Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Facile fabrication of Ir/CNT/rGO nanocomposites with enhanced electrocatalytic performance for hydrogen evolution reaction

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Experimental Section

Materials

All chemicals were purchased commercially and used without any other purification. Ethylene glycol (≥99%), NaOH (≥96%), H_2O_2 (30%), acetone, concentrated hydrochloric acid and anhydrous ethanol were purchased from Sinopharm Chemical Reagents Co. Ltd. Concentrated sulfuric acid, concentrated nitric acid, and $KMnO_4$ were purchased from Beijing Chemical Industry Group Co. Ltd. $IrCl_3 \cdot 3H_2O$ was purchased from Aladdin Reagents Co. Ltd. The active carbon was provided by Shenzhen Kejingzhida Company. High purity argon gas (99.999%) was supplied by Beijing Gas Company. Commercial CNT was purchased from Chengdu Organic Chemicals Co. Ltd. Graphite was purchased from Qindao Yubo Graphite Technology Co. Ltd. Nafion solution (5 wt%) was purchased from Dupont China Holding Co. Ltd. All carbon nanomaterials were pre-treated respectively with acid condition to improve water dispersibility, the procedures of which were according to the conventional methods.[1–2]

Physical characterizations

Fourier transform infrared (FTIR) spectra were collected on a microinfrared spectrometer (spotlight 200i). Raman spectra were measured on a laser confocal Raman spectrometer (Renishaw inVia plus). X-ray diffraction (XRD) patterns were tested on an X-ray diffractometer (Rigaku, D/MAX-TTRIII, 40 KV, 200 mA, Cu Kα radiation λ=0.154178 nm). X-ray photoelectron spectra (XPS) were tested on an ESCALAB 250Xi equipped with *ex situ* treatment chamber and the binding energy of C1s (284.8 eV) was used as the reference to correct the measured binding energy. The loading percentages of Ir in the prepared electrocatalysts were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 7000DV). Scanning electron microscopy (SEM) images were obtained on a cold-field emission Hitachi SU8200. High resolution transmission electron microscopy (HRTEM) images and elemental mapping results were obtained on a Tecnai G2 F20 U-TWIN.

Electrochemical measurements

All electrochemical tests were conducted with a standard three-electrode system on a Multi Autolab M204 workstation (Metrohm, Switzerland). All the potentials in this paper were referenced to a reversible hydrogen electrode (RHE) according to $E(\text{RHE}) = E(\text{Hg/HgO}) + 0.2422 + 0.059\ \text{pH}$. In the preparation of a working electrode, 2.0 mg prepared electrocatalyst and 50 mL Nafion solution were dispersed in 150 mL anhydrous ethanol by ultrasonication for 1 hour to form a homogeneous ink. Then, 5.0 μL of the ink was loaded onto the surface of a glassy carbon electrode (3.0 mm in diameter) and dried at room temperature. Before electrochemical tests, the fresh working electrode was cycled 1,000 cycles to stabilize the current. Linear sweep voltammetry (LSV) was tested in 1 M KOH at a scan rate of 5 mV s^{-1} without *IR*-correction, and the electrolyte was H_2-saturation. A Hg/HgO electrode and graphite rod were used as the reference electrode and counter electrode, respectively. Additionally, cyclic voltammograms (CV) were obtained from 0.4 to 0.5 V with sweep rates of 25, 50, 75, 100, 125, 150, 175 and 200 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) was performed at various overpotentials with frequency from 10^{-2} to 10^{6} Hz with an AC voltage of 5 mV.

Preparation of Ir colloid solution

The preparation of Ir colloid solution was referred with the reported literature.[3–5] Typically, 1.0 g $IrCl_3 \cdot 3H_2O$ was dissolved in 150 mL ethylene glycol under stirring and 0.25 mol/L NaOH ethylene glycol solution was added to adjust the pH value to 10.0. The mixed solution was heated at 160 °C for 3 hours under flowing Ar and brown Ir colloid solution (0.39 wt%) can be obtained after cooling to room temperature. The morphological characteristic of the Ir nanoparticles in the colloid solution was observed by TEM (**Fig. S1a-1b**), the TEM samples were prepared by adding additional concentrated hydrochloric acid into the colloid solution and dispersing the deposition by acetone.

Preparation of AC dispersion

2.0 g commercial active carbon was dispersed in 50 mL concentrated nitric acid and stirred at 60 °C for 3 hours. Later, adding deionized water and filtrating the dispersion. The filter cake was washed by deionized water for several times until the filtrate was neutral. After oven drying for 24 h, the AC was finally obtained. The AC dispersion was prepared by dispersing the collected solid of AC into deionized water with stirring and ultrasonic treatment, so that the AC dispersion (1.0 g L^{-1}) was obtained for further utilization. The morphological characteristic of AC was observed by SEM, the SEM samples were prepared by freeze drying (**Fig. S2a-2b**).

