

Electronic Supplementary Material (ESI) for ChemComm.  
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## Electronic Supplementary Information

### **Ultrafine ruthenium nanocrystal with extremely high activity for hydrogen evolution reaction in both acidic and alkaline medium**

Yutong Li, Fuqiang Chu,\* Yang Liu, Yong Kong, Yongxin Tao, Yongxin Li, and Yong Qin\*

Jiangsu Key laboratory of Advanced Catalytic Materials and Technology, School of Petrochemical Engineering, Changzhou University, Changzhou, Jiangsu, China

\*Corresponding authors:

E-mail: cfq@cczu.edu.cn

E-mail: qinyong@cczu.edu.cn

## Experimental Section

### *Preparation of graphene*

GO was prepared from natural graphite flakes using an improved Hummers' method. Typically, graphite flakes (1.0 g) and  $\text{KMnO}_4$  (6.0 g) were added into a mixture of 120 mL concentrated  $\text{H}_2\text{SO}_4$  and 13.3 mL  $\text{H}_3\text{PO}_4$ , producing a slight exotherm to  $35^\circ\text{C}$ . The mixture was then heated to  $50^\circ\text{C}$  and kept there under stirring for 12 h. The reaction was cooled to room temperature and poured into ice water (150 mL) with 30%  $\text{H}_2\text{O}_2$  (10 mL). The mixture was sifted through a polyester fiber. The filtrate was centrifuged (4000 rpm for 4 h), and the supernatant was decanted away. The remaining solid material was then washed in succession with 200 mL of water, 200 mL of 30% HCl, and 200 mL of ethanol. The eventual solution was centrifuged (4000 rpm for 4 h) and the supernatant was decanted away. The solid was vacuum-dried overnight at room temperature, resulting 1.8 g GO. 150 mg GO was dispersed in 15 mL water to form a concentrated GO suspension, which was mixed with 1 mL formaldehyde solution (37% wt) and 0.35 g melamine. The mixture was then transferred into an autoclave and hydrothermally treated at  $180^\circ\text{C}$  for 12 h. The obtained composite hydrogel was dried at  $80^\circ\text{C}$  for 24 h in an oven. The dry aerogel was subsequently calcined at  $750^\circ\text{C}$  for 5 h in  $\text{N}_2$  atmosphere to obtain the final graphene product.

### *Preparation of PtNC*

1.25 mL  $\text{H}_2\text{PtCl}_6$  solution (4 mg  $\text{mL}^{-1}$ ) was added into 20 mL ethylene glycol to form a homogeneous mixture, and then 20 mg graphene was added into the above mixture and dispersed. The dispersion was kept for 12 h at  $140^\circ\text{C}$ . After steps of rinsing with ethanol and drying in air, the resultant PtNC-graphene was obtained.

### *Preparation of RuNC-2*

3 mg tris(2, 2'-bipyridine) ruthenium dichloride and 30 mg cyanuric acid were first dissolved in 0.5 ml DMF. 20mg graphene was then dispersed in the above solution. The dispersion was transferred into an open Teflon vessel and let the solvent volatilize slowly at 70 °C. The obtained solid was annealed at 700 °C under for 3 hours under Ar atmosphere.

### *Preparation of RuNC-5*

20 mg graphene was dispersed in 10 mL phosphate buffer solution (pH 8.5) followed by addition of 2.6 mL  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  water solution ( $4 \text{ mg mL}^{-1}$ ), 40 mg dopamine hydrochloride, and 300 mg cetyl trimethyl ammonium bromide (CTAB). The mixture was treated at 140 °C for 6 hours. Afterwards, it was centrifuged at 3000 rpm. The obtained solid was washed by water and ethanol, subsequently dried and annealed at various temperatures for 3 hours under Ar atmosphere.

