Electronic Supplementary Information

Activated carbon nanotubes: a high-active metal-free electrocatalyst for hydrogen evolution reaction

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Experimental section

Materials

MWCNTs and SWCNTs were purchased from Boyu Gaoke New Material Company (Beijing, China); HNO_3 was purchased from Aladdin Ltd. (Shanghai, China). Pt/C (20 wt% Pt on Vulcan XC-72R) and Nafion (5 wt%) were purchased from Sigma-Aldrich. All chemicals were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

Acidic oxidation of MWCNTs

100 mg MWCNTs were treated in 150 mL 70 % HNO_3 at 120 ℃ for different hours (0.5, 1, 2, 4, 8 hours). The products were washed with deionized water until neutral and collected via centrifugation at 10000 rpm for 10 min, and then dried at 60 ℃. SWCNTs-ao-4 was prepared using the same method.

Characterizations

Transmission electron microscopy (TEM) measurements were made on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. The sample for TEM characterization was prepared by placing a drop of sample solution on carbon-coated copper grid and dried at room temperature. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. Gas chromatography measurements were carried out on GC–2014C (Shimadzu Co.) with thermal conductivity detector and nitrogen carrier gas.

Electrochemical measurements

Electrochemical measurements are performed with a CHI614D electrochemical analyzer (CH Instruments, Inc., Shanghai). A three-electrode cell is used, including a glassy carbon electrode (geometric area = 0.07 cm^2) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a graphite plate as the counter electrode. The electrolyte (0.5 M H_2SO_4) was degassed by bubbling N_2 for at least 30 min before the electrochemical measurements. To prepare the working electrode, 5 mg of the catalyst and 10 μL of 5 wt% Nafion solution were dispersed in 1 mL of water/ethanol (49:50 v/v) mixed solvent, followed by ultrasound at least 30

min. Then 5 μL of the ink was dropped onto the glassy carbon electrode (loading: 0.36 mg cm^{-2}). Before electrochemical measurements, all working electrodes were pretreated at -2.0 V (vs. SCE) for 4 h. Linear sweep voltammograms (LSVs) measurements were performed with a scan rate of 2 mV s^{-1} in a range from 0 V to -0.8 V vs. SCE in N_2 saturated aqueous solution of 0.5 M H_2SO_4. Durability test was then carried out by cyclic voltammograms (CVs) from -0.8 to 0 vs. SCE with a scan rate of 100 mV s^{-1}. All the potentials reported in our work were vs. the reversible hydrogen electrode (RHE). In 0.5 M H_2SO_4, E (RHE) = E (SCE) + 0.279 V.

Exchange current density calculation

The exchange current density (j_0) is obtained from extrapolation methods. Tafel plots are fit into the Tafel equation (η = b log (j) + a, where b is the Tafel slope). The Tafel equation of p-MWCNTs-ao-cp is η/V=0.128 + 0.0713lg[j /(mA cm^{-2})]. When η = 0 V，j_0 is calculated to be 16.0×10^{-3} mA cm^{-2}.