Preparation of Ir/AC

50 mL as-prepared AC dispersion was added into 7.0 g as-prepared Ir colloid solution and the mix was refluxing as well as stirring for 3 h. After cooling down to room temperature, the mix was centrifuged and washed with deionized water for four times. The solid of Ir/AC was collected after freeze drying for 2 days. The morphological characteristic of the prepared Ir/AC was observed by SEM (**Fig. S2c-2d**) and TEM (**Fig. 1a-1c**).

Preparation of CNT dispersion

1.0 g commercial CNT were dispersed in 12 mL concentrated sulfuric acid and concentrated nitric acid solution (H_2SO_4:HNO_3=3:1 *v*/*v*) under stirring and refluxing at 90 °C for 4 hours. Deionized water was added slowly for attenuation and the prepared CNT were collected by suction filtration after the pH value of the dispersion was adjusted to 7.0 by deionized water. The CNT dispersion was prepared by dispersing the collected solid of CNT into deionized water with stirring and ultrasonic treatment, so that the CNT dispersion (1.0 g L^{-1}) was obtained for further utilization. The morphological characteristic of CNT was observed by SEM, the SEM samples were prepared by freeze drying (**Fig. S2e-2f**).

Preparation of Ir/CNT

50 mL as-prepared CNT dispersion was added into 43.8 g as-prepared Ir colloid solution and the mix was refluxing as well as stirring for 3 h. After cooling down to room temperature, the mix was centrifuged and washed with deionized water for four times. The solid of Ir/CNT was collected after freeze drying for 2 days. The morphological characteristic of the prepared Ir/CNT was observed by SEM (**Fig. S2g-2h**) and TEM (**Fig. 1e-1g**).

Preparation of GO dispersion

1.0 g commercial graphite and 30 mL concentrated sulfuric acid were mixed in a cooled beaker in ice bath under stirring. 0.15 g $KMnO_4$ was added slowly to the dispersion with the temperature keeping below 10 °C. After 30 min stirring, 3.0 g $KMnO_4$ was added and the temperature was kept no more than 20 °C. The mix continued stirring at 30 °C for 12 h and a mash liquid was obtained. Later, 45 mL deionized water was added with a heating treatment at 95 °C for 15 min. 30 mL 30% H_2O_2 was added and light yellow suspension liquid was obtained. Filtering the suspension liquid and collecting the tawny filter cake, which was further washed by hydrochloric acid (3%) for 3 times. Filter cake was dispersed in 400 mL deionized water and centrifuged to obtain the sediment. After vacuum drying at 60°C for 24 h, GO solid was collected. The GO dispersion was prepared by dispersing GO into deionized water with stirring and ultrasonic treatment, so that the GO dispersion (1 g L^{-1}) was obtained for further utilization. The morphological characteristic was observed by SEM, the SEM samples were prepared by freeze drying (**Fig. S2i-2j**).

Preparation of Ir/rGO

50 mL as-prepared GO dispersion was added into 6.3 g as-prepared Ir colloid solution and the mix was refluxing as well as stirring for 3 h. After cooling down to room temperature, the mix was centrifuged and washed with deionized water for four times. The solid of Ir/rGO was collected after freeze drying for 2 days. The morphological characteristic of the prepared Ir/rGO was observed by SEM (**Fig. S2k-2l**) and TEM (**Fig. 1g-1i**).

Preparation of CNT/GO dispersion

100.0 mg prepared CNTs were dispersed in 100 mL deionized water by stirring and ultrasonic treatment for 2 h. Then, slowly dropping the CNTs suspension into 100 mL GO dispersion under stirring. The mix was kept stirring and ultrasonic treatment for 12 h so that the CNT/GO dispersion was finally obtained. The morphological characteristic was observed by SEM (**Fig. S3m-3n**) and TEM (**Fig. S1i-1k**), the SEM samples were prepared by freeze drying.

Preparation of Ir/CNT/rGO

50 mL as-prepared CNT/GO dispersion was added into 6.8 g as-prepared Ir colloid

solution and the mix was refluxing as well as stirring for 3 h. After cooling down to room temperature, the mix was centrifuged and washed with deionized water for four times. The solid of Ir/CNT/rGO was collected after freeze drying for 2 days. The morphological characteristic of the prepared Ir/CNT/rGO was observed by SEM (**Fig. S2o-2p**) and TEM (**Fig. 1m-1o**).