### *Electrochemical measurements*

The electrochemical measurements were conducted on an electrochemical cell with conventional three-electrode system. 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. The graphite rod electrode and the saturated calomel electrode (SCE) served as the counter electrode and the reference electrode, respectively. The working electrodes were fabricated by the following procedure: the suspensions (in water,  $6 \text{ mg mL}^{-1}$ , 10  $\mu\text{L}$ ) of the as-prepared materials were drop coated onto a glassy carbon disk with the diameter of 3 mm (loading  $\sim 0.86 \text{ mg cm}^{-2}$ ) and dried at room temperature in air for 6 h. Then 5  $\mu\text{L}$  Nafion solution (0.02 wt.%) were cast on the electrode surface to adhere the materials on

electrodes. The potential versus saturated calomel electrode were converted into the potential versus reversible hydrogen electrode (RHE) according  $E_{vs\ RHE} = E_{vs\ SCE} + E^0_{SCE} + 0.059\ pH$ . Cu-upd method was applied to determine the ECSA of the catalysts. The calibration test was conducted in a 0.25 M  $H_2SO_4$  solution containing 10 mM  $CuSO_4$  with saturated  $N_2$  during the whole test. The electrode was first cycled between 0.23 and 0.7 V in 0.25 M  $H_2SO_4$  with scan speed of  $10\text{mV s}^{-1}$  for many scans as the background. Then the solution was changed into mixture of 0.25 M  $H_2SO_4$  and 10 mM  $CuSO_4$  with scan speed of  $10\text{mV s}^{-1}$ . And the ECSA was calculated after 20 times CV scan. The ECSA was calculated by the following formula:

$$ECSA_{(cm^2\ metal\ /g\ metal)} = \frac{Q_{Cu}}{M_{metal} \times 420\mu C\ cm^{-2}}$$

Where, the  $M_{metal}$  is the numerous loading of Ru nanoparticles on the working electrode;  $Q_{Cu}$  is the average charge calculated from area under the voltragram of the Cu-upd CV curve as shown in Fig. S3. The ECSA of RuNC-2 catalyst calculated by current Cu-upd method is  $77.78\text{m}^2\ \text{g}^{-1}$ , the ECSA of the RuNC-5 is  $51.78\ \text{m}^2\ \text{g}^{-1}$  and the ECSA of the PtNC is  $35.1\ \text{m}^2\ \text{g}^{-1}$ .

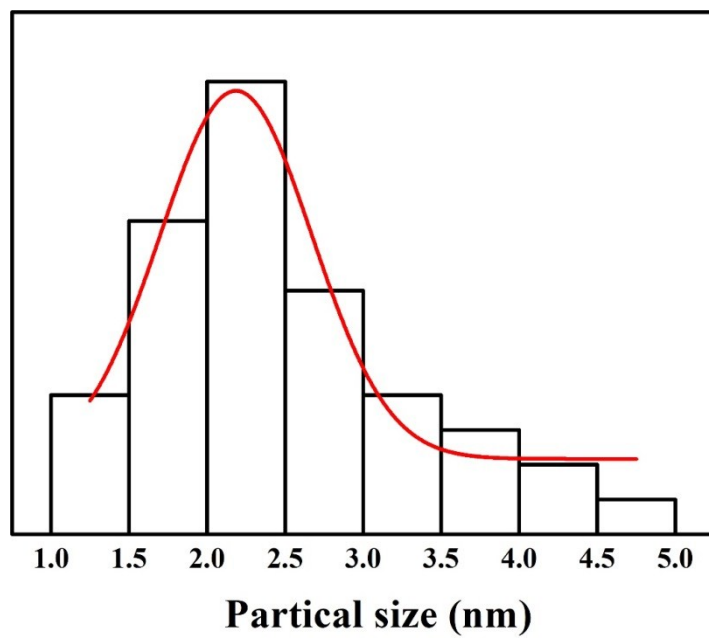
Afterwards, the HER turnover frequency (TOF) is defined as:

$$TOF = \frac{\text{total hydrogen turnovers/cm}^2\ \text{geo}}{\text{total active sites / cm}^2\ \text{geo}}$$

The upper hydrogen turnovers per geometric electrode area can be calculated by the hydrogen evolution current density under a certain overpotential:

$$H_2 = \left( j \frac{mA}{cm^2_{geo}} \right) \times \left( \frac{1C/s}{1000mA} \right) \times \left( \frac{1mol\ e^-}{96485C} \right) \times \left( \frac{1mol\ H_2}{2mol\ e^-} \right) \times 6.02 \times 10^{23} = j \times 3.12 \times 10^{15}\ H_2 / s / cm^2_{geo}$$

The total active sites per geometric electrode area can be calculated through the precalculated ECSA above.



