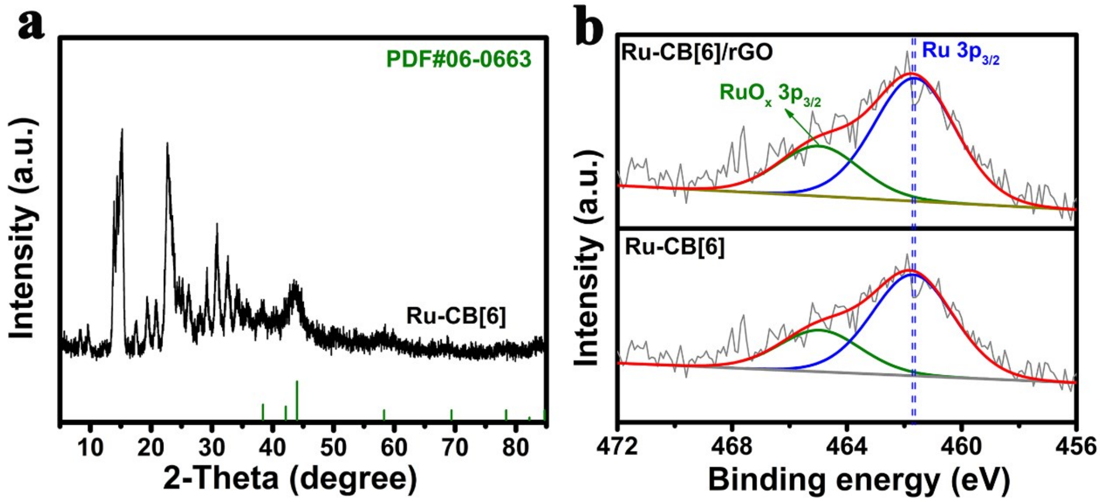


**Fig. S6** (a) XRD pattern of Ru-CB[6], and (b) XPS patterns of Ru-CB[6] of Ru-CB[6]/rGO.

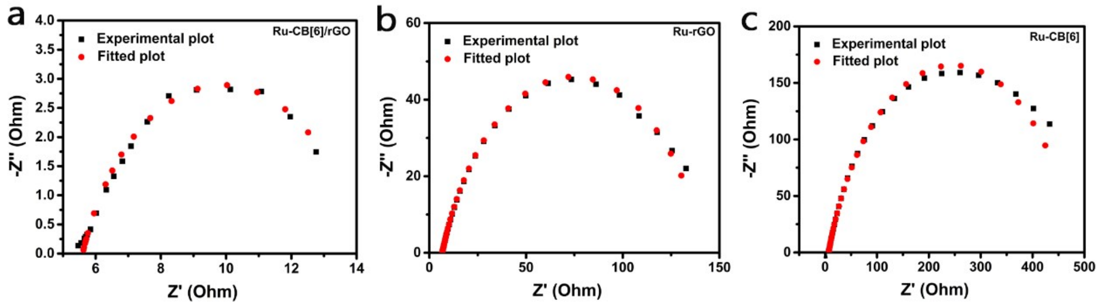


**Fig. S7** EIS Nyquist plots of Ru-CB[6]/rGO, Ru- rGO and Ru-CB[6]. The black and red dots are experimental data and fitted data, respectively.