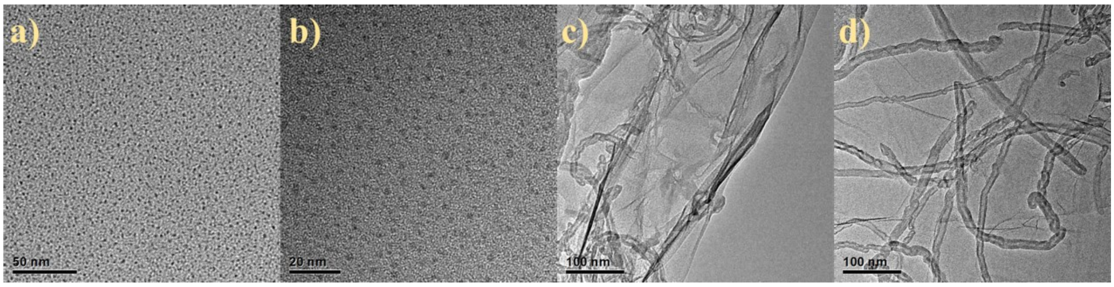

Fig. S1. TEM images of the prepared Ir nanoparticles in the colloid solution (a–b) and the as-prepared composite of CNT/GO (c–d), respectively.

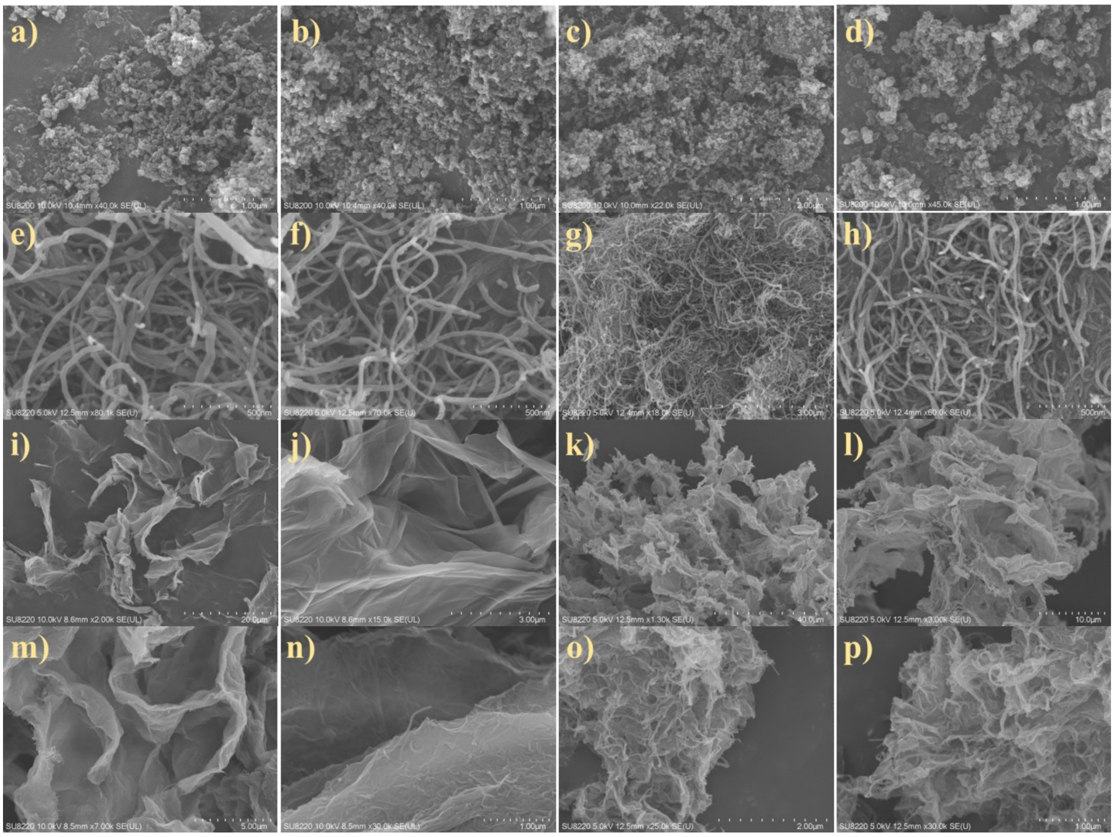

Fig. S2. SEM images of prepared AC (a-b), Ir/AC (c–d), CNT (e–f), Ir/CNT (g–h), GO (i–j), Ir/rGO (k–l), CNT/GO (m–n), and Ir/CNT/rGO (o–p), respectively.

