SUPPORTING INFORMATION

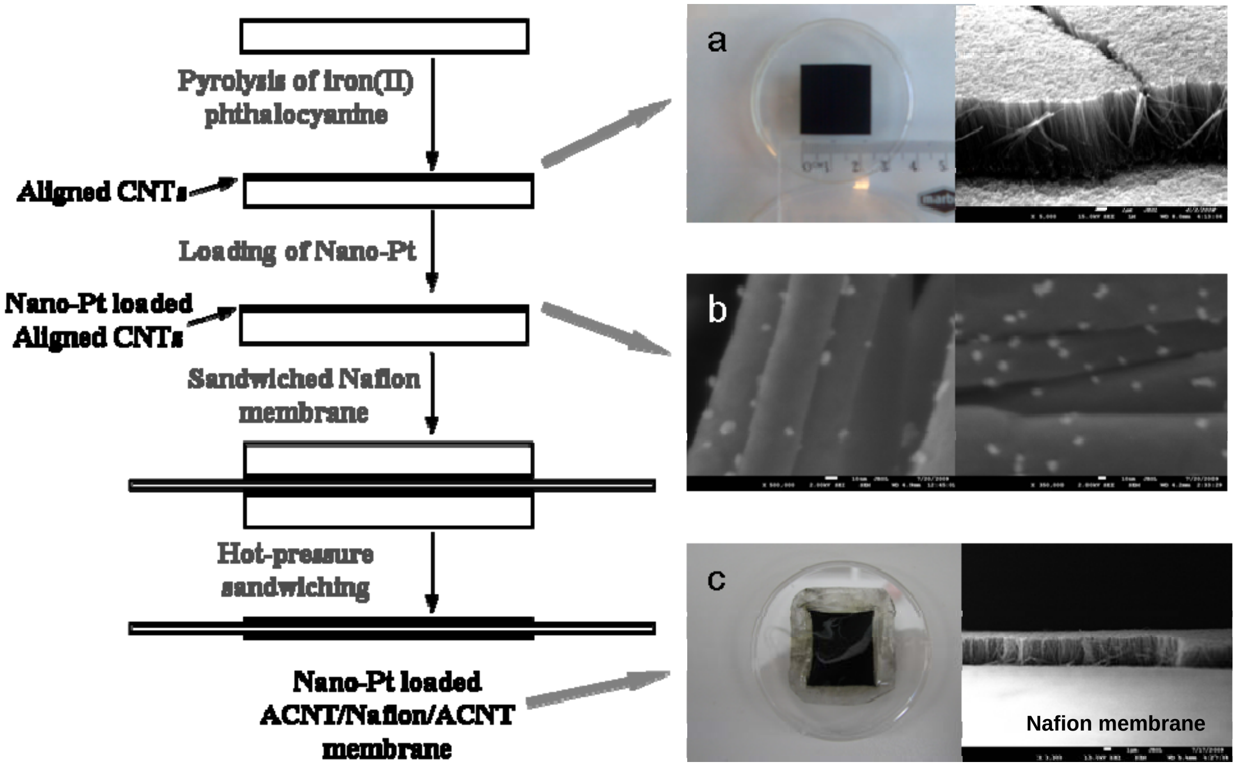

Figure S1. Schematic procedures of the preparation of Nano-Pt loaded ACNT/Nafion/ACNT membrane electrodes. Digital and SEM images of (1a) aligned CNT arrays; (1b) Nano-Pt loaded ACNTs; (1c) Nano-Pt loaded ACNT/Nafion/ACNT membrane.

Preparation of Nano-Pt loaded ACNT/Nafion/ACNT Membrane Electrode

Figure S1 displays the schematic procedures involved in preparing a free-standing sandwich-structure, nano-Pt-loaded ACNT/Nafion/ACNT membrane electrode for use in a PEM fuel cell. Firstly, short-length (3-4 μm), aligned CNT arrays were deposited onto a quartz plate (5 cm^2, the size required for testing in a single fuel cell) (Figure S1a, top left image) via the pyrolysis of iron(II) phthalocyanine,[17] with controlled CVD growth time (Figure S1a, right SEM image). Pt nanoparticles were then loaded onto the aligned CNT arrays by controlled chemical reduction from 5 mM H_2PtCl_6 solution using $NaBH_4$ (20 mM) as the reductant. The SEM images in Figure S1b clearly show that nanosized Pt particles were successfully deposited onto individual nanotubes in the aligned CNT arrays. **2.5 mL of 0.05 wt% diluted Nafion solution in isopropanol was uniformly cast onto the nano-Pt loaded ACNT arrays.** Then two pieces of nano-Pt-loaded ACNT modified quartz plates (5 cm^2 each) were then fabricated into a sandwich structure with a Nafion membrane in the middle (Nafion$^{@}$115, 0.005in thick, from Aldrich). The entire sandwich fabrication was placed in a PHI (model 210C) hot hydraulic compression press system at 160 ºC with an external pressure of 5,000 *psi* for 2 min in order to transfer the nano-Pt loaded ACNT arrays from the quartz plates to the Nafion membrane. Finally, the free standing sandwich-structure nano-Pt-loaded ACNT/Nafion/ACNT membrane electrode was peeled off from the quartz plates, after which it was cooled down to room temperature. Figure S1c shows the digital (left) and SEM (right) images of the resulting membrane electrode, which maintained the aligned CNT array structure. This kind of 3D nano-Pt-loaded ACNT/Nafion/ACNT PEM membrane electrode was then ready to be tested in a single fuel cell.