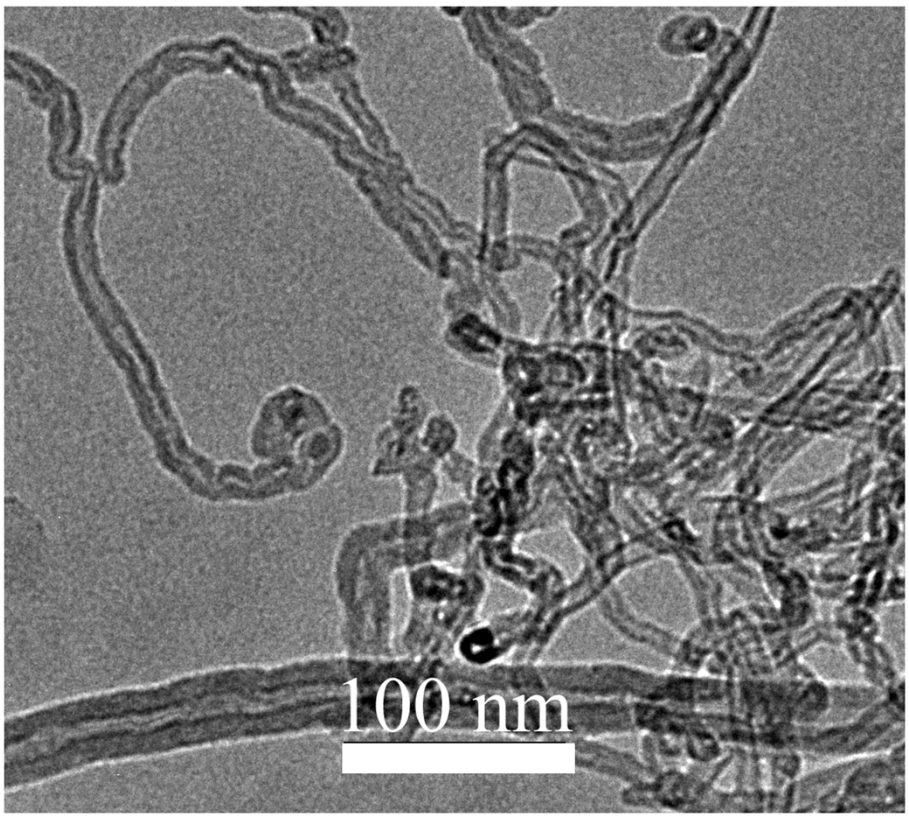

Fig. S1 TEM image of p-MWCNTs.

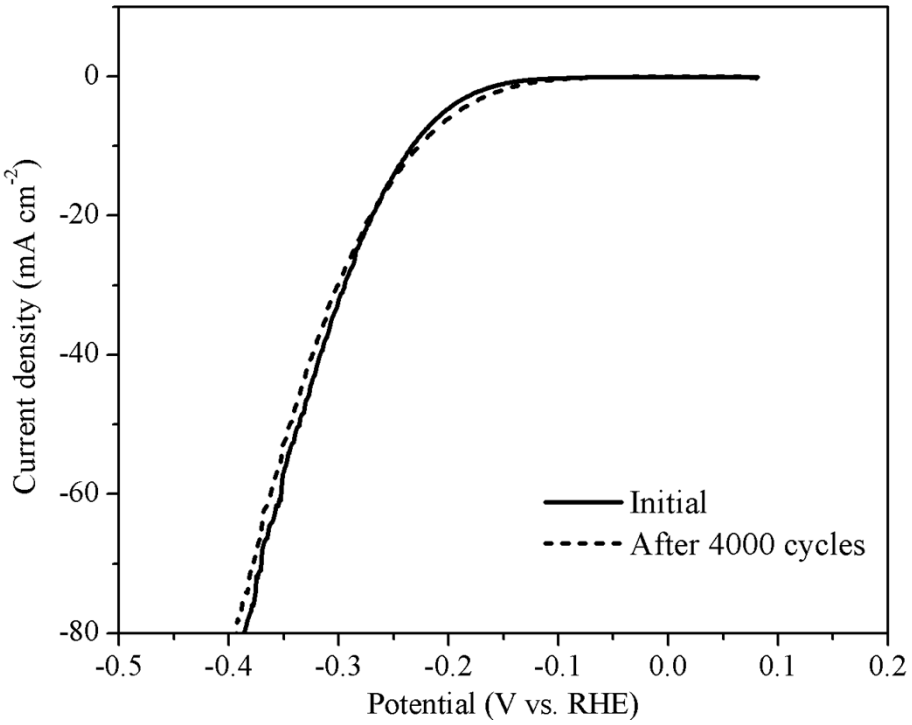

Fig. S2 Durability test for the p-MWCNTs-ao-cp catalyst for 4000 cycles in 0.5 M H_2SO_4.