**Fig.S1** The particle size distribution of RuNC-2

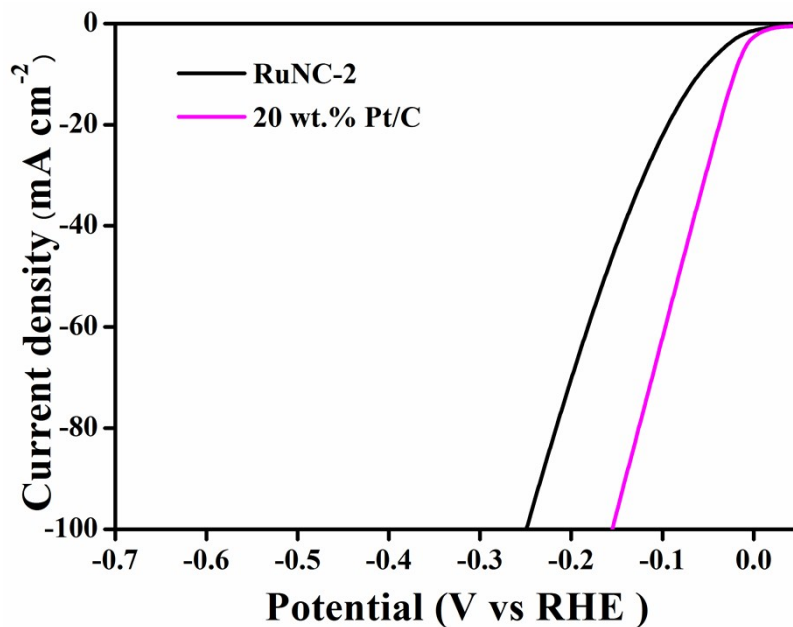


Fig.S2 The comparison of HER activity of RuNC-2 with the state-of-the-art 20 wt.% Pt/C

