

Electronic Supplementary Information

Hierarchically structured Pt/CNT@TiO₂ nanocatalysts with ultrahigh stability for low-temperature fuel cells

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1. Experimental section

1.1 Synthesis of hybrid CNT@TiO₂.

Acid-treated (HNO₃ and HCl mixed solution at 120 °C) multi-walled carbon nanotubes (CNTs, 50 mg) were dispersed into 40 mL of isopropyl alcohol (IPA) with sonication for 10 minutes, and then diethylenetriamine (DETA, 0.03 mL) was added into the mixture. After gentle stirring for 2 minutes, 1.8 mL of titanium (IV) isopropoxide (TIP) was added into the obtained solution, which was subsequently transferred into a 60 mL Teflon-lined stainless steel autoclave and kept in an electric oven at 200 °C for 24 h. The autoclave was then taken out of the oven and left to cool down to room temperature. The black precipitate was collected by centrifugation, washed thoroughly with ethanol and dried at 60 °C overnight. The as-prepared CNT@TiO₂ was treated at 400 °C in air for 2 h with a heating rate of 1 °C min⁻¹ to obtain highly crystalline phase.

1.2 Preparation of Pt nanocatalysts.

Pt nanocatalysts on the different supports (CNT, TiO₂ nanosheets (NSs), CNT@TiO₂) were prepared using the polyol process. Firstly, the support powder was dispersed into ethylene glycol (EG) by ultrasonication. Then, a predetermined amount of a Pt

precursor ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) dissolved in EG was added slowly. The mixed solution was heated at a desired temperature of around 140 °C for 3 hours under continuous magnetic stirring. After cooling to room temperature, the material was then filtered, dried at 80 °C for 24 h and stored for further studies. The Pt loading on the support was controlled to be 50 wt. %. Such catalysts prepared using CNT, TiO_2 NSs and $\text{CNT}@\text{TiO}_2$ as supports are denoted as Pt/CNT, Pt/ TiO_2 and Pt/ $\text{CNT}@\text{TiO}_2$, respectively.

1.3 Electrochemical Measurements.

The electrochemical activities of Pt nanocatalysts were characterized by cyclic voltammetry (CV) and chronoamperometry (CA) techniques. The experiments were performed using a three-electrode cell with a CHI660 electrochemical workstation at ambient temperature. The working electrode was a glassy carbon (GC) cylinder with a diameter of 5 mm, and the Pt loading on the GC electrode was controlled to be 0.2 mg cm^{-2} . A saturated calomel electrode (SCE) and a large-area Pt plate were used as the reference electrode and the counter electrode, respectively. The CV profiles were recorded at a scan rate of 20 mV s^{-1} within the potential range from -0.241 to 1V vs. SCE in a 0.5 M H_2SO_4 solution. Methanol oxidation experiments were carried out in 1 M $\text{CH}_3\text{OH} + 0.5$ M H_2SO_4 electrolyte at a scan rate of 10 mV s^{-1} from the potential of -0.241 to 1V vs. SCE.

1.4 Materials Characterization.

The product morphology and microstructure were studied by field-emission scanning electron microscopy (FESEM; JEOL, JSM-6700F, 5 kV), transmission electron microscopy (TEM; JEOL, JEM-2010, 200 kV) and high-resolution transmission electron microscopy (HRTEM; JEOL, JEM-2100F, 200 kV). Selected area electron diffraction (SAED) was performed to study the crystalline and structure of the Pt nanoparticles. Energy dispersive X-ray spectroscopy (EDX) was carried out to analyze the chemical compositions of the samples. Powder X-ray diffraction (XRD) experiments were performed to study the crystallographic information of the samples. XRD patterns were recorded using a Bruker diffractometer with Cu K α radiation (The Bruker, D8 Advance X-ray diffractometer, Cu K α , $\lambda = 1.5406$ Å, 40 kV and 40 mA).