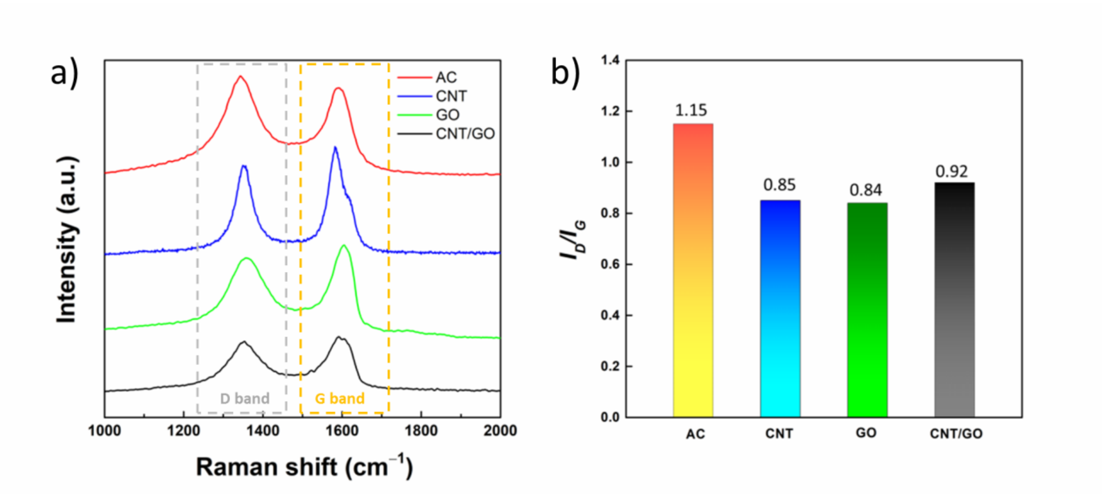

Fig. S3. (a) Raman spectra and (b) I_D/I_G values of the prepared AC, CNT, GO, CNT/GO, respectively.

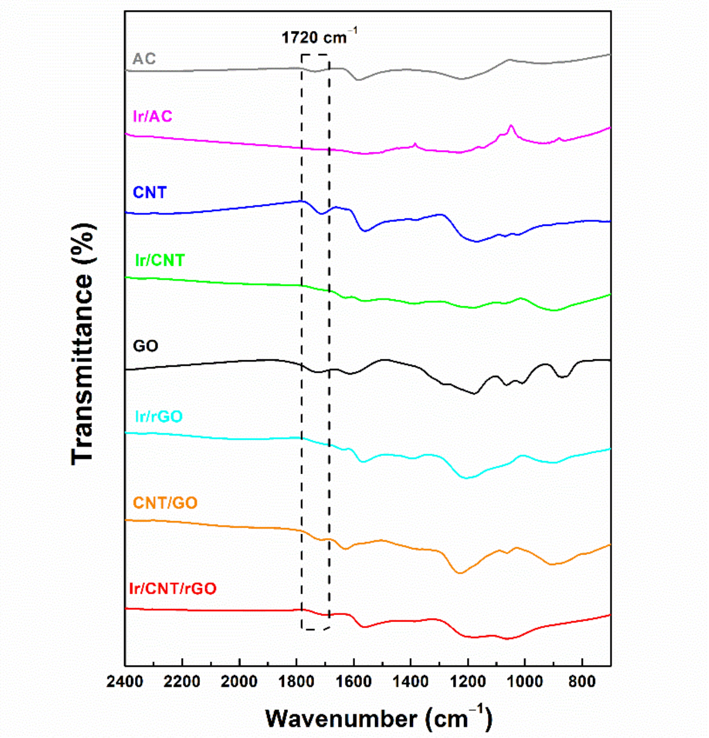

Fig. S4. FTIR spectra (700 cm^{-1}–2400 cm^{-1}) of prepared AC, CNT, GO, CNT/GO, Ir/AC, Ir/CNT, Ir/rGO, and Ir/CNT/rGO, respectively. The peak at 1560 cm^{-1} is the skeleton vibration of graphene-like structure, the peak at 1200 cm^{-1} is the signal of C–OH functional groups, and the peak at 1050 cm^{-1} is the signal of epoxyl groups attaching on benzene ring. –COOH (1720 cm^{-1}), C–O (1050 cm^{-1}), and C–O–C (983 cm^{-1}), disappear and the graphene skeleton (1570 cm^{-1}) and C–OH (shift from 1230 to 1200 cm^{-1}). (refer to Liang, M., Wang, J., Luo, B., Qiu, T., & Zhi, L. (2012). High-Efficiency and Room-Temperature Reduction of Graphene Oxide: A Facile Green Approach Towards Flexible Graphene Films. Small, 8(8), 1180–1184. doi:10.1002/smll.201101968)

