

Supporting Information

High dispersion of platinum-ruthenium nanoparticles on the 3, 4, 9, 10-perylene tetracarboxylic acid-functionalized carbon nanotubes for methanol electro-oxidation

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1. Experimental Details

Pristine multi-walled carbon nanotubes (CNTs) (length 5-15 μm , diameter 20-60 nm) were purchased from Shenzhen Nanotech Port Co. Ltd., China. 3, 4, 9, 10-perylene tetracarboxylic dianhydride (PTCDA, 98%) was purchased from Alfa Aesar. Ultra-pure N_2 were used for the deaeration of the electrolytes. Other chemicals were of analytical grade and used as received.

3, 4, 9, 10-perylene tetracarboxylic acid (PTCA) was obtained by hydrolyzing PTCDA in a minimal volume of 1.0 M sodium hydroxide [1]. Red deposits appeared in the yellow-green solution and were collected by centrifugation and dried under vacuum at room temperature.

The procedure for the non-covalent functionalization of CNTs with PTCA was as follows: the pristine CNTs (200 mg) were ultrasonicated in 100 mL of ethanol containing 40 mg of PTCA for 2 h, then the pH value of the mixture solution was adjusted to about 9 with 1.0 M KOH aqueous solution. The solution was stirred continuously for 5 h at ambient temperature and held still overnight. After that, the

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mixture was filtered through a nylon 66 membrane, and washed three times with distilled water. The final products, denoted as CNTs-PTCA, were then dried in vacuum oven at 60°C for 12 h. CNTs surface-functionalized with PTCA were characterized by Fourier transform infrared (FTIR) spectroscopy, and Raman spectroscopy.

Acid oxidized-CNTs (CNTs-AO) were obtained by refluxing CNTs in a mixed acid ($\text{H}_2\text{SO}_4:\text{HNO}_3$ in 1:3 v/v ratio) solution at 140 °C for 5 h.

Deposition of PtRu NPs on the CNTs-PTCA was carried out via microwave-assisted reduction process in ethylene glycol solution [2]. The details were as follows: 20 mg of CNTs-PTCA was mixed with 438 μL H_2PtCl_6 (38.6 mM) and 350 μL RuCl_3 (48.2 mM) in ethylene glycol solution under ultrasonication for 30 min. The pH value of the solution was adjusted to 8-9 with 1.0 M KOH aqueous solution. Then, the mixture was placed in a microwave oven and heated by microwave irradiation (800 W) for 10 min at 120 °C. The products were centrifuged and washed three times with distilled water. The obtained PtRu electrocatalysts supported on the CNTs-PTCA, denoted as PtRu/CNTs-PTCA, were dried in vacuum oven at 60 °C for 12 h. For comparison, PtRu NPs supported on the CNTs-AO, labeled as PtRu/CNTs-AO, were prepared under the same procedure as described above. The PtRu loading mass for the PtRu/CNTs-PTCA (or PtRu/CNTs-AO) was determined by Inductively Coupled Plasma-Atom Emission Spectroscopy (ICP-MS), the corresponding results are shown in *Table S1*. Transmission electron microscopy

(TEM, JEM-3010, Jeol, Japan) was applied to characterize the morphology and particle size distribution of PtRu NPs on CNTs.

Table S1. The results of ICP-MS for different CNTs-based nanohybrids

nanohybrids	Pt (wt. %)	Ru (wt. %)
PtRu/CNTs-PTCA	12.94	4.65
PtRu/CNTs-AO	12.68	4.24

For electrochemical investigation, a glassy carbon (GC, 5 mm diameter) electrode was polished with the slurry of 0.5 and 0.03 μm alumina successively and washed ultrasonically in double-distilled water prior to use. The catalyst ink was prepared by dispersing 5 mg of catalyst in 5 mL of water by sonication. When a dark homogeneous dispersion was formed, 40 μL of the ink was dropped onto the glassy carbon electrode using micro-syringe. After dried in air, the electrode was coated with 10 μL of 0.05 wt. % Nafion ethanol solution to fix the catalyst powder.

The electrochemical surface area (ESA) and the electrochemical performance of the electrocatalysts were evaluated by cyclic voltammetry. All electrochemical measurements were performed on a CHI660B electrochemical workstation (Chenhua Instrument Company of Shanghai, China), except the ESA measurement (Autolab PGSTA12). A conventional three electrode glass cell was used with a platinum wire as the counter electrode and a saturated calomel electrode (SCE) as the reference

electrode. All the potentials reported herein were in respect to SCE. Double-distilled water was used throughout.