Thermogravimetric analysis (TGA) was carried out under a flow of air with a temperature ramp of 5 °C min⁻¹ from room temperature to 750 °C. The weight ratio of Pt to support for each catalyst was controlled by stoichiometric calculation and confirmed by TGA.

N₂ adsorption/desorption experiments using BET analyzer (Quantachrome Instruments, Autosorb AS-6B) were conducted to investigate the porosity of the as-prepared samples. All samples were outgassed at 200 °C for 6 h prior to the measurement. Nitrogen adsorption/desorption data was recorded at the liquid nitrogen temperature (77K). The specific surface area was calculated according to the BET method from the adsorption data in the relative pressure from 0.01 to 0.35. The pore size distribution was determined by the Barrett-Joyner-Halenda (BJH) method calculated from the desorption branch.

2. The calculation of the electrochemical active specific surface area (ESA)

The ESA of Pt nanocatalysts is calculated with the coulombic charges accumulated during the hydrogen desorption after the deduction of the contribution of the charge from the electric double layer:^[1-4]

$$\text{ESA} = Q_{\text{H}} / (0.21 \times M_{\text{Pt}})$$

Where Q_{H} is the charge due to the hydrogen desorption, 0.21 mC cm⁻² is the electrical charge associated with monolayer adsorption of hydrogen on Pt, and M_{Pt} is the Pt loading on the working electrode.

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3) E. Antolini, L. Giorgi, A. Pozio, E. Passalacqua, *J. Power Sources* **1999**, *77*, 136-142;

4) E. P. Lee, Z. Peng, D. M. Cate, H. Yang, C. T. Campbell, Y. Xia, *J. Am. Chem. Soc.* **2007**, *129*, 10634-10635

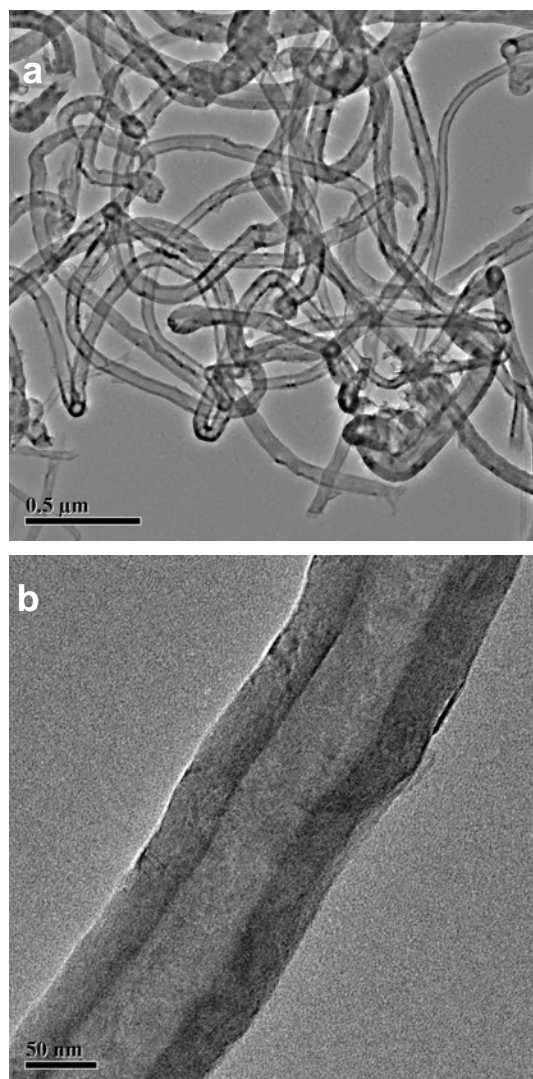


Figure S1. TEM images of multi-walled carbon nanotubes (MWCNT). The average outer diameter of CNTs is ~150 nm.