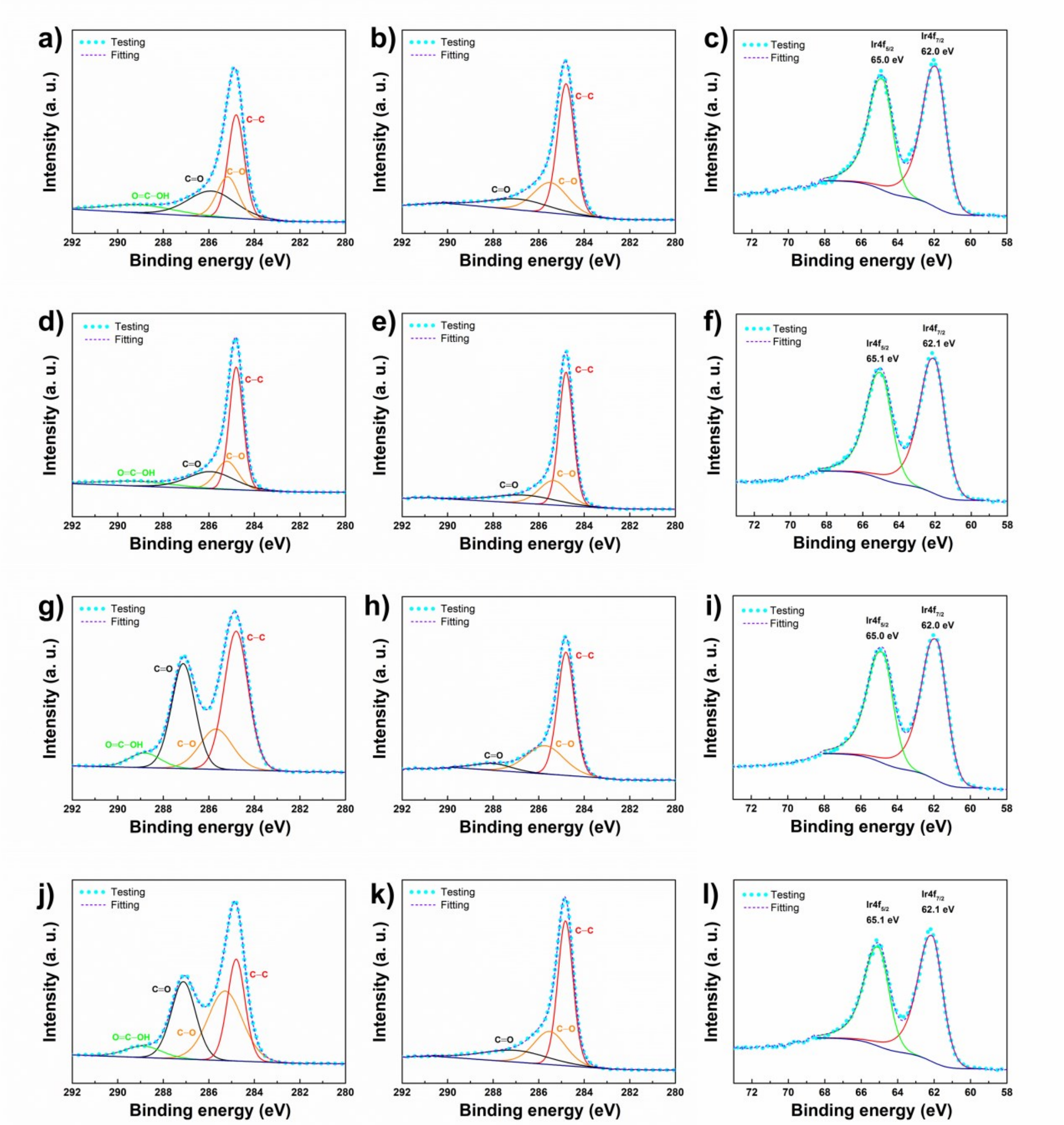

Fig. S5. XPS C1s spectra of prepared AC (a), Ir/AC (b), CNT (d), Ir/CNT (e), GO (g), Ir/rGO (h), CNT/GO (j), Ir/CNT/rGO (k), respectively. XPS Ir4f spectra of prepared Ir/AC (c), Ir/CNT (f), Ir/rGO (i), and Ir/CNT/rGO (l), respectively.