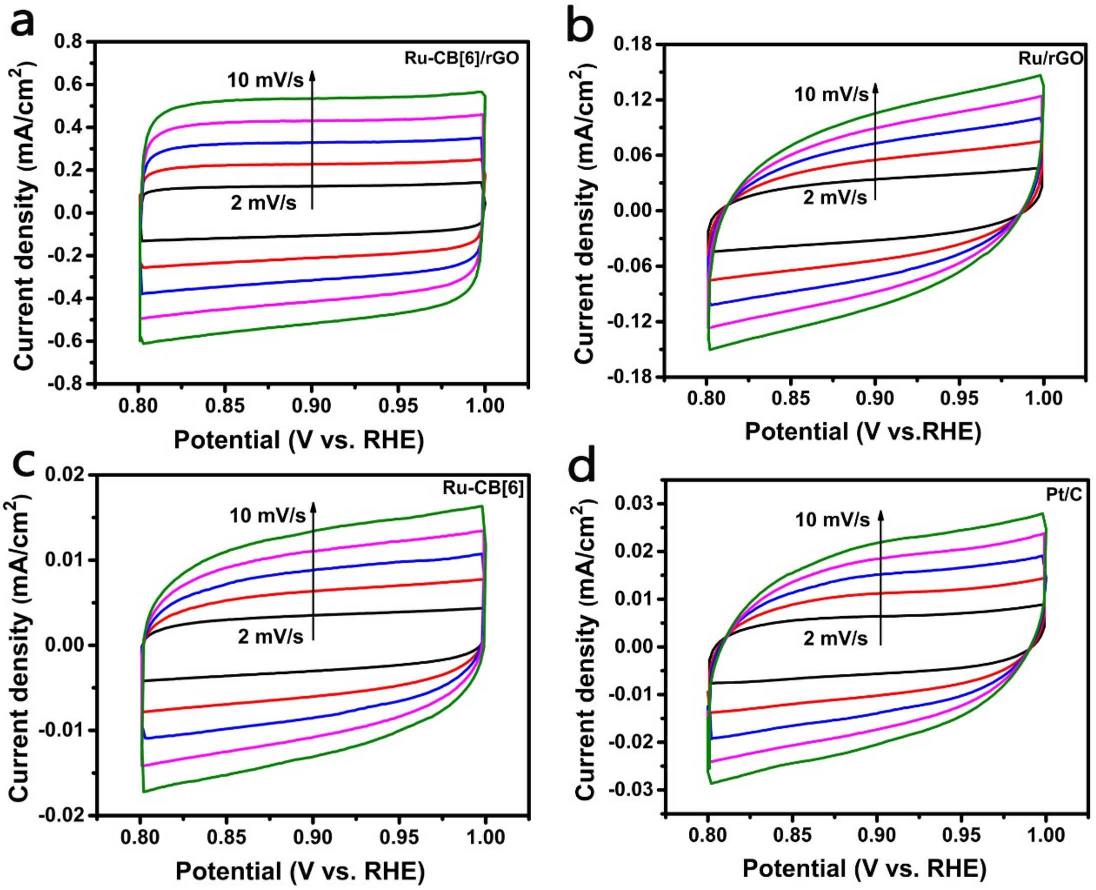


**Fig. S8** CV curves for (a) Ru-CB[6]/rGO, (b) Ru- rGO, (c) Ru-CB[6] and (d) Pt/C in the region of 0.8 ~ 1.0 V vs. RHE at various scan rates.