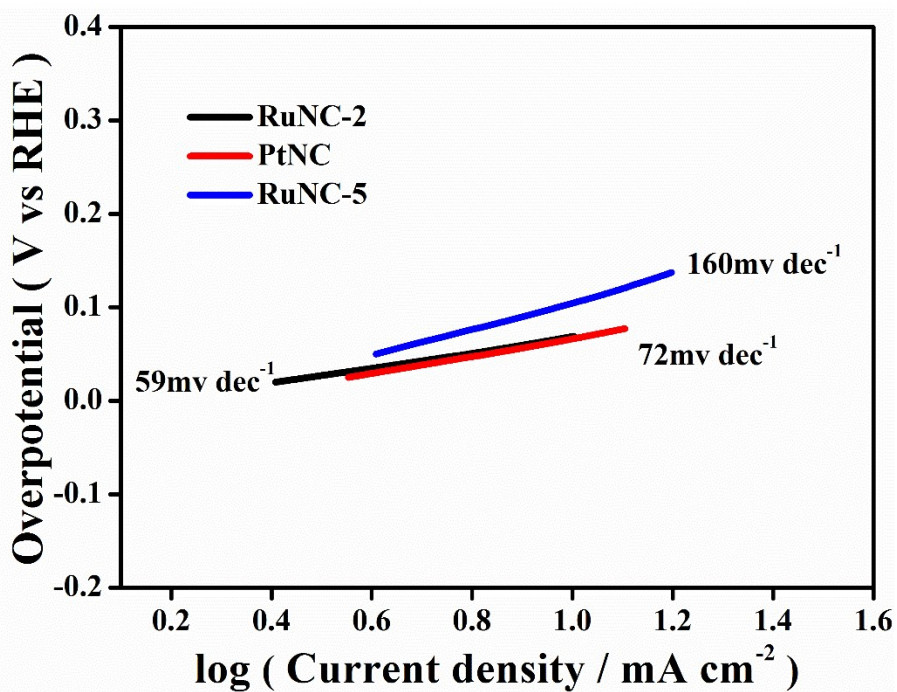
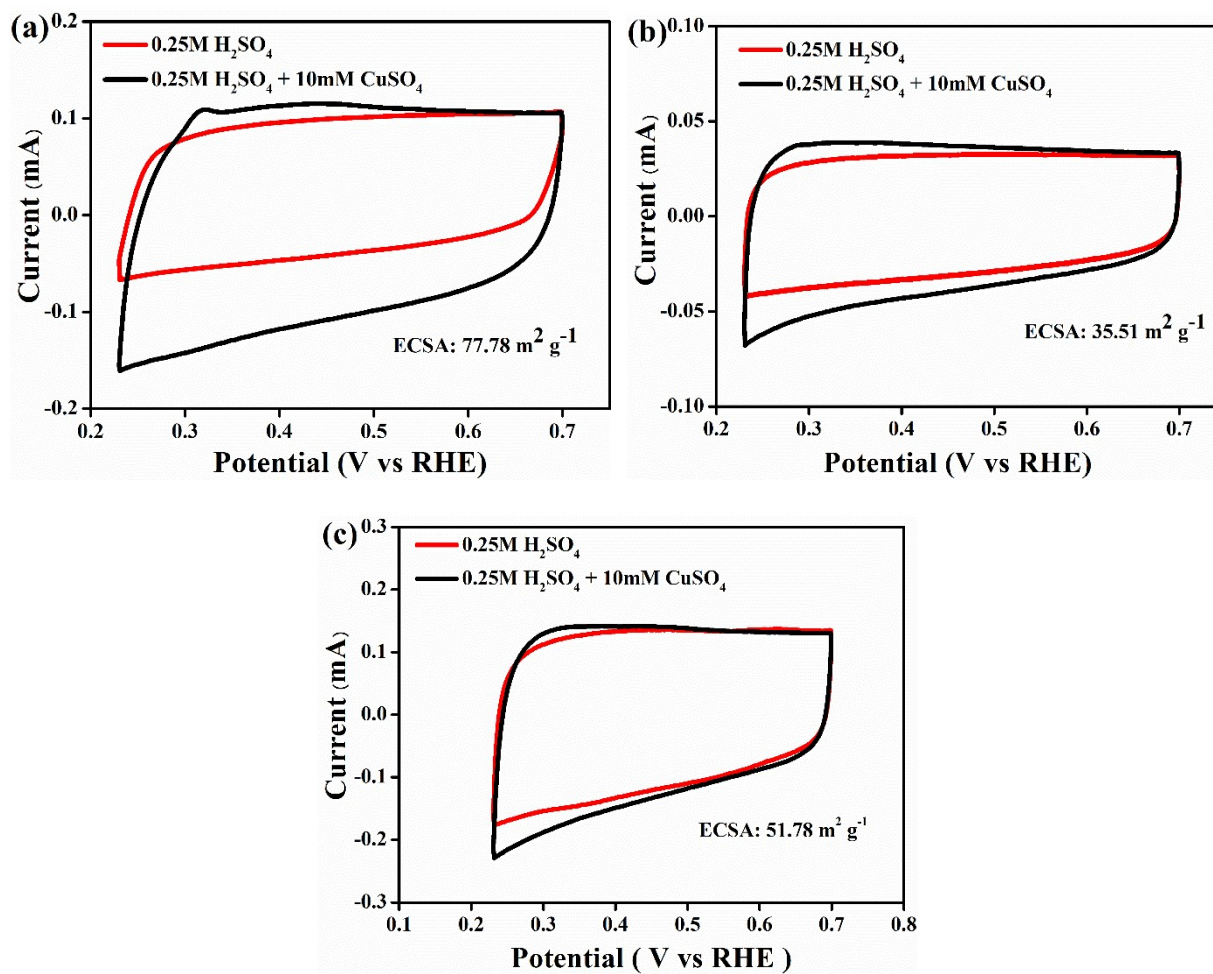


