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Electronic Supplementary Information

Highly Dispersed Ruthenium Precursors via Self-Assembly Assist Synthesis of Uniform Ruthenium Nanoparticles for Superior Hydrogen Evolution Reaction

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contents

Materials and Preparation of the Catalysts

Melamine (99%, CAS: 108-78-1), Cyanuric acid (98%, CAS: 108-80-5), $RuCl_3 \cdot 3H_2O$ (99%, CAS: 14898-67-0), Nafion (5 wt% in a mixture of lower aliphatic alcohols and water, contains 15-20% water. CAS: 31175-20-9), H_2SO_4 (CAS: 7664-93-9), KOH (CAS: 1310-58-3), 20 wt% Pt/C (CAS: 7440-06-4).

Preparation of Ru/CNO by three methods

(a) Grinding-calcination method: melamine (200 mg), $RuCl_3 \cdot 3H_2O$ (10 mg) and cyanuric acid (200 mg) were weighed in a mortar, fully ground, transferred to a quartz boat, and calcined at 550 ^oC for 4 h with a heating rate of 2 ^oC min^{-1} under a N_2 atmosphere.
(b) Stirring-calcination method: melamine (200 mg) and $RuCl_3 \cdot 3H_2O$ (10 mg) were stirred in distilled water for 1 hour, then cyanuric acid (200 mg) aqueous solution was added and stirred for another hour. Then the turbid reaction solution was filtered and the product was dried at 80 ^oC, subsequently transferred to quartz boat and calcined at 550 ^oC for 4 h with a heating rate of 2 ^oC min^{-1} under a N_2 atmosphere.
(c) Hydrothermal-calcination method: melamine (200 mg) and $RuCl_3 \cdot 3H_2O$ (10 mg) were stirred in distilled water for 1 hour, then cyanuric acid (200 mg) aqueous solution was added and stirred for another hour. Then the turbid reaction solution was transferred to a reactor and reacted at 180 ^oC for 6 hours. After cooling down to room temperature naturally, the turbid reaction solution was filtered and the product was dried at 80 ^oC, subsequently transferred to quartz boat and calcined at 550 ^oC for 4 h with a heating rate of 2 ^oC min^{-1} under a N_2 atmosphere.

Preparation of Ru/CNO-0,1,5,10,15.

Stirring-calcination method: melamine (0.2 g) and $RuCl_3 \cdot 3H_2O$ (0, 1, 5, 10, 15 mg) were dissolved in 40 ml distilled water and stirred for 1 hour at room temperature, then cyanuric acid aqueous solution (0.2 g in 40 ml distilled water) was added and stirred for another hour. Then the turbid reaction solution was filtered and the product was dried at 80 ^oC, subsequently transferred to quartz boat and calcined at 500 ^oC, 550 ^oC, 600 ^oC for 4 h with a heating rate of 2 ^oC min^{-1} under a N_2 atmosphere.

Electrochemical measurements

All electrochemical experiments were investigated on a CHI660E electrochemical workstation (Shanghai Chenhua Co., China) with a standard three electrode cell at room temperature. A glassy carbon electrode with coated catalysts was used as the working electrode, a saturated calomel electrode as the reference electrode and a graphite rod was used as the counter electrode. Preparation of working electrode: a certain amount of catalysts (1 mg) were dispersed in an aqueous solution containing water (85 μL), ethanol (85 μL) and Nafion solution (10 uL) under sonication for about 30 minutes to make it sufficiently dispersed. Subsequently, the obtained uniform catalyst inks (4 μL) was dropped onto the glassy carbon electrode (3 mm in

diameter) and dried naturally to form a film. The mass loading was 0.28 mg cm^{-2} in 0.5 M H_2SO_4 or 1.0 M KOH unless otherwise noted and the commercial Pt/C electrode was also prepared using the same procedure for comparison.

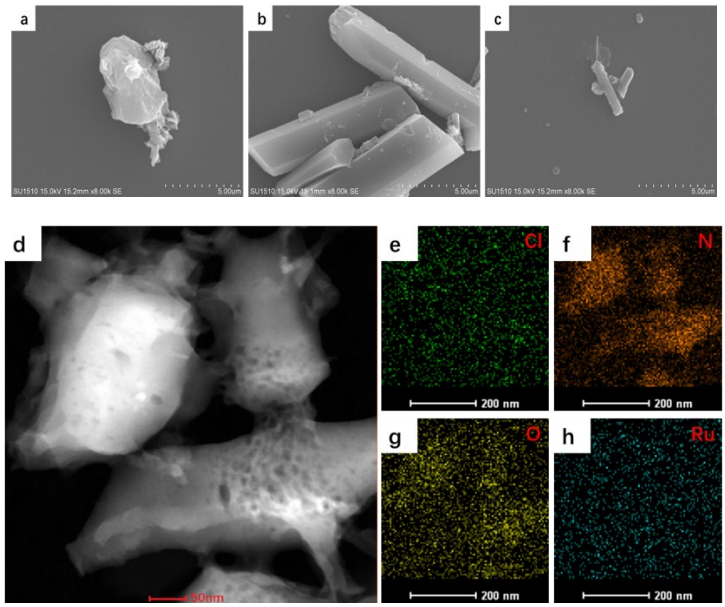

Fig. S1 Methods of (a) Grinding-calcination. (b) Hydrothermal-calcination. (c) Stirring-calcination. (d) STEM-EDX mapping images of (e) Cl, (f) N, (g) O,and (h) Ru in Ru-CAM precursors.

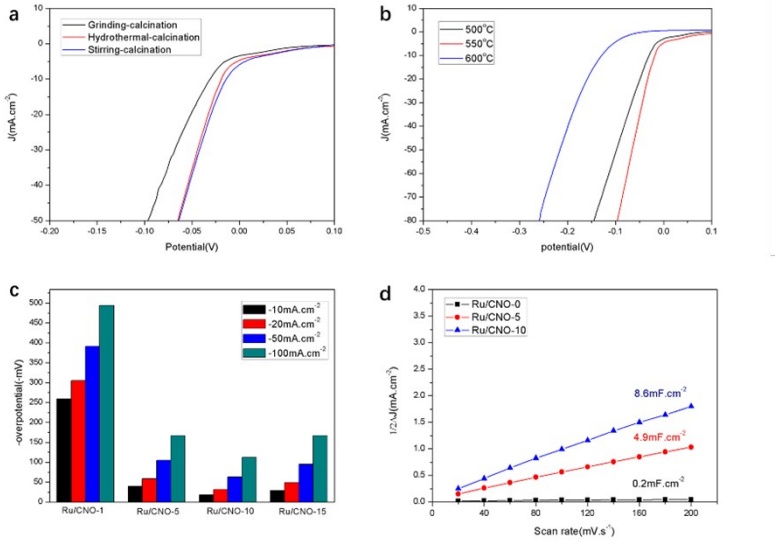

Fig. S2 (a) Polarization curves of Ru/CNO-10 with different synthesis methods in 0.5 M H_2SO_4. (b) Polarization curves of Ru/CNO-10 with different calcination temperatures in 0.5 M H_2SO_4. (c) Overpotentials of Ru/CNO-1,5,10,15 at -10, -20, -50 and -100 mA cm^{-2} in 0.5 M H_2SO_4. (e) Current density differences (Δj= (ja-jc)/2) at 0.10 V as a function of the scan rate for Ru/CNO-0,5,10.

Tab. S1 BET of three precursors

	Grinding	Hydrothermal	Stirring
BET Surface Area	1.9005 m^2/g	2.2364 m^2/g	7.9866 m^2/g