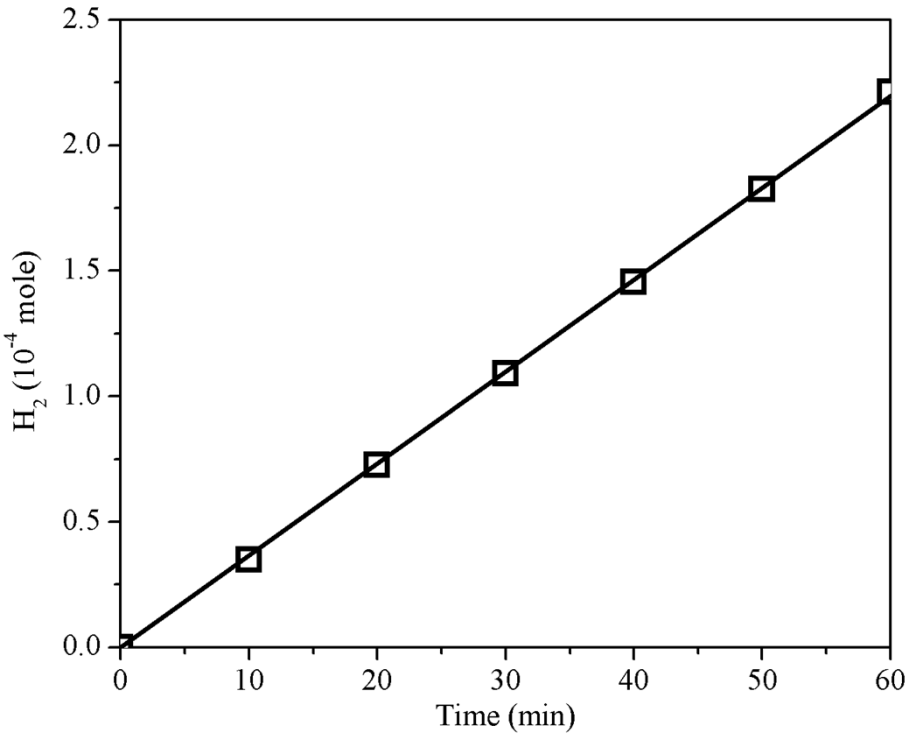

Fig. S3 The amount of calculated (solid) and experimentally measured (square) hydrogen versus time for p-MWCNTs-ao-cp at an overpotential of 150 mV for 60 min.

Active sites calculation： The number of active sites (n) is examined using CVs with pH=7 phosphate buffer at a scan rate of 50 mV s^{-1}. When the number of voltammetric charges (Q) is obtained after deduction of the blank value, n (mol) can be calculated with the following equation:

$$n= Q/2F$$

where F is Faraday constant (96480 C mol^{-1}). For the sample of p-MWCNTs-ao-cp, Q is 1.04×10^{-3} C (obtained from Figure S4A), n (mol) = $1.04\times10^{-3}/(2\times96480)$ mol= 5.39×10^{-9} mol.

Turnover frequency (TOF) calculation： The TOF (s^{-1}) is calculated with the following equation:

$$TOF= I/(2Fn)$$

where I (A) is the current of the polarization curve obtained from the LSVs measurements. Two electrons are required to form one hydrogen molecule, thus the value should divided by two.