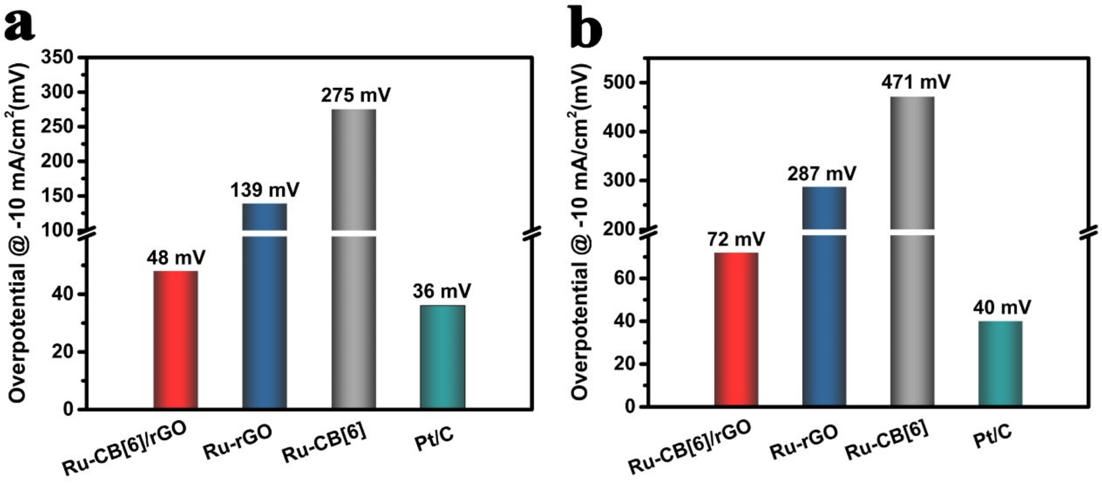


**Fig. S9** Histograms of the required overpotential at -10 mA/cm$^2$ in (a) 1 M KOH, (b) 1M PBS.

**Table S1.** Comparison of HER performance of Ru-CB[6]/rGO with other electrocatalysts in acidic electrolytes[a].

| Catalyst | Loading (μg/cm$^2$) | Onset potential[b] (mV) | η @ -10 mA/cm$^2$ (mV) | Tafel slope (mV/dec) | Ref. |
|---|---|---|---|---|---|
| **Ru-CB[6]/rGO** | **20 (Ru)** | **-10** | **44** | **58.6** | **This work** |
| Ru-NGC | 23.6 (Ru) | -9.5 | 25 | 40 | *Chem. Commun.*, 2019, **55**, 965 |
| $Ru_2P$@NPC | 233 (Ru) | - | 38 | 38 | *Angew. Chem. Int. Ed.*, 2017, **56**, 11559-11564 |
| Pt/$WO_3$@CFC | 6.75 | - | 42 | 61 | *J. Mater. Chem. A*, 2019, **7**, 6285 |
| Ru-NC | 17.2 (Ru) | - | 61 | 59 | *Chem. Comm.*, 2018, **54**, 13076-13079 |
| $MoS_2$–Au | 220 | -17 | 66 | 40 | *J. Mater. Chem. A*, 2017, **5**, 4122 |
| Ru/$C_3N_4$/C | 41 (Ru) | - | 70 | - | *J. Am. Chem. Soc.*, 2016, **138**, 16174 |
| NFP/C-3 | 400 | -22 | 72 | 62 | *Sci. Adv.*, 2019, **5**, eaav6009 |
| CoP/NPC/TF | 1.5*103 | - | 91 | 54 | *Adv. Energy Mater.*, 2019, **9**, 1803970 |
| $NiCo_2P_x$/CF | - | -11 | 104 | 60 | *Adv. Mater.* 2017, **29**, 1605502 |
| $Ni_5P_4$-$Ni_2P$ NS | 68.2*10$^3$ | -54 | 120 | 79 | *Angew. Chem.* 2015, **127**, 8306 |
| $C_3N_4$-Ru-F | 153 | - | 140 | 57 | *J. Mater. Chem. A*, 2017,**5**,18261-18269 |
| Ru/$Co_xP$@NC | 570 | -41 | 165 | 74 | *ACS Sustainable Chem. Eng.*, 2019, **7**, 9737 |
| EA-2H/1T/RGO | 500 | -103 | 186 | 49 | *Small*, 2019, **15**, e1804903 |
| MS-CS NTs | 570 | -148 | 206 | 45 | *J. Mater. Chem. A*, 2018, **6**, 7842 |

(Ru) means the loading amount of Ru.

a. The acidic electrolyte is 0.5 M $H_2SO_4$.

b. We defined the potential at a HER current density of 1 mA/cm$^2$ as the onset potential.

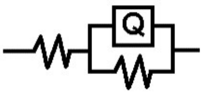
| The equivalent circuit used to fit the EIS data | Sample name | $R_s$ (Ω) | $Q$-Yo (F) | $Q$-n (F) | $R_{ct}$ (Ω) |
|---|---|---|---|---|---|
|  | Ru-CB[6]/rGO | 5.60 | $2.19*10^{-2}$ | 0.80 | 8.58 |
| | Ru-rGO | 6.69 | $5.04*10^{-4}$ | 0.76 | 136 |
| | Ru-CB[6] | 6.83 | $5.87*10^{-5}$ | 0.80 | 481 |

**Table S2**. Detail information of EIS fitting data.

$R_s$ stands the resistance of the electrolyte and intrinsic resistance of the active materials coated on the electrode.

$R_{ct}$ represents for the electron or charge transfer resistance, which determines the interfacial electron.

