

Supporting Information for

Pt-Covered Multiwall Carbon Nanotubes for Oxygen Reduction in Fuel Cell Applications

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Synthesis of amine-functionalized multiwall carbon nanotube (MWNTs).

Amine-functionalized MWNTs were synthesized *via* the procedures described in detail elsewhere.¹ 1 g of raw MWNT (95% purity, NANOLAB) was refluxed in a solution consisting of 150 mL of H₂SO₄ (96.7%) and 50 mL of HNO₃ (68 ~ 70%) at 70 °C for 2 hours with stirring, which was then washed in 5% of HCl solution. The oxidized MWNT dispersion was filtrated at least 3 times using a filter paper having 0.5 mm of pore size (PC, Whatman®), which was subsequently dried in air. Carboxylic acid groups on the oxidized MWNTs were chlorinated in 100 mL of thionyl chloride (SOCl₂, Sigma-Aldrich) at 70 °C for 24 hours with stirring and reflux in N₂. After removing remaining SOCl₂ solution by a distillation, the MWNTs were aminated by slowly injecting 5 mL of ethylenediamine (NH₂(CH₂)₂NH₂, 99.5%, Sigma-aldrich) into 100 mL of anhydrous toluene (99.8%, Sigma-aldrich) and stirring at 70 °C for 24 hours under N₂-purged reflux condition. The amine-functionalized MWNT (MWNT-NH₂) powders were dried in vacuum at 50 °C for 24 hours after 3 times of washing steps with ethanol and deionized (DI) water (R = 18.2 MΩ).

Direct current plasma-atomic emission spectroscopy (DCP-AES) analysis.

DCP-AES was used to analyze the weight loading of Pt on the MWNTs using a Beckman spectra Span VI DCP-AES instrument. The Pt on the MWNTs samples were dissolved in concentrated aqua regia and then diluted for analysis. Calibration curves were made from dissolved standards solution in the same acid matrix as the unknowns. This analysis was conducted by Luvac INC.

X-ray photoemission spectroscopy (XPS) characterization of amine- functionalized MWNTs.

XPS analysis was performed to investigate surface chemistry of amine-functionalized MWNTs, as shown in Figure S1. In wide scan survey, O_{1s} and N_{1s} peaks are clearly detected on amine-functionalized MWNTs. The XPS analysis of N_{1s} of MWNT-NH₂ indicates the presence of amide bonds N-C=O (399.8 eV), and amines NH₂ (NH₃⁺) (401.6 eV), showing successful introduction of primary amine groups *via* the formation of amide bonds.¹

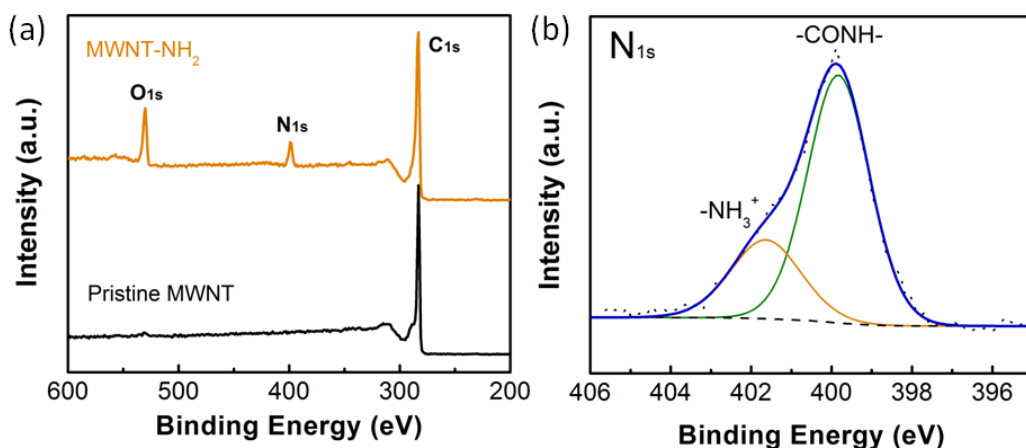


Figure S1. X-ray photoelectron spectroscopy (XPS) spectra of MWNTs. (a) Wide scan survey, (b) MWNT-NH₂ N_{1s} spectra.