Fig.S3 Tafel plots of the catalysts in acidic medium



**Fig.S4** ECSA of the RuNC-2 (a), PtNC (b), and RuNC-5 (c) determined by Cu-upd method.

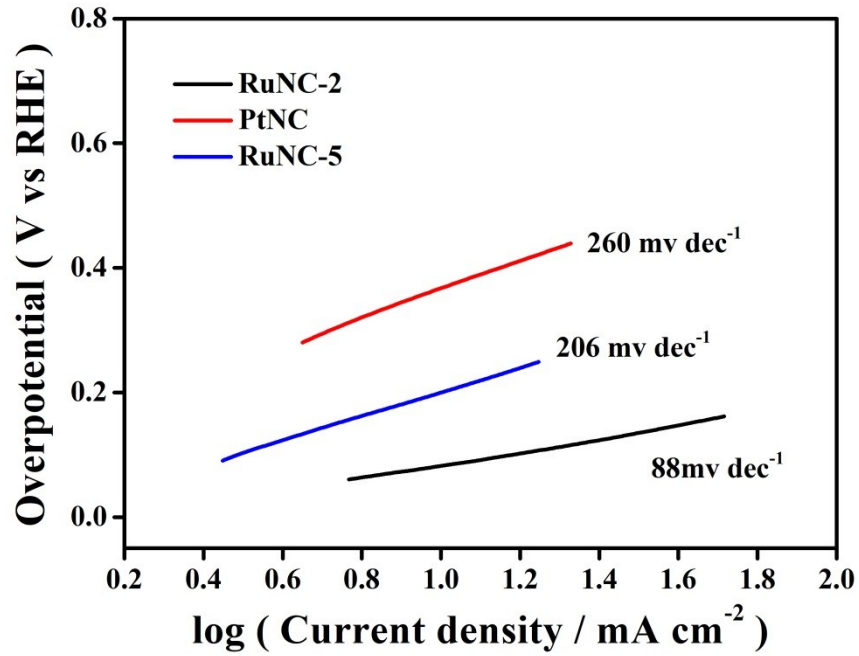


Fig. S5 Tafel plots of the catalysts in alkaline medium.

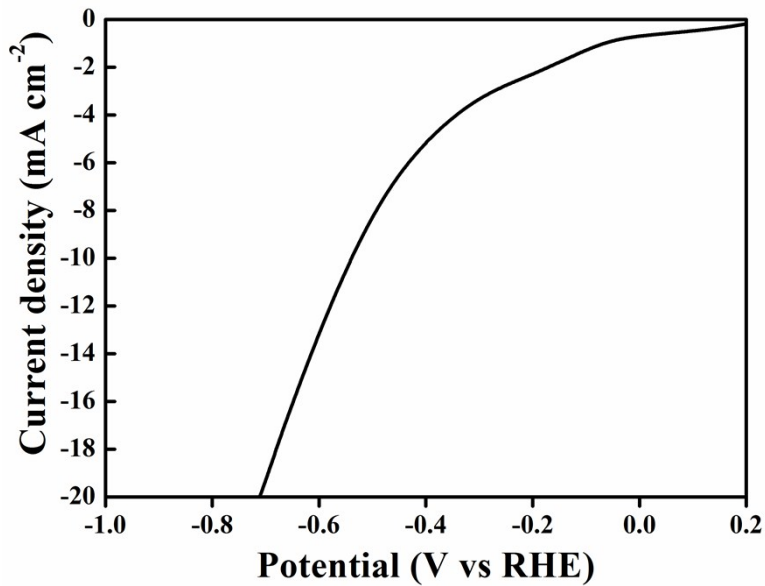


Fig. S6 LSV curves of RuNC-2 in neutral medium (phosphate buffer solution, pH=7).