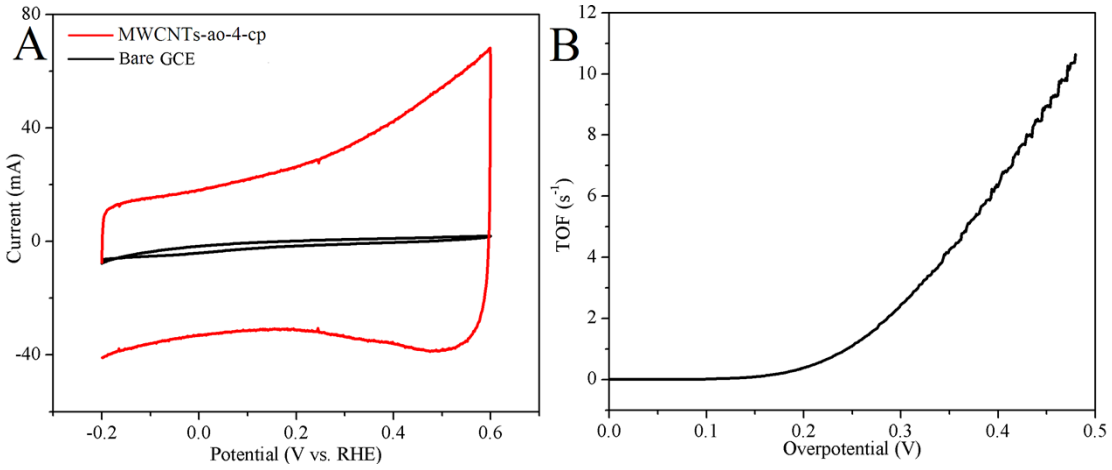

Fig. S4 (A) CVs of bare GCE and the p-MWCNTs-ao-cp catalyst in pH=7 phosphate buffer between -0.2 V and 0.8 V vs. RHE with a scan rate of 0.05 V s^{-1}. (B) Turnover frequencies of the p-MWCNTs-ao-cp catalyst in 0.5 M H_2SO_4.

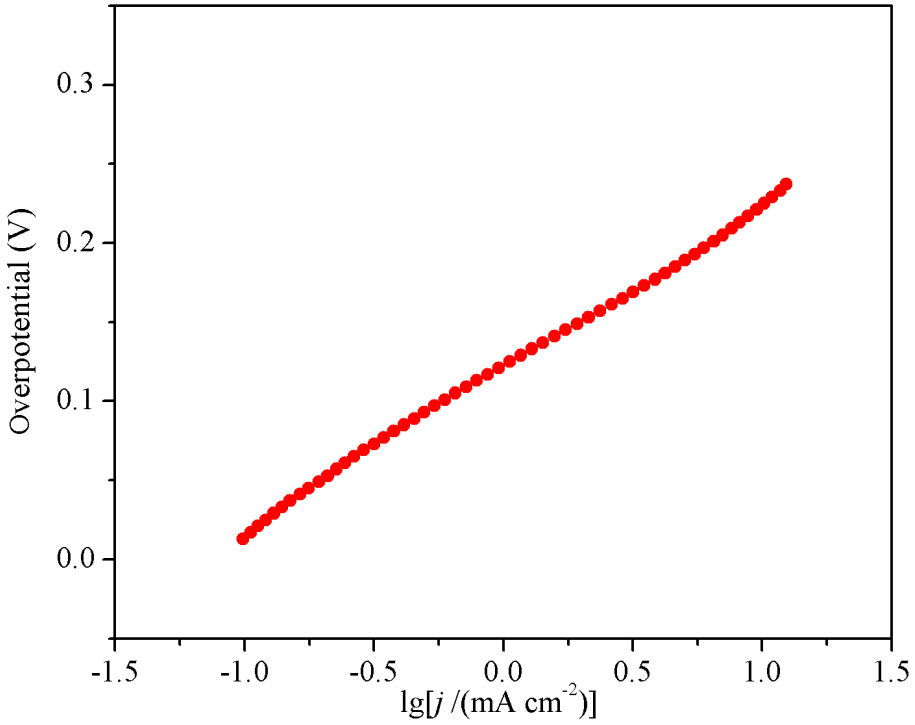

Fig. S5 Tafel plot for p-SWCNTs-ao-cp.