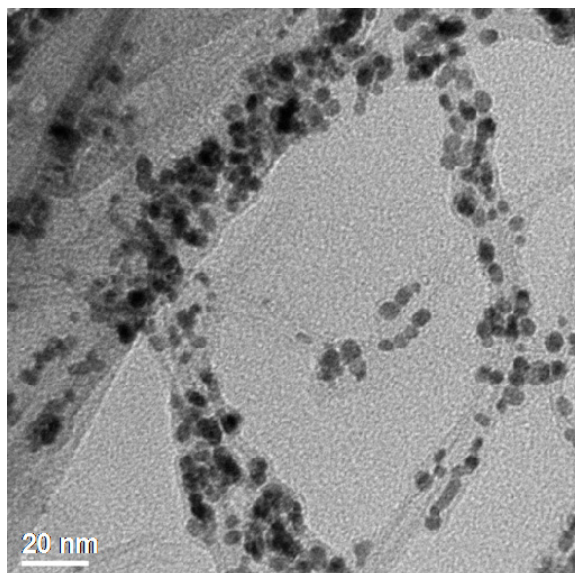


Figure S2. Representative TEM image of Pt NPs on pristine MWNTs following the same ethanol-based polyol process described in this work.

Electrode preparation and electrochemical measurements.

Freshly prepared Pt NPs/MWNTs electrodes were used to measure ORR activity. At first, Pt NPs/MWNT samples were dispersed in Milli-Q (18 M Ω) water *via* ultrasonicator (Sonics & Materials, Inc). Uniform, thin Pt NPs/MWNTs electrodes were prepared on the glassy carbon electrode (5 mm in diameter) by dropping 20 μ L of suspension of Pt NPs/MWNTs. After evaporation of water, dropping 10 μ L of a dilute Nafion[®] solution (0.025 wt%), which was prepared from 5 wt% Nafion[®] solution (Ion Power, Inc.), was followed. Pt loading amount on the glassy carbon electrode is 14.5 μ g_{Pt}/cm²_{electrode}. The SCE potential scale was calibrated with the RHE scale using H₂ electro-oxidation. Cyclic voltammetry experiments were performed in 0.1 M HClO₄ electrolyte with oxygen free condition that was obtained by bubbling ultra high-purity Ar (Airgas) for at least 30 minutes. Cycling was continued with the potential range between 0.05 and 1.1 V vs. RHE to reach steady-state cyclic voltammograms at a scan rate of 50 mV/s.

Determination of electrochemical surface area (ESA) of Pt.

The charge associated with hydrogen under-potential deposition on Pt was obtained from integrating current in the CV data (Figure S3) after double layer current subtraction. Based on 210 μ C/cm²_{Pt} for H_{upd} reported previously,² the ESA of Pt was calculated.

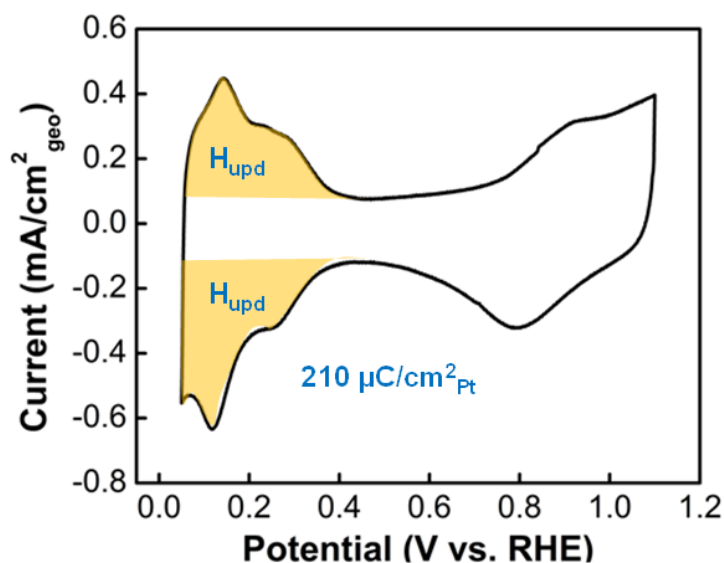


Figure S3. Calculation of electrochemical active surface area (ESA) of Pt.