According to the following equation [3], the ESA value can be obtained from the area of the hydrogen adsorption-desorption peaks after correcting for the double layer charging current from the cyclic voltammograms shown in Fig. 3a.

$$\text{ESA} = Q_{\text{H}} / (0.21 \times [\text{Pt}]) \quad (1)$$

where Q_{H} ($\text{mC}\cdot\text{cm}^{-2}$) represents the mean value between the amounts of charge exchanged during the electro-adsorption (Q_1) and desorption (Q_2) of H_2 on Pt sites, $[\text{Pt}]$ is the Pt loading ($\text{mg}\cdot\text{cm}^{-2}$) on the electrode and 0.21 ($\text{mC}\cdot\text{cm}^{-2}$) represents the charge required to oxidize a monolayer of H_2 on bright Pt. From Fig. 3a, the ESA values of PtRu/CNTs-PTCA and PtRu/CNTs-AO nanohybrids were calculated and summarized in *Table S2*.

Table S2 Hydrogen adsorption and desorption charges and the electrochemical surface area (ESA) of different catalysts

catalysts	[Pt] ($\mu\text{g}\cdot\text{cm}^{-2}$)	Q_1 ($\text{mC}\cdot\text{cm}^{-2}$)	Q_2 ($\text{mC}\cdot\text{cm}^{-2}$)	Q_{H} ($\text{mC}\cdot\text{cm}^{-2}$)	ESA ($\text{m}^2\cdot\text{g}^{-1}$ Pt)
PtRu/CNTs-PTCA	26.38	1.654	2.978	2.316	41.8
PtRu/CNTs-AO	25.85	0.455	2.085	1.270	23.4

2. Raman Spectroscopic Characterization of Carbon Nanotubes with PTCA

Modification

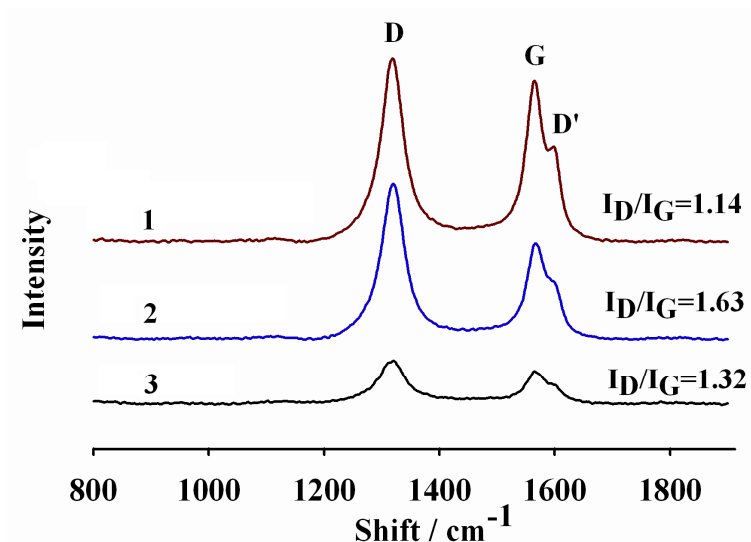


Fig. S1 The Raman spectra of the CNTs-PTCA (1), CNTs-AO (2) and pristine CNTs (3).

The Raman spectroscopy was used to study the structure damage of the pristine CNTs, CNTs-PTCA and CNTs-AO. The corresponding results are shown in *Fig. S1*. It is noted that the peak at 1320 cm⁻¹ should be assigned to the A_{1g} breathing mode of disorder graphite structure (i.e., the D band), and the peak at ~1564 cm⁻¹ assigned to the E_{2g} structure mode of graphite (i.e., the G band). The G band reflects the structure of the sp² hybridized carbon atoms. An additional side band at ~1600cm⁻¹ was also observed, which was assigned as the D' band. Both the D and the D' bands are due to the defect sites in the hexagonal framework of graphite materials [4]. The extent of the defects in graphite materials can be quantified by the intensity ratio of the D to G bands (i.e., I_D/I_G). It is noted from *Fig. S1* that the values of the I_D/I_G ratio are 1.32,

1.63 and 1.14 for the pristine CNTs, CNTs-AO and CNTs-PTCA, respectively. The I_D/I_G value of the pristine CNTs (1.32) is in agreement with that reported in literature [5]. It is notable that the I_D/I_G ratio of the PTCA functionalized-CNTs is smaller than that of the pristine CNTs, indicating that immobilization or wrapping of PTCA on the sidewalls of CNTs via π - π stacking has no detrimental effect on the structure of carbon nanotubes. Rather, the original defect sites on the surface of the pristine CNTs are covered by the PTCA molecules, which may result in the decrease of the I_D/I_G ratio, as reported in literature for the 1-Aminopyrene-Functionalized CNTs [5]. However, as reported previously [5], the value of I_D/I_G ratio of CNTs-AO is higher than that of the pristine CNTs, indicating that the harsh acid treatment causes significant structural damage of CNTs, which would decrease the electronic conductivity of CNTs. The results from *Fig. S1* imply that the CNTs-PTCA should be the promising catalyst support for noble metal NPs in fuel cells.

Reference

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