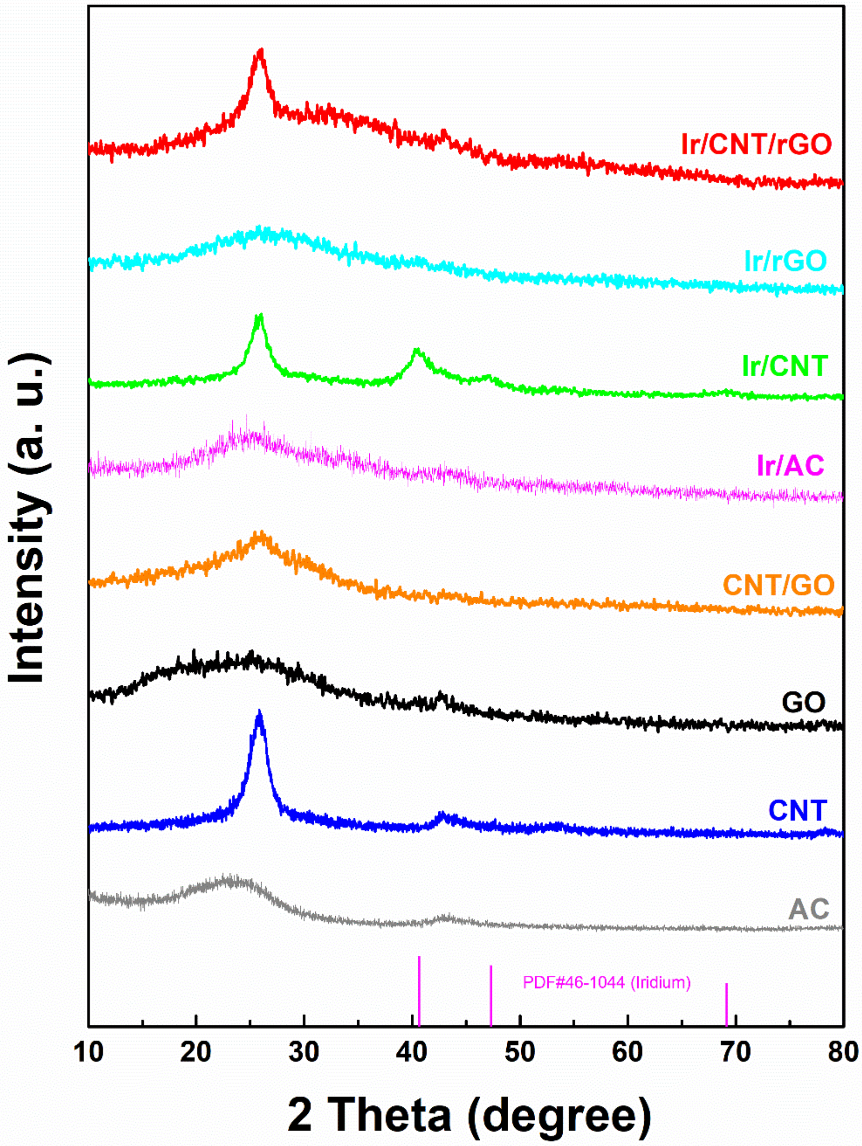

Fig. S6. XRD of prepared CNT, GO, CNT/GO, Ir/CNT, Ir/rGO, and Ir/CNT/rGO, respectively.