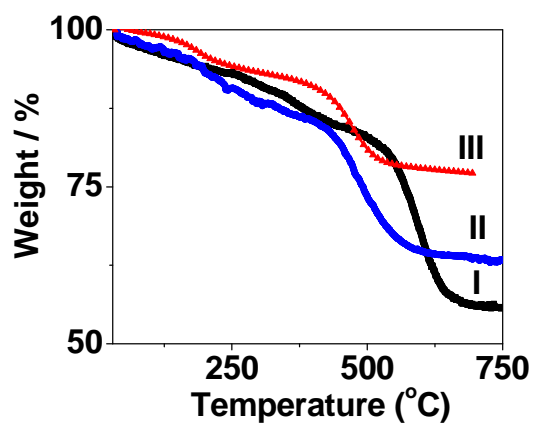


Figure S2. Thermogravimetric analysis (TGA) of CNT@TiO₂ (Sample I) and different Pt nanocatalysts. TGA results indicate that the loading of Pt is about 48 and 18 wt% on CNT@TiO₂, which agree well with the designed amounts (Sample II: 20% Pt/CNT@TiO₂, III: 50% Pt/CNT@TiO₂).

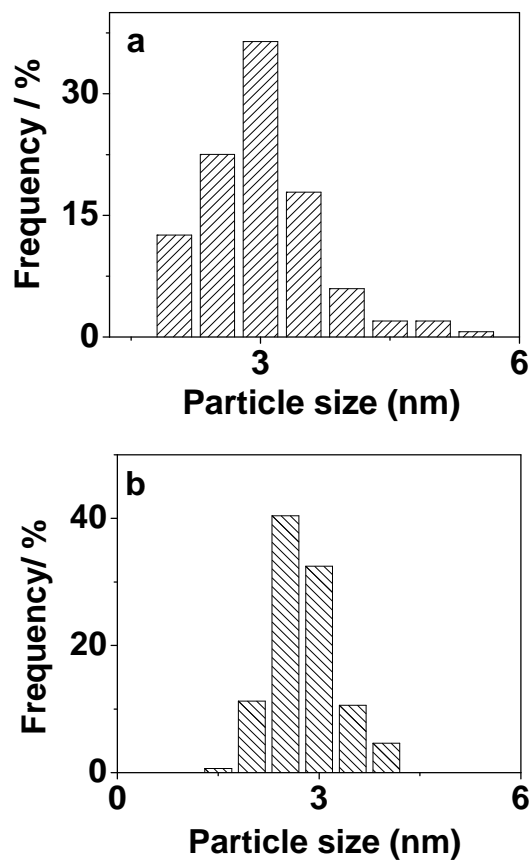


Figure S3. The size distribution of Pt nanoparticles deposited on hybrid CNT@TiO₂ support with different Pt loading (a) 50% and (b) 20%.