Analysis of the kinetic current from RDE measurements (Koutecky-Levich analysis).

The oxygen reduction reaction (ORR) activity of Pt NPs/MWNTs samples was measured by sweep voltammetry in O₂-saturated HClO₄ using a rotating disk electrode at room temperature. After the electrolyte was purged with pure oxygen (O₂) for at least 30 min, polarization curves were recorded between 0.1 and 1.1 V (RHE) under a voltage sweep rate of 10 mV/s at room temperature. The Pt specific kinetic activity (j_k , mA/cm²_{Pt}) of Pt NPs/MWNTs was calculated from Koutecky-Levich analysis and ESA of Pt. All the shown ORR currents were obtained after background current subtraction and used for Koutecky-Levich analysis.

In order to obtain insights into the electrocatalytic kinetics of ORR on the prepared 1-dimensional Pt NPs/MWNTs, analysis of the data in Figure 3(b) using Koutecky-Levich equation³ (1) was performed, assuming that the geometric RDE current density (mA/cm²_{geo}) consists of kinetic (i_k) and diffusion (i_d) components:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} = \frac{1}{nFAkC_{O_2}} + \frac{1}{0.62nFAD_{O_2}^{2/3}\nu^{-1/6}C_{O_2}\omega^{1/2}} = \frac{1}{i_k} + \frac{1}{Bc_{O_2}\omega^{1/2}} \quad (1)$$

where i is the measured current after background subtraction in the positive sweep direction, n is the number of electrons in the O₂ reduction reaction, F is the Faraday constant (96485 C/mol), A is the geometric electrode area, D is the diffusion coefficient of O₂ (1.93×10^{-5} cm²/s) in solution, ν (1.00×10^{-2} cm²/s) is the kinematic viscosity of the electrolyte, C_{O_2} (1.22×10^{-6} mol/cm³) is the O₂ solubility in the electrolyte, and ω is the rotation rate.² Equation (1) can be simply formed by equation (2).

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{Bc_{O_2}^b\omega^{1/2}} \quad (2)$$

The Koutecky-Levich plots (i^{-1} vs $\omega^{-1/2}$) at four different potentials 0.85 V, 0.80 V, 0.75 V and 0.70 V vs. RHE in the positive sweep are shown in Figure 3(c), where kinetic currents for O₂ reduction, i_k , were calculated based on the equation (1); having these Bc_{O_2} values, Equation (2), kinetic currents (i_k) as a function of potential were calculated from equation (3).

$$i_k = \frac{i \times i_d}{i_d - i} \quad (3)$$

The linearity and parallelism of the plots is usually taken as an indication of first-order reaction kinetics with respect to dissolved O_2 (Figure 3(c)). Finally, the calculated i_k was normalized by the ESA of Pt to compare specific activity of the ORR as shown in Figure 3(d). The specific activity in Figure 3(d) is the uncompensated ohmic electrolyte resistance ($\sim 35 \Omega$) measured *via* high frequency ac impedance in O_2 -saturated 0.1 M $HClO_4$ by the following equation: $E_{iR-corrected} = E_{applied} - iR$, where i is ORR current and R is the uncompensated ohmic electrolyte resistance.