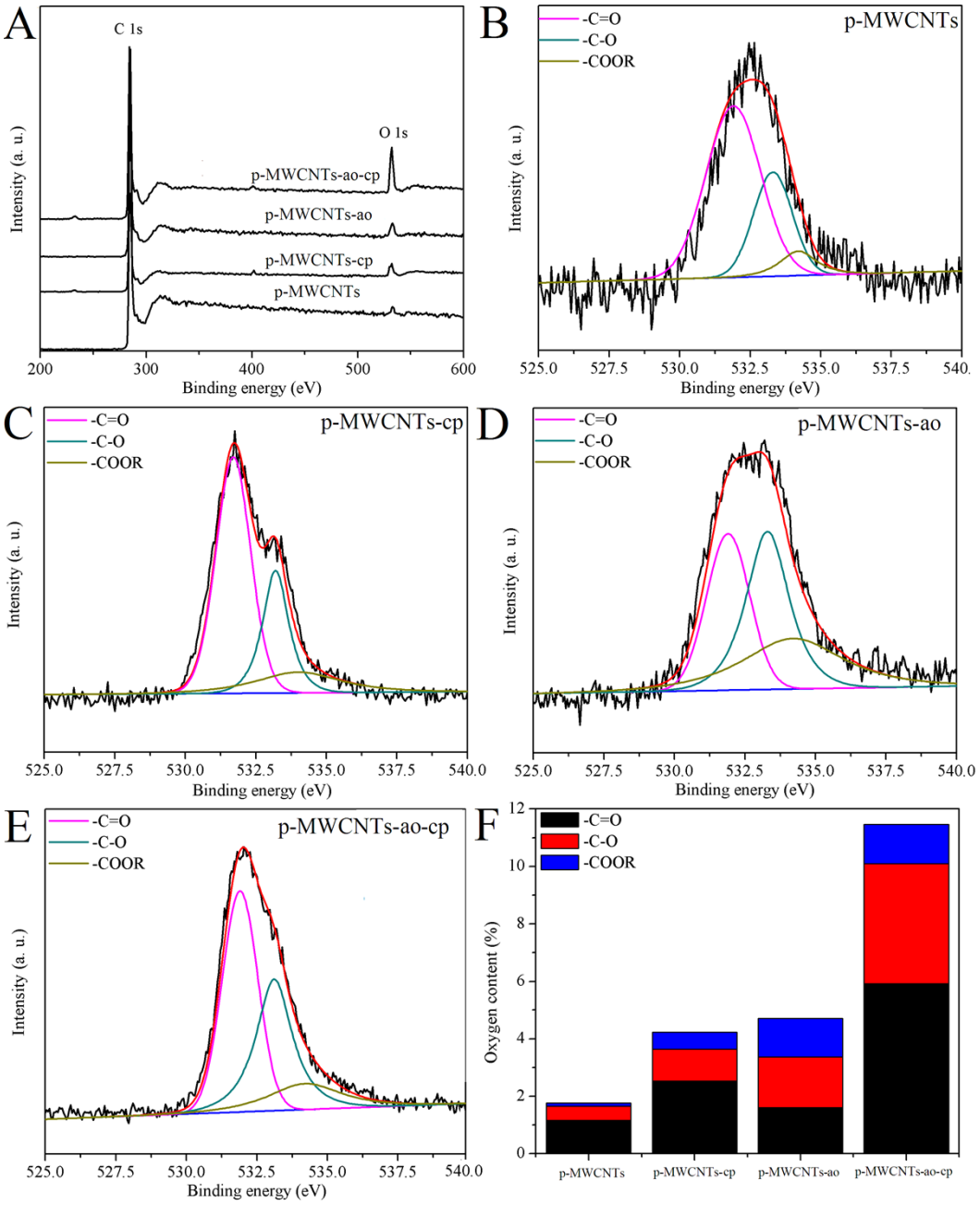

Fig. S6 (A) The XPS survey spectra of p-MWCNTs, p-MWCNTs-cp, p-MWCNTs-ao and p-MWCNTs-ao-cp. The high resolution O 1s XPS spectra of (B) p-MWCNTs, (C) p-MWCNTs-cp, (D) p-MWCNTs-ao and (E) p-MWCNTs-ao-cp. (F) The oxygen functionalities percentage of these four samples.