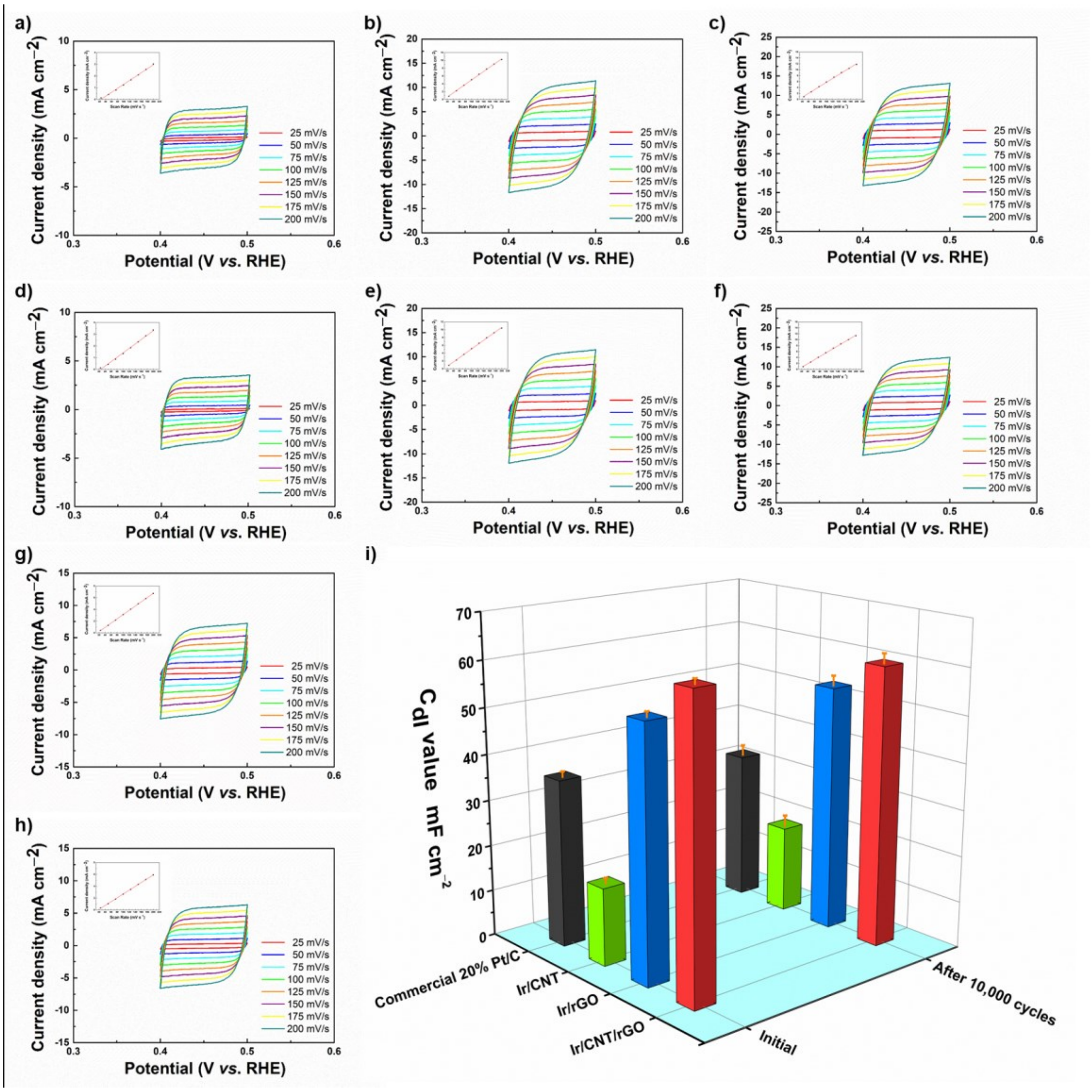

Fig. S7. CV curves of the electrocatalysts of Ir/CNT, Ir/rGO, Ir/CNT/rGO, and commercial 20%Pt/C in initial cycle (a–c,g) and after 10,000 cycles (d–f,h) at different scan rates respectively. (i) The evaluated C_{dl} values of these electrocatalysts before and after 10,000 cycles.

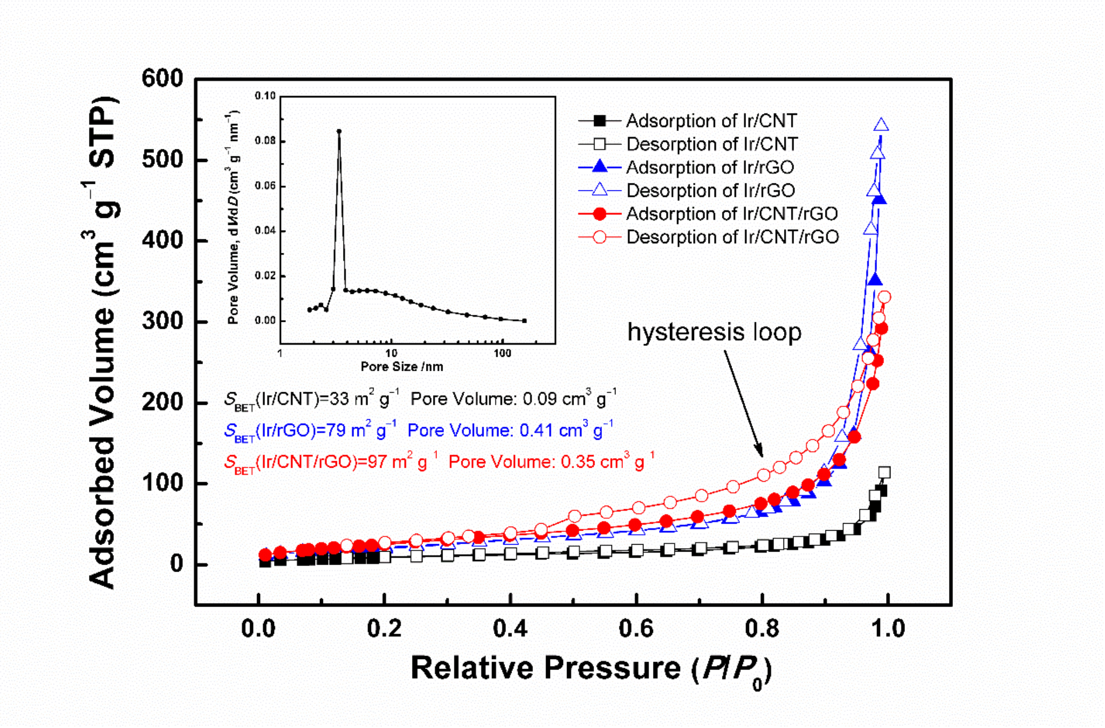

Fig. S8. BET of Ir/CNT, Ir/rGO, and Ir/CNT/rGO. Insert figure: distribution of pore sizes of Ir/CNT/rGO.