**Table S3.** Comparison of HER performance of Ru-CB[6]/rGO with other electrocatalysts in alkaline electrolytes.

| Catalyst | Loading ($\mu g/cm^2$) | Onset potential (mV) | η @ -10 $mA/cm^2$ (mV) | Tafel slope (mV/dec) | Ref. |
|---|---|---|---|---|---|
| **Ru-CB[6]/rGO** | **20 (Ru)** | **-12** | **48** | **46.4** | **This work** |
| Mo-NiO/Ni | 500 | - | 50 | 86 | *ACS Energy Lett.* 2019, **4**, 3002-3010 |
| $Ru/C_3N_4/C$[a] | 41 (Ru) | - | 79 | - | *J. Am. Chem. Soc.,* 2016, **138**, 16174 |
| Ru-NC | 17.2 (Ru) | - | 81 | 88 | *Chem. Comm.,* 2018, **54**, 13076-13079 |
| $Ru/Y(OH)_3$[a] | 283 | 0 | 100 | 66 | *Chem. Commun.,* 2018, **54**, 12202 |
| $R-TiO_2:Ru$[a] | 12.5 (Ru) | -82 | 150 | 95 | *J. Am. Chem. Soc.* 2018, **140**, 5719-5727 |
| $Ni/Mo_2C$-PC | 500 | -60 | 179 | 101 | *Chemical science,* 2017, **8**, 968 |
| CoP@BCN | 400 | - | 215 | 52 | *Adv. Energy Mater.* 2017, **7**, 1601671 |
| $CoO_x$@CN | 120 | -85 | 232 | 115 | *J. Am. Chem. Soc.* 2015, **137**, 2688 |
| Co-N-$MoO_2$ | 204 | -69 | 258 | 126.8 | *Nano Energy,* 2017, **41**, 772-779 |
| NFPGNS | $2.55*10^3$ | -120 | 330 | 109 | *J. Mater. Chem. A,* 2017,**5**, 7784-7790 |

(Ru) means the loading amount of Ru.

a. The alkaline electrolyte is 0.1 M KOH, and other's is 1.0 M KOH

**Table S4.** Comparison of HER performance of Ru-CB[6]/rGO with other electrocatalysts in neutral electrolytes.

| Catalyst | Loading (μg/cm$^2$) | Onset potential (mV) | η @ -10 mA/cm$^2$ (mV) | Tafel slope (mV/dec) | Ref. |
|---|---|---|---|---|---|
| **Ru-CB[6]/rGO** | **20 (Ru)** | **-16** | **72** | **83.2** | **This work** |
| Ru/MeOH/THF[a] | 92 (Ru) | - | 83 | 80 | *Chem. Comm.*, 2017, **53**, 11713-11716 |
| s-RuS$_2$/S-rGO | 112 (Ru) | -13 | 93 | 41 | *ACS Appl. Mater. Interfaces,* 2018, **10**, 34098 |
| MoP/CNT | 500 | - | 102 | 115 | *Adv. Funct. Mater.* 2018, **28**, 1706523 |
| Ru-CN | 7.85 (Ru) | -9 | 100 | - | *Energy Environ. Sci.,* 2018, **11**, 800-806 |
| L-RP/C | 2*10$^3$ | -8 | 95 | 54 | *ChemSusChem*, 2018, **11**, 743-752 |
| CoP@BCN | 410 | - | 122 | 59 | *Adv. Energy Mater.* 2017, **7**, 1601671 |
| MoP NA/CC | 2.5*10$^3$ | -90 | 187 | 94 | *Appl. Catal. B-Environ.,* 2016, **196**, 193-198 |
| MoP700 | 250 | -75 | 196 | 79 | *ACS Catal.* 2019, **9**, 8712-8718 |

(Ru) means the loading amount of Ru.

a. The neutral electrolyte is 0.1 M PBS, and other's is 1.0 M PBS.

## Reference

1. D. Bardelang, K. A. Udachin, D. M. Leek and J. A. Ripmeester, *CrystEngComm*, 2007, **9**, 973-975.
2. D. Meng, S. Jiang, Y. Zeng, Y. Li, S. Yan, J. Geng and Y. Huang, *J. Mater. Chem.*, 2012, **22**, 21583-21591.