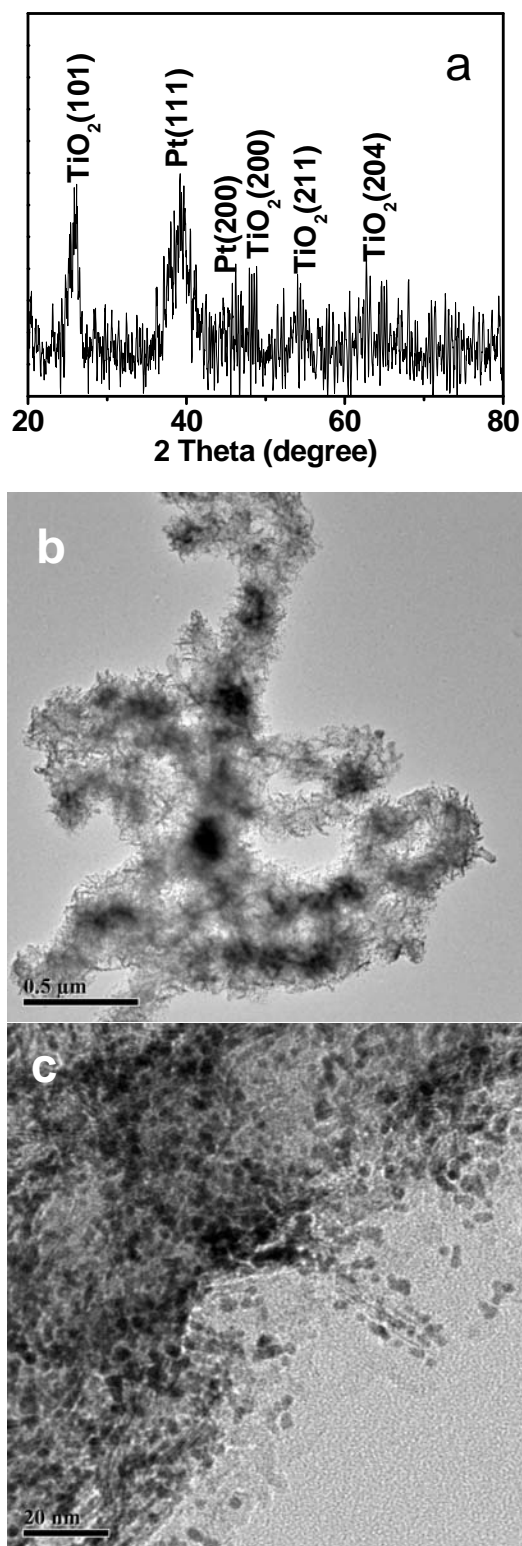


Figure S4. XRD pattern (a) and TEM images (b, c) of 20 wt. % Pt /CNT@TiO₂. The TiO₂ nanosheets grafted on the CNT backbone can be observed clearly, and Pt nanoparticles are dispersed uniformly on these tailored hybrid support.

