Supporting information

Accelerated galvanic interaction for the fabrication of core-shell nanowire to boost hydrogen evolution reaction

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1 Reagents

Polyvinylpyrrolidone (PVP, MW = 360000, analytical grade) was ordered from Sigma-Aldrich. Silver nitrate (AgNO₃, 99%) was obtained from Alfa Aesar. Ferric chloride hexahydrate (FeCl₃ \bigcirc 6H₂O, analytical grade) was purchased from McClean. Ethylene glycol (EG, analytical grade) was subscribed from Xilong Scientific Co., Ltd. Ruthenium trichloride hexahydrate (RuCl₃ \bigcirc 6H₂O, analytical grade) was ordered from Aladdin. RuO₂ (99 wt%), Pt/C (20 wt%) and Nafion solution (5 wt%) were purchased from Sigma-Aldrich. All reagents were used without further modification.

2 The synthesis process of Ag NWs

To synthesize Ag NWs, 0.2 g of PVP was gradually dissolved in 7 mL of EG solution at 60 °C. After cooling down at 20 °C, 0.25 g of AgNO₃ was further ultrasonically dissolved in the abovementioned solution, followed by the addition of 1.75 mL of 0.6 M FeCl₃ EG. After rigorously stirring for 1 minute, transferring to an oven and reacting for 1 hour at 150 °C to generate a black gel. The obtained black gel was further dialyzed to remove impurities. Finally, the Ag NWs were grasped after lyophilization.

3 The preparation of Ru@Ag/AgCl catalysts

To prepare Ru@Ag/AgCl catalysts, first, 2 mg of Ag NWs was mixed with 2 mL of deionized water to form a homogeneous solution under ultrasonication for 30 minutes. Subsequently, 30 μ L of the obtained solution was dropwise added on the pre-treated glass carbon electrode (0.19625 cm⁻²), dried at 25 °C, and then used as the

working electrode (0.152 mg cm⁻²). Carbon rod and Hg/HgO electrode were worked as counter and reference electrodes, respectively. The deposition of Ru on the surface of Ag NWs was obtained by the CV operating from 0.28 to 0.6 V (vs. RHE) at 50 mV s⁻¹ in 0.1 M RuCl₃ solution. After 100, 200, 300, and 400 cycles of CV operation, the obtained Ru(a)Ag/AgCl-100, Ru(a)Ag/AgCl-200, Ru@Ag/AgCl-300, and Ru@Ag/AgCl-400 catalyst used as the working electrode for the following electrochemical measurements conducted in 1 M KOH, respectively. For the other control experiments, 2 mg of commercial Pt/C was evenly dissolved in a mixed solution containing ethyl alcohol and water to form a catalyst ink. Then, 25 µL of the obtained catalyst ink was to dropwise added on the pre-treated glass carbon electrode. The Ru electrode was prepared by the deposition of Ru³⁺ on the pre-treated glassy carbon electrode. The potential window of CV ranges from 0.28 to 0.6 V (vs. RHE) at the scanning rate of 50 mV s⁻¹.

4 Electrochemical measurements

The Ru@Ag/AgCl modified working electrode for HER was executed in 1 M KOH solution. The CV operation at -0.3 to 0 V (vs. RHE) was executed to activate the prepared catalysts. Then, linear sweep voltammetry (LSV) was used to evaluate the electro-catalysis performance of the obtained samples. The potential window ranges from -0.3 to 0 V (vs. RHE), and the sweep rate was 5 mV s⁻¹. The electrical conductivity of catalysts was achieved by using electrochemical impedance spectroscopy (EIS). Meanwhile, the values of double-electrochemical-layer (C_{dl}) of the prepared catalysts were obtained by the multiple CV measurements in a given potential

window (0.2 - 0.3 V vs. RHE) under different scan rates (40, 60, 80, 100, and 120 mV s⁻¹). The durability of catalysts was assessed by chronopotentiometry (CP) and CV. The displayed potential was converted into reversible hydrogen electrode (RHE) according to the previous reports.¹⁻⁴

5 Water splitting measurements

To synthesize the RuO₂-coated electrode for water splitting, 1 mg of RuO₂ was evenly dispersed in a mixed solution containing 475 μ L of EG and 25 μ L of Nafion. Then, 15 μ L of mixed solution was dripped onto the pre-treated glass carbon electrode, which possesses a load capacity of 0.152 mg cm⁻². Differing in the aforementioned electrochemical measurements, the water splitting measurement was conducted using a two-electrode system that Ru@Ag/AgCl-200 catalyst worked as the cathode and RuO₂ catalysts used as the anode. Chronoamperometry (CA) was utilized to detect the stability of prepared catalysts for water splitting.



Fig. S1. (a) Transmission electron microscope (TEM), (b) high-resolution transmission electron microscope (HR-TEM) and (d-f) energy dispersive spectroscopy (EDS) mapping images for Ag nanowires (NWs) soaking RuCl₃ 9H₂O solution for 5 h.



Fig. S2. (a) Scanning electron microscopy (SEM), (b) TEM, (c) X-ray diffraction (XRD) patterns of Ag NWs.



Fig. S3. Multi-CV images of (a) Ru@Ag/AgCl-100, (b) Ru@Ag/AgCl-200, (c) Ru@Ag/AgCl-300, (d) Ru@Ag/AgCl-400, (e) Ru, (f) Pt/C and (g) Ag NWs.



Fig. S4. (a) TEM, (b) HR-TEM and (c) EDS-Mapping for Ru@Ag/AgCl-100.



Fig. S5. Comparative (a) XRD, (b) X-ray photoelectron-spectroscopy (XPS), (c) Ru 3p and (d) Ag 3d images of Ru@Ag/AgCl-100 and Ru@Ag/AgCl-200.

Table S1. Inductively coupled plasma mass spectrometry (ICP-MS) results of Ru@Ag/AgCl-100 and Ru@Ag/AgCl-200.

Catalyst	Total mass (mg)	Ru content (at %)
Ru@Ag/AgCl-100	1 mg	6.891
Ru@Ag/AgCl-200	1 mg	9.635



Fig. S6. Ag 3d image of Ru@Ag/AgCl-400 catalysts.

Table. S2. The comparative atomic retention rate of Ru in Ru@Ag/AgCl-200 catalysts and recent report values after CP measurements.

Catalyst	Retention rate after CP test	Electrolyte	Refferences
Ru(OH) _x /Ag/NF	96.79 %	1M KOH	5
Mo _x /Ru/C-3	61.00 %	1M KOH	6
Ru hcp	87.50 %	1M KOH	7
Ru/meso-NC-300 °C	29.00 %	1M KOH	8
Ru@Ag/AgCl-200	99.00 %	1M KOH	This article



Fig. S7. (a) TEM, (b) HR-TEM, and (c-f) EDS-Mapping images of Ru@Ag/AgCl-200 after stability measurements for HER.

Table S3. Atomic ratio of Ru in Ru@Ag/AgCl-200 before and after stability measurement measured by ICP-MS.

Ru@Ag/AgCl-200	Total mass (mg)	Ru content (at %)
Before	1 mg	9.635
After	1 mg	8.897

Table S4. A comparison of Ru concentration in the electrolyte after the stability test of Ru@Ag/AgCl-200 and Ru catalysts by ICP-MS.

Electrolyte	Volume (L)	The concentration of Ru ($\mu g/L$)
Ru	0.05	333.151
Ru@Ag/AgCl-200	0.05	143.632

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