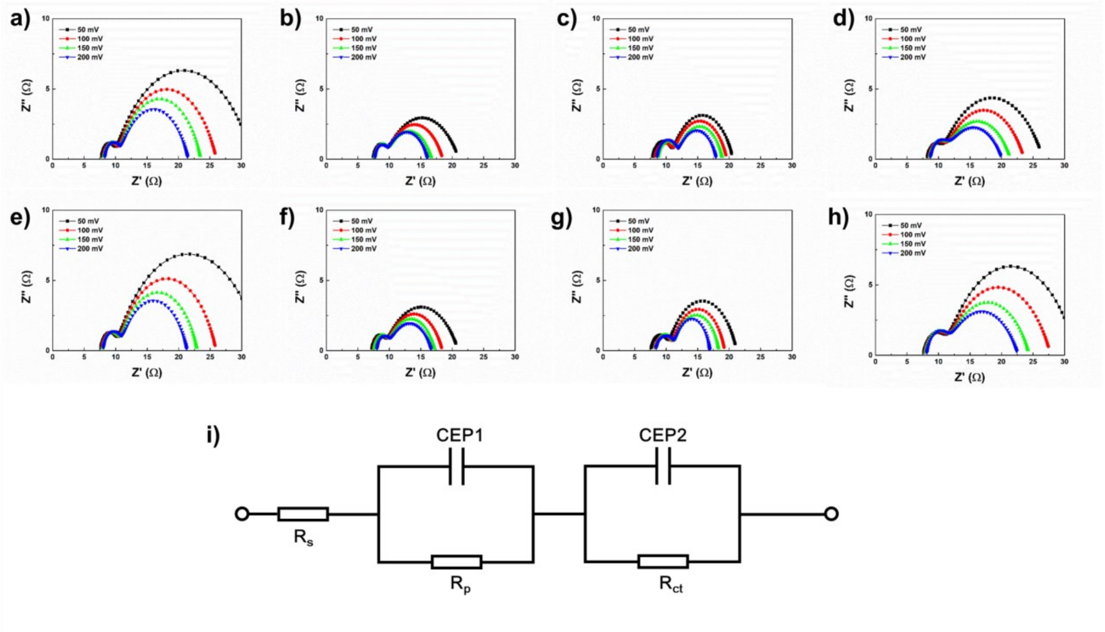

Fig. S9. Nyquist plots of the electrocatalysts of Ir/CNT, Ir/rGO, Ir/CNT/rGO, and commercial 20%Pt/C in the initial cycle (a–d) and after10,000 cycles (e–h) at different overpotentials respectively. (i) the two time-constant model equivalent circuit used for data fitting of EIS spectra (R_s represents the overall series resistance, CPE1 and CPE2 represent the constant phase element and resistance related to surface porosity R_p, and R_{ct} represents the charge transfer resistance related to HER process).

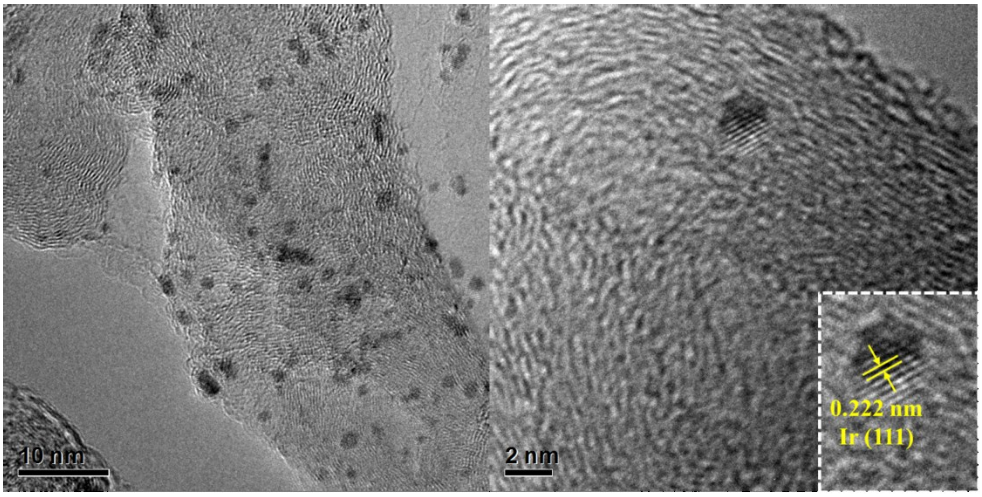

Fig. S10. TEM images of the Ir/CNT/rGO after 10,000 cycles.

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