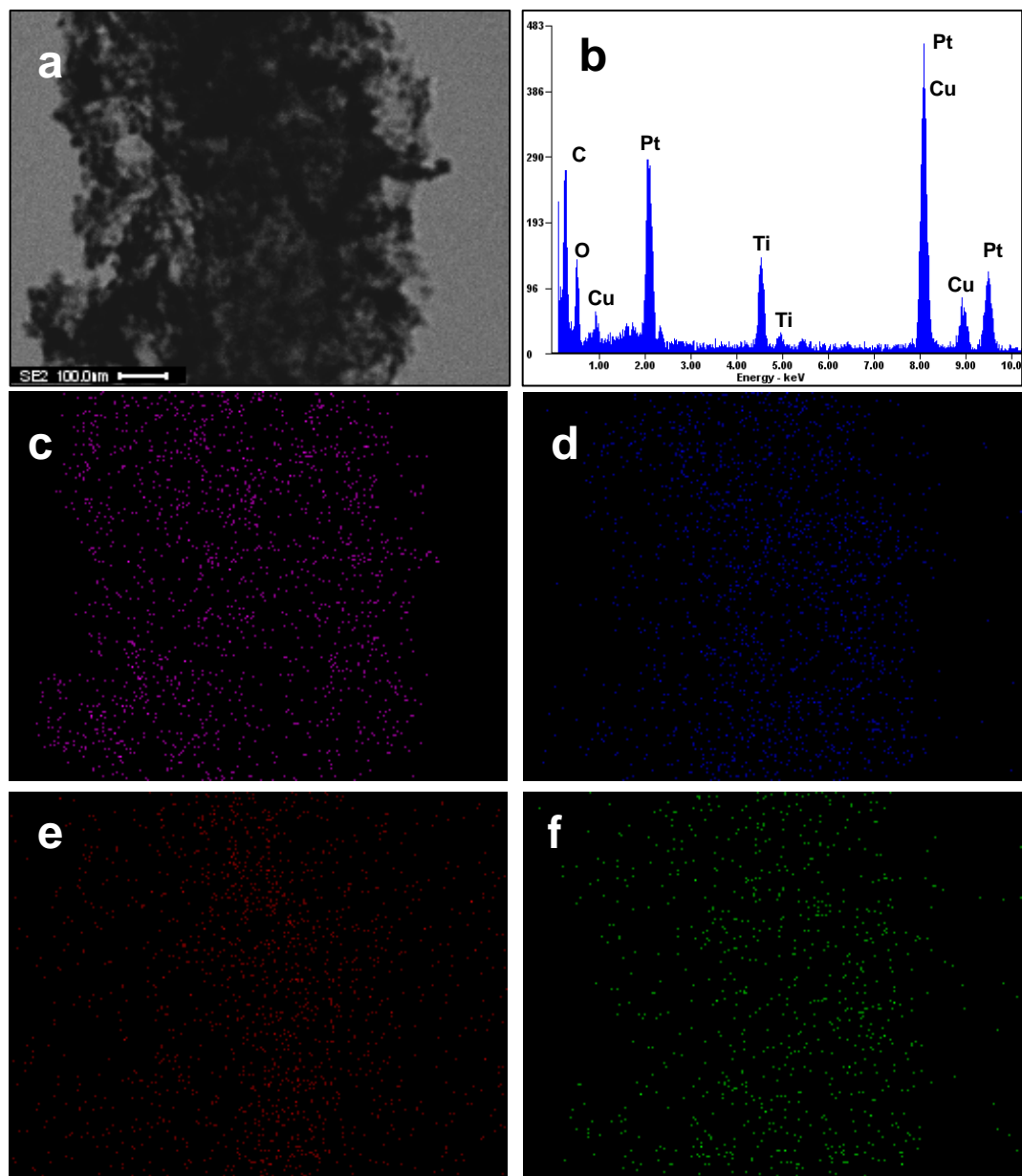


Figure S5. a) TEM image of 50 wt.% Pt/CNT@TiO₂; b) the corresponding EDX pattern; elemental mapping images for: Pt (c), Ti (d), C (e), O (f)