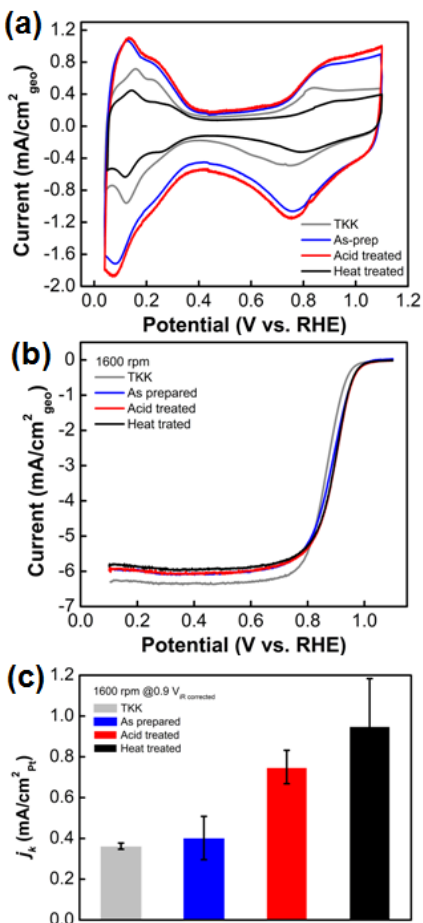


Figure S4. Intrinsic ORR activity comparison at room temperature. (a) cyclic voltammetry of 46 wt% Pt/C (gray, TKK, $9.9 \mu g_{Pt}/cm^2_{geo}$), as-prepared, acid-treated (blue) and acid-treated (red), heat-treated 31 wt% Pt NPs/MWNTs (black, $14.5 \mu g_{Pt}/cm^2_{geo}$) in Ar-saturated 0.1 M $HClO_4$ and at a scan rate of 50 mV/s, (b) ORR measurements by RDE at 1600 rpm, a scan rate of 10 mV/s in O_2 -saturated 0.1 M $HClO_4$, all the shown ORR measured currents are after background current subtraction and (c) specific activity comparison at 0.9 V_{iR corrected}.

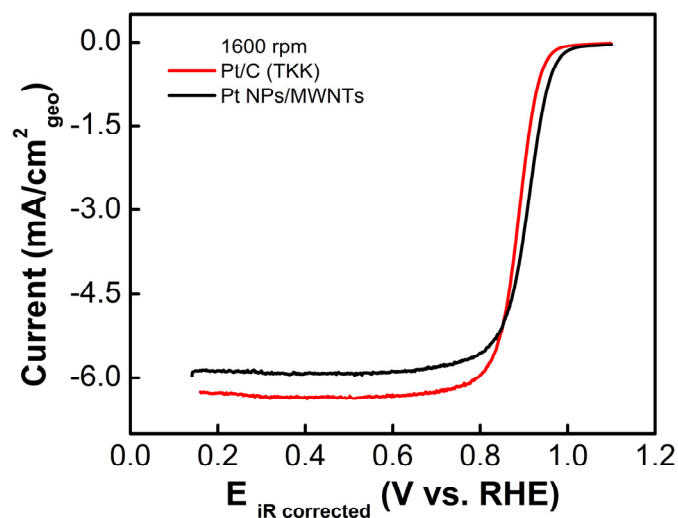


Figure S5. Oxygen reduction polarization curves (46 wt% Pt/C, TKK; $9.9 \mu\text{g}_{\text{Pt}}/\text{cm}^2_{\text{geo}}$ and acid-treated, heat-treated 31 wt% Pt NPs/MWNTs, $14.5 \mu\text{g}_{\text{Pt}}/\text{cm}^2_{\text{geo}}$) collected from a positive-going potential sweep at a 10 mV/s scan rate in 0.1 M HClO_4 , at room temperature. The potential was obtained after iR correction from high frequency ac impedance measurement in O_2 -saturated 0.1 M HClO_4 .

References

1. Lee, S. W.; Kim, B.-S.; Chen, S.; Shao-Horn, Y.; Hammond, P. T. Layer-by-Layer Assembly of All Carbon Nanotube Ultrathin Films for Electrochemical Applications. *J. Am. Chem. Soc.* **2009**, *131*, 671-679.
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