

Supplementary Data

1. Synthesis of supported Pt catalysts

The supported Pt catalysts were prepared by the ethylene glycol reduction as reported previously. In a typical process, 50 mg of the carbon supports was ultrasonically dispersed in 50 mL EG for half hour. Then 370 μL EG solution of H_2PtCl_6 (33.6 mg Pt/mL) and 270 μL EG solution of NaOH (1.0 mol/L) were added with magnetic stirring. The whole solution was heated at 120 $^\circ\text{C}$ for 2 h with magnetic stirring. The catalyst product was vacuum-filtered and washed by a large amount of deionized water, then dried at 60 $^\circ\text{C}$ in air for 2 h. The weight calculation showed that the Pt loading was consistent with the nominal content (20 wt%), indicating a complete metal loading.

2. Characterization

Transmission electron microscopy (TEM) was performed on JEOL-2100F operated at 200KV. To prepare the TEM sample, a small amount of catalyst was ultrasonically dispersed in ethanol. A drop of such suspension was dropped onto a 200 mesh Cu grid with holey carbon film and then dried in air completely. Powdered X-ray diffraction (XRD) was performed with a filtered Cu-K α radiation. The 2θ angular range between 15 $^\circ$ and 90 $^\circ$ was explored at a scanning rate of 4 $^\circ$ /min in the resolution of 0.02 $^\circ$.

3. Electrochemical measurements

The electrochemical measurements were performed on Solartron 1280 electrochemical workstation in a single compartment with three-electrode cell at room temperature. A glassy carbon electrode (GCE) with geometric surface area of 0.07 cm^2 was used for the preparation of working electrode. A powder sample of 10 mg was dispersed in the solution containing 900 μL isopropanol and 100 μL Nafion solution (5wt %, EI DuPont), and then ultrasonically dispersed for 15 min to form a uniform suspension. Then 1.0 μL portion of the suspension was dropped onto the GCE to form a uniform catalyst layer and then dried at 60 $^\circ\text{C}$ for 30 min. Measurements on rotating disk electrode (RDE) were carried out on a BAS RDE-2 rotator (Bioanalytical Systems, Inc.). A Pt wire was used as the counter electrode and Hg/Hg $_2\text{SO}_4$ electrode was used as the reference electrode. All potentials referred in this paper are with respect to the normal hydrogen electrode (NHE). Accelerated durability tests (ADT) were performed by repeated cyclic voltammetry between 0 and 1.2 V at a scanning rate of 100 mV/s in 0.1 mol/L HClO $_4$ or 0.1 mol/L HClO $_4$ containing 0.01 mol/L methanol under air. After a certain cycles, voltammogram were recorded at a scanning rate of 50 mV/s in N $_2$ saturated 0.1 mol/L HClO $_4$ or 0.1 mol/L HClO $_4$ containing 0.01 mol/L methanol.

4. Single fuel cell test

The single cell performance was evaluated using a DMFC single cell with a 10 cm^2 cross-sectional catalyst area. The anode (PtRu/Vulcan catalysts, 2.0 mg cm^{-2} of PtRu,) and cathode (0.8 mg cm^{-2} of Pt) catalyst layers were formed on carbon paper (TGP-H-090, Toray) substrates using catalyst slurries containing 15 wt% and 10 wt% Nafion, respectively. The membrane electrode assembly was fabricated by hot-pressing (135 $^\circ\text{C}$, 5 MPa, 2 min) a Nafion 117 membrane (DuPont) with anode and cathode on each side. A 2.0 mol L $^{-1}$ methanol solution was pumped through the anode at a rate of 3.0 mL min $^{-1}$, while pure O $_2$ gas was fed to the cathode at a rate of 500 mL min $^{-1}$.

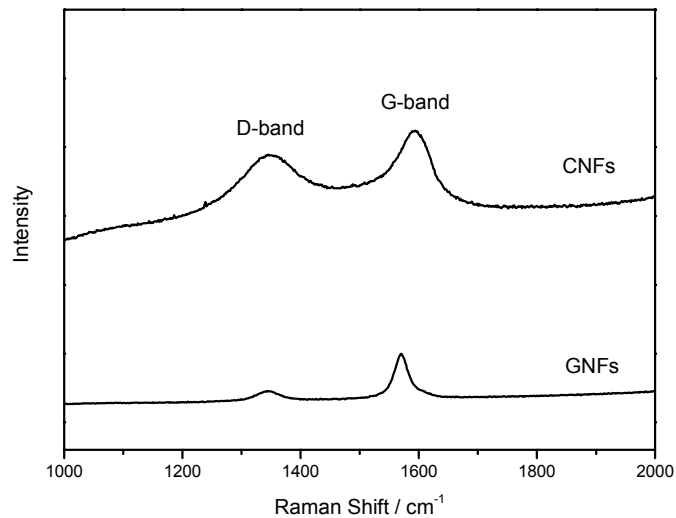


Fig. S1 Raman spectra of CNFs and GNFs. The intensity ratio of G-band to D-band for GNFs is 5.5, which is much higher than that for CNFs (1.4), suggesting a higher graphitization degree of GNFs.