Preparation of Pt/C MEA and the Fuel Cell Testing

Pt/C coated MEA was prepared by the conventional brushing method. The platinum loading level on both sides was 0.142 mg Pt cm^{-2} in order to compare with nano-Pt loaded ACNT/Nafion/ACNT. The fuel cell testing was performed using a 850e fuel cell test system (Scribner Associates, Inc., USA) in a single fuel cell hardware assembly (Fuel Cell Technologies, Inc., USA) according to the same procedure as that of nano-Pt loaded ACNT/Nafion/ACNT. The fuel cells were fed with fully humidified pure H_2 and O_2, respectively. The dimension of the MEAs used in the testing single-cell was 5 cm^2. The gas flow rates were fixed at 0.08 L min^{-1}. The fuel cell measurements were carried out at 80 ℃ under 100 kPa back pressure. The polarization curves were recorded using a scan current method by holding the cell at each current-density value for 60 s in order to obtain the steady-state voltage value.

Electrochemically Active Surface Area (ECSA)

In this study, in situ cyclic voltammetry (CV) measurements were performed to determine the catalytic activity using a special "hydrogen-pump-mode" configuration. In these measurements, high purity nitrogen gas was passed through the cathode instead of oxygen, while the anode was supplied with hydrogen. The CV measurements were conducted using an EG&G 283 potentiostat/galvanostat (Princeton Applied Research, USA) by sweeping the voltage of the testing single fuel cell between 0.08 V and 1.00 V with respect to the anode, at a scan rate of 25 mV s^{-1}. Figure S2 shows in situ cyclic voltammograms for H adsorption on a nano-Pt-loaded electrode and a commercial Pt/CB electrode. Characteristic peaks in the region 0.1 - 0.4 V are attributed to atomic hydrogen adsorption/desorption on the Pt surface and indicate the electrochemically active surface area (ECSA) of the Pt. The integrated area of the cyclic voltammogram represents Q_H, which can be used to determine the ECSA using the expression:[19,20]

$$\mathrm{ECSA[cm^2/g]} = \frac{Q_{\mathrm{H}}[\mu\mathrm{C/cm^2}]}{2\times\{210[\mu\mathrm{C/cm^2}]\times\mathrm{Pt\,loadings[gPt/cm^2]}\}}$$

The nano-Pt-loaded membrane electrode displayed an increased specific charge transfer for the characteristic peaks when compared with the commercial Pt/CB electrode having the same Pt loading level. The ECSA of nano-Pt loaded electrode and commercial Pt/CB electrode were calculated to be 78.72 m^2 g^{-1} Pt and 52.22 m^2 g^{-1} Pt, respectively.

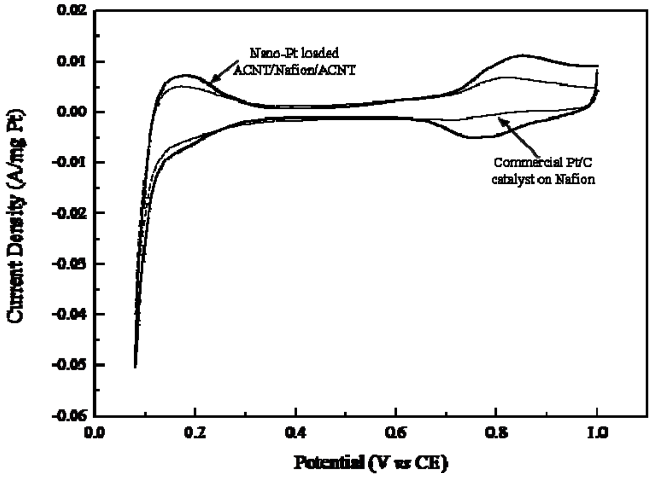

Figure S2. The in-situ cyclic voltammograms of nano-Pt-loaded ACNT/Nafion/ACNT and commercial Pt/CB-loaded electrodes obtained by sweeping the voltage of the testing single fuel cell between 0.08 V and 1.00 V with respect to the anode, at a scan rate of 25 mV s^{-1}.

Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectra for the fuel cell with nano-Pt-loaded electrodes operating under fully humidified conditions (100 % RH) are shown in Figure S3. A built-in 880 impedance analyzer (Scribner Associates, USA) was used to perform electrochemical impedance spectroscopy (EIS) measurements in the range of 10 k-0.1 Hz at 100 mA cm^{-2}. The perturbing amplitude was 10% of the DC current applied to the cell. The EIS spectra (Figure S3) show that the single fuel cell using nano-Pt-loaded ACNT/Nafion/ACNT membrane electrodes has much lower kinetic resistance (relative to the whole cell reaction) compared to the one using Pt/CB catalyst.

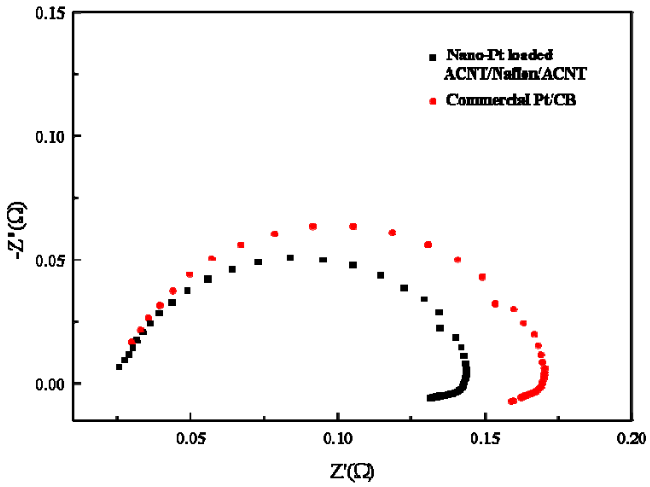

Figure S3. Electrochemical impedance spectra of the tested single fuel cells using nano-Pt-loaded ACNT/Nafion/ACNT and commercial Pt/CB-loaded electrodes.