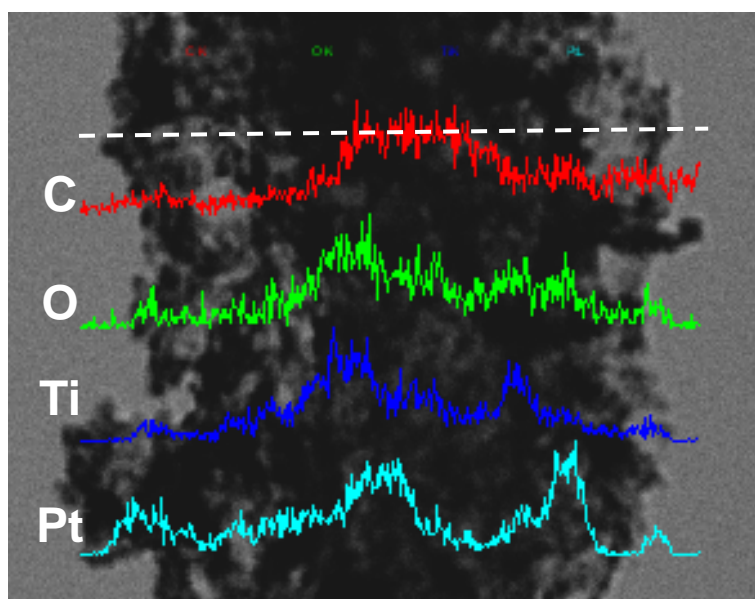


Figure S6. The corresponding line mapping image for 50 wt. % Pt/CNT@TiO₂

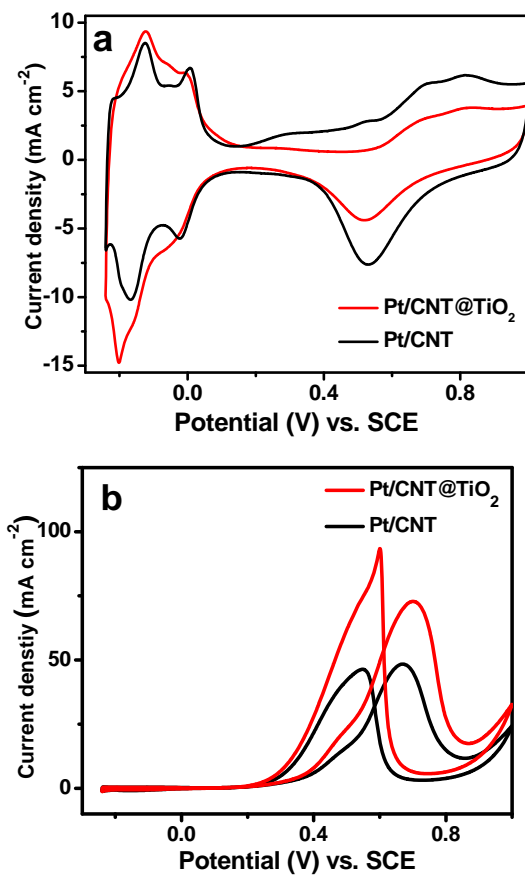


Figure S7. CVs of Pt/CNT and Pt/CNT@TiO₂ in 0.5M H₂SO₄ with a 50 mV s⁻¹ sweep rate (a) and 0.5M H₂SO₄+ 1M CH₃OH solution with a 10 mV s⁻¹ sweep rate. The Pt loading on the electrode is 0.4 mg cm⁻².

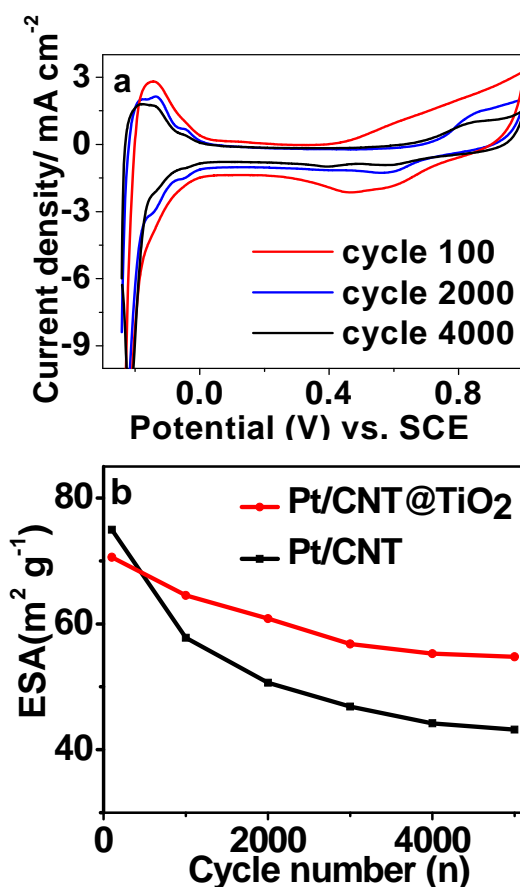


Figure S8. a) CVs for Pt/CNT@TiO₂ recorded at different cycles; b) ESA variation with the cycling number.

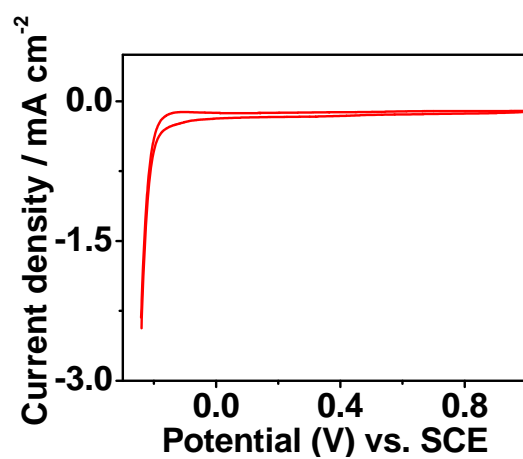


Figure S9. CV for Pt/TiO₂ in 0.5 M H₂SO₄, scanning rate: 20 mV s⁻¹