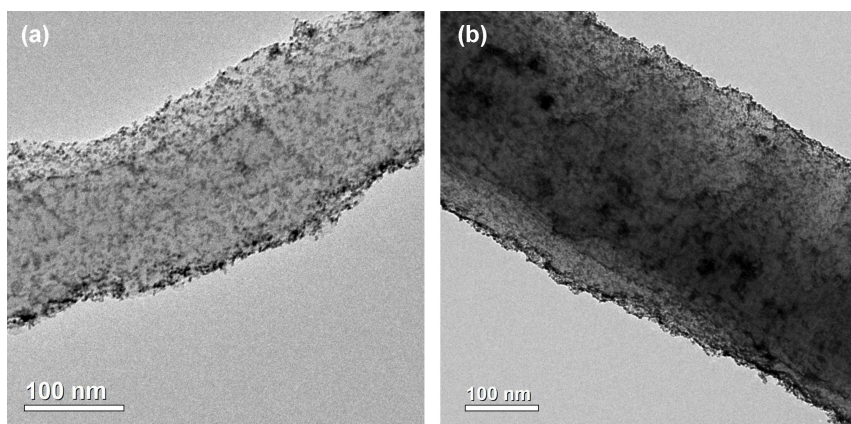


Fig. S2 TEM images of Pt/CNF (a) and Pt/GNF (b) catalyst

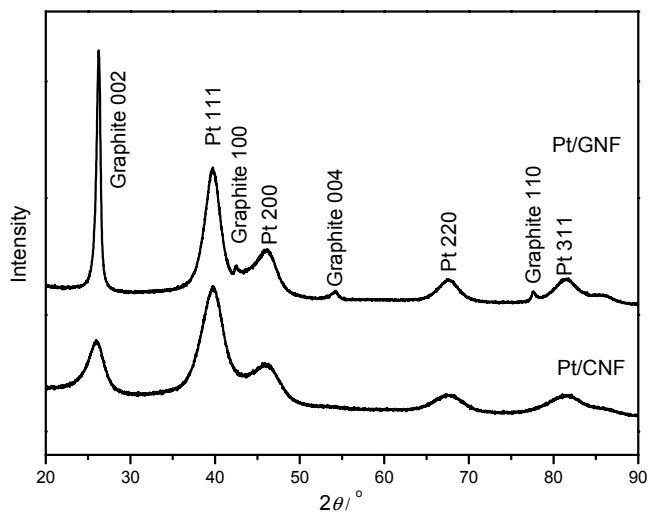


Fig. S3 XRD patterns of the Pt/GNF and Pt/CNF catalyst.

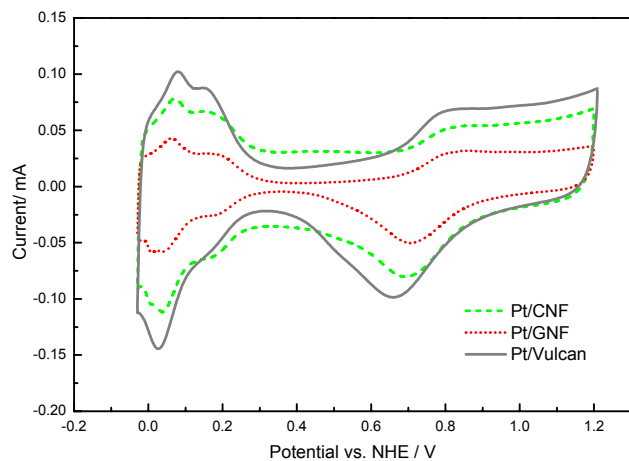


Fig. S4 Cyclic voltammogram of different catalysts in N_2 saturated 0.1 mol/L $HClO_4$ aqueous solution at a scanning rate of 50 mV/s. The electrochemical surface area (ESA) of Pt evaluated from the hydrogen adsorption and desorption for Pt/CNF, Pt/GNF and Pt/Vulcan catalyst are 42, 39 and 76 m^2/g , respectively.

