# **Supporting Information**

# Joule-heating synthesis of highly dispersed Pt single atoms anchored on carbon nanotubes for efficient hydrogen evolution

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#### **Experimental section**

## Materials and chemicals

Carbon nanotubes, Chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O), and Ethanol (99.5%) were purchased from Shanghai Aladdin. Co. Ltd. Ultrapure water (18.2 M $\Omega$ ·cm) was applied for washing and centrifugation of the samples.

### **Physical and Chemical Characterization**

The chemical composition and surface valence were determined using X-ray diffraction (XRD, Rigaku, Smartlab) with Cu Ka radiation ( $\lambda = 1.5418$  Å), X-ray photoelectron spectroscopy (XPS, PHI 5000 Versaprobe) with an Al Ka X-ray source, and Raman spectrum (LabRam HR Evolution). The microstructure and morphology are characterized by scanning electron microscopy (SEM, JEOL JSM-6701F), spherical aberration corrected transmission electron microscope (AC-TEM, Thermo Fisher Scientific Themis-G2), high-resolution transmission electron microscopy (HRTEM), and the high-angle annular dark-field scanning STEM (HAADF-STEM). Inductively coupled plasma-optical emission spectroscopy (ICP-OES, PerkinElmer Optima 7300DV) was conducted to reveal the Pt loading of each catalyst sample. The X-ray absorption near-edge structure (XANES) spectra and the extended X-ray absorption fine structure (EXAFS) spectra were acquired at the BL 07A beamline of the National Synchrotron Radiation Research Center in Shanghai.

### **Preparation of Pt SAs-CNTs**

First, 60 mg of carbon nanotubes were ultrasonically dispersed in 50 mL of deionized water. Then, a certain amount of chloroplatinic acid was added and ultrasonically dispersed evenly. The solution was stirred for 12 hours at room temperature, and then washed with deionized water and absolute ethanol. It was dried in a vacuum oven at 40°C for 12 hours. After that, the dried powder was put into a Joule - heating device and instantaneously heated to 600°C in a vacuum environment, and thus Pt SAs-CNTs could be obtained.

## **Preparation of Pt NCs-CNTs**

First, 60 mg of carbon nanotubes were ultrasonically dispersed in 50 mL of deionized water. Then, a certain amount of chloroplatinic acid was added and

ultrasonically dispersed evenly. The solution was stirred for 12 hours at room temperature, and then washed with deionized water and absolute ethanol. It was dried in a vacuum oven at 40°C for 12 hours. Then, the dried powder was placed in a magnetic boat and vacuum-heated in a tube furnace. The temperature was raised to 400°C at a heating rate of 2°C/min, maintained at this temperature for 1 hour, and then allowed to cool down naturally.

## **Electrochemical measurements**

All the electrochemical measurements were carried out under the CHI760E (CH Instruments) in 1 M KOH with the typical three-electrode system. Specifically, the saturated Hg/HgO electrode and graphite rod were respectively served as the reference electrode and counter electrode. Working electrodes for HER measurements were prepared by a controlled drop-casting method. The carbon paper coated by 10  $\mu$ L catalyst ink was used as the working electrode. The detailed synthesis of catalyst ink is as following: typically, 10 mg catalyst powder was homogeneously dispersed into the mixture of 330  $\mu$ L ultrapure water, 330  $\mu$ L ethanol, 330  $\mu$ L isopropanol and 10  $\mu$ L Nafion solution under sonication. All potentials in this paper were calculated to the reversible hydrogen electrode (RHE) via the following equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.098 + 0.059 \times pH$$

Linear sweep voltammetry was recorded at 1 mV/s in 1 M KOH. Tafel slopes were determined by plotting the overpotential vs. the logarithm of current density  $(\log |j|)$ . CV curves were obtained in 1 M KOH solution with potential window between 0.03 V and 0.16 V vs. RHE and CV tests were performed at different sweep rates of 10, 20, 30, 40, 50, 60, 70 and 80 mV/s. EIS measurements were carried out from 0.1 to 100,000 Hz with a constant voltage. The double-layer capacitance (C<sub>dl</sub>) was determined from the CV curves with different scan rates (10, 20, 30, 40, 50, and 60 mV/s) measured in a non-faradic potential range. The electrochemically active surface area (ECSA) was calculated by following formula:

$$ECSA = C_{dl} / C_s$$

Where the  $C_s$  is the specific capacitance of the corresponding surface smooth sample under the same conditions (~ 40  $\mu$ F/cm<sup>2</sup>).



Fig. S1 (a) SEM image of CNTs. (b) SEM image of Pt NCs-CNTs. (c) SEM image of Pt SAs-CNTs.



Fig. S2 (a) CV curves for (a) CNTs, (b) Pt NCs-CNTs, and (c) Pt SAs-CNTs catalysts in the non-Faradaic region of 0.1-0.25 V *vs*. RHE with scan rates of 10, 20, 30, 40, 50, 60, 70 and 80 mV/s in 1 M KOH solution.



Fig. S3 (a) SEM image and (b) AC-HADDF-TEM image of Pt SAs-CNTs after the 50-hour stability test.



Fig. S4 XPS spectra of Pt SAs-CNTs after the 50-hour stability test: (a) High-resolution spectrum of C 1s; (b) High-resolution spectrum of Pt 4f.



Fig. S5 Raman spectrum of Pt SAs-CNTs after the 50-hour stability test.



Fig. S6 Comparison with HER performance of Pt SAs-CNTs measured using GC rotating disk electrodes: (a) LSV curves. (b) Tafel slope.



Fig. S7 Pt SAs-CNTs with different initial Pt loads:(a) LSV curves. (b) Tafel slope. (c) The actual Pt single atom loadings by ICP.

Catalysts	Overpotential (mV) at 10 mA/cm <sup>2</sup>	Tafel slope (mV/dec)	Reference
Pt SAs-CNTs	62.8	47.9	This work
Ni-MoB <sub>2</sub>	65.4	58.3	[1] ACS Energy Lett. 2023, 8, 5175
Pt-NiCo LDO	92	73	[2] Adv. Funct. Mater. 2024, 34, 2405919
0.22Pt–HMoS <sub>2</sub>	123	76.71	[3] Small, 2022, 18, 2104824
RuSAs/Ni(OH) <sub>2</sub> @FeOOH	105	72	[4] Chemical Engineering Journal, 2024, 479, 147500
Pt/VG Ar-5	124	36	[5] Adv. Funct. Mater., 2022, 32, 2203067
Cu@Cu <sub>3</sub> P-Ru/CCG-500	102.5	63	[6] Appl. Catal. B- Environ. 2023, 326, 122402
PtRu/CNT@SnO <sub>2-x</sub>	53	48	[7] J. Am. Chem. Soc. 2024, 146, 21453
Co <sub>SA</sub> /CNFs	89	143	[8] Chem Asian J. 2023, 18, e202300393
TM SAs-MoS <sub>2</sub>	80	82.6	[9] Adv. Energy Mater. 2024, 14, 2401716
Ru-Co <sub>2</sub> P@Ru-N-C	69	65	[10] Adv. Funct. Mater. 2024, 34, 2316709

**Table. S1.** Performance comparisons of Pt SAs-CNTs electrode with recently reportedHER electrocatalysts in 1 M KOH.

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