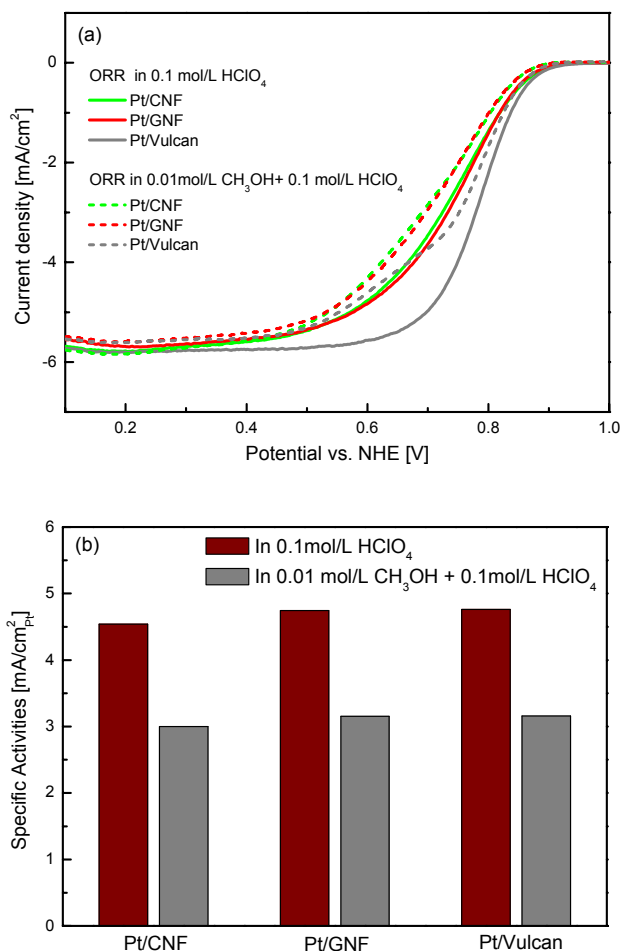


Fig. S5 (a) Voltammogram of different catalysts on rotating disk electrode at 1600 rpm with a scanning rate of 20 mV/s in O₂ saturated 0.1 mol/L HClO₄ (solid line) and 0.1 mol/L HClO₄ containing 0.01 mol/L CH₃OH (dash line). The currents were normalized to the geometric surface area of the electrode (0.07 cm²). (b) Comparison of ORR specific activities of different catalysts. The specific activity was estimated from the kinetic reduction current i_k at 0.8V ($i_k = i_d / (i_d - i)$, where i_d is diffusion-limited current and i is the apparent current) that was then normalized to the ESA of Pt.

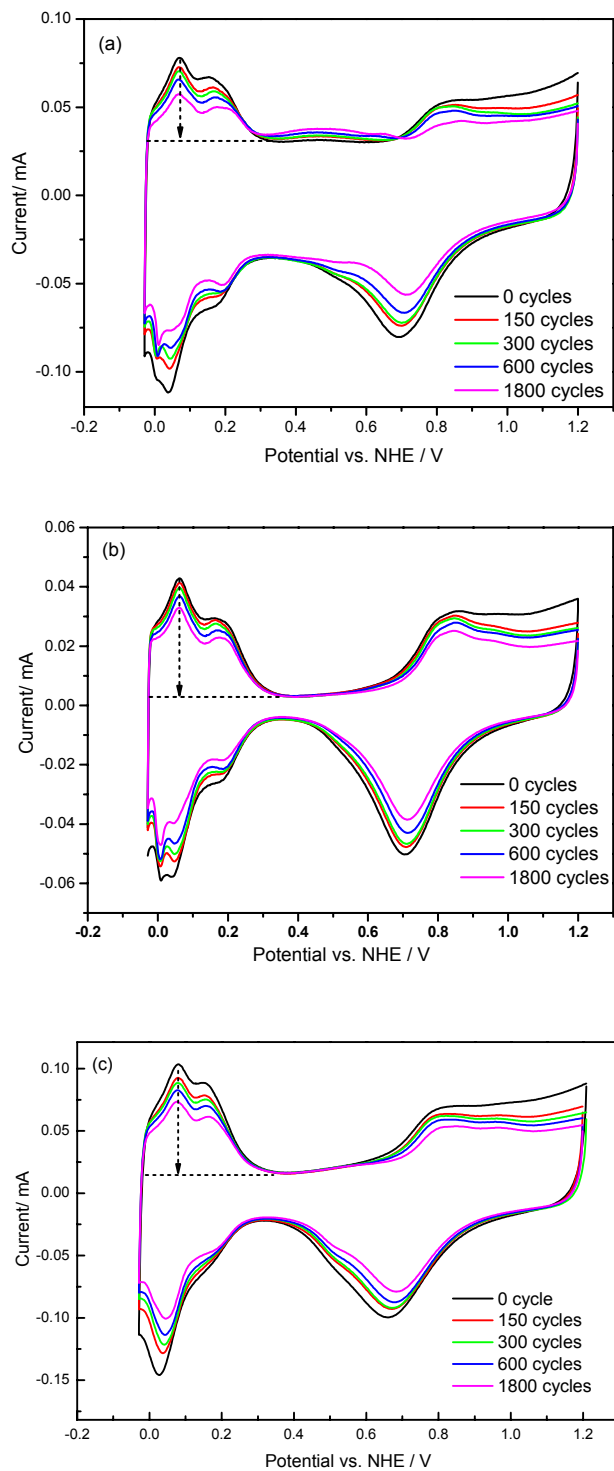


Fig. S6 Voltammogram of (a) Pt/CNF, (b) Pt/GNF and (c) Pt/Vulcan catalyst at the scanning rate of 50 mV/s in N_2 saturated 0.1 mol/L $HClO_4$ aqueous after 150, 300, 600 and 1800 cycles of ADT tests. The dash arrows show decreasing currents associated with hydrogen desorption, indicating decreasing ESA during the ADT tests.

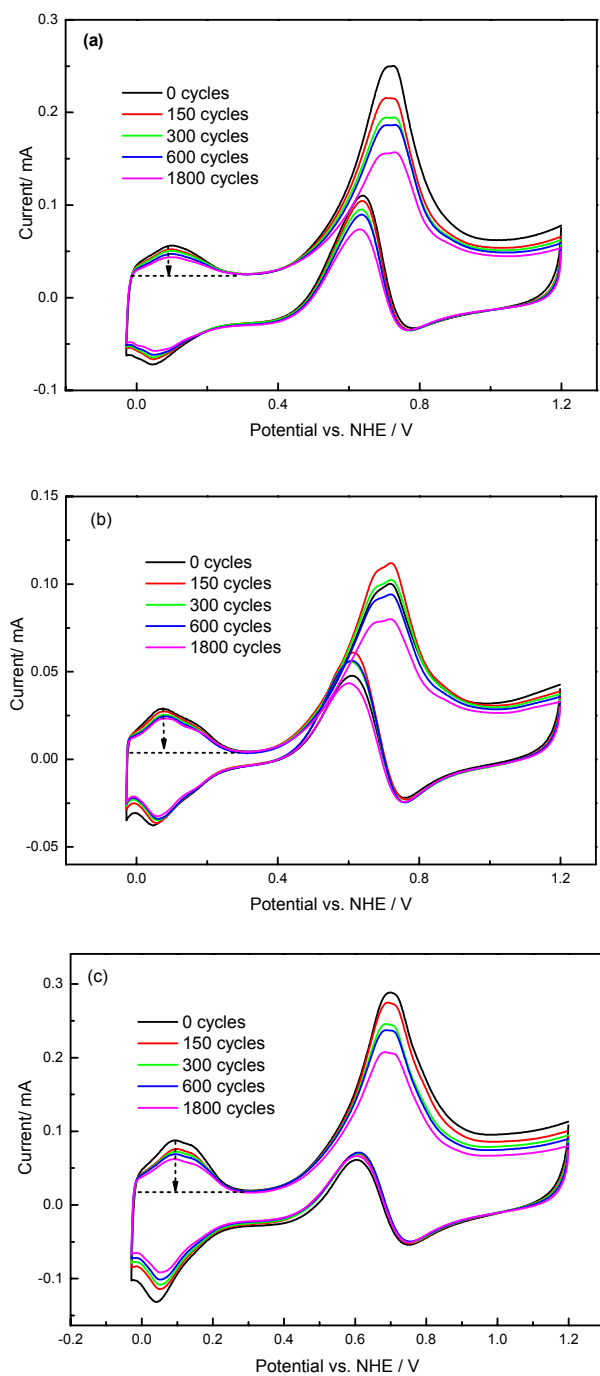


Fig. S7 Voltammogram of (a) Pt/CNF, (b) Pt/GNF and (c) Pt/Vulcan catalyst at the scanning rate of 50 mV/s in N_2 saturated 0.1 mol/L $HClO_4$ containing 0.01 mol/L CH_3OH after 150, 300, 600 and 1800 cycles of ADT tests.