

## Supplementary Materials for N-doped carbon nanomaterials are durable catalysts for oxygen reduction reaction in acidic fuel cells

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## Supplementary Materials

### N-Doped Carbon Nanomaterials Are Durable Catalysts for Oxygen Reduction Reaction in Acidic Fuel Cells

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#### Materials and Methods

##### *Synthesis of vertically-aligned nitrogen doped CNT (VA-NCNT), nitrogen doped graphene (N-G), CNT (N-CNT) and their composite (N-G-CNT)*

VA-NCNT was synthesized by pyrolysis of iron(II) phthalocyanine according to our previously published procedures (*Ref.1*). The N-G-CNT composite and its component N-G and N-CNT were synthesized according to the following procedures.

Graphene oxide, the precursor of N-G, was prepared by modified Hummers' method (*Ref.31*). Specifically, graphite flakes (3.0 g, purchased from Alfa Aesar) were added into the mixture of concentrated H<sub>2</sub>SO<sub>4</sub> (70 mL) and NaNO<sub>3</sub> (1.5 g) in an ice bath. Thereafter, KMnO<sub>4</sub> (9.0 g) was added into the mixture, followed by stirring at 35 °C for 48 hours. Deionized water (150 mL) was added slowly into the mixture and then they were together poured into a beaker containing 500 mL deionized water and 15 mL 30% H<sub>2</sub>O<sub>2</sub>. Then, the solid in the mixture was recovered by filtration and

washed with HCl (1 M) and deionized water. The solid was added to 300 mL water and sonicated for 1 hour for exfoliation of graphene oxide. The resultant graphene oxide was collected through filtration and washed copiously with deionized water. Typically, 40 mL of graphene oxide solution ( $2.5 \text{ mg mL}^{-1}$ ) was freeze-dried to obtain the GO foam. N-G foam was prepared by annealing the freeze-dried GO foams in a horizontal quartz tube in a tube furnace under ammonia gas ( $100 \text{ mL min}^{-1}$ ) at  $800 \text{ }^\circ\text{C}$  for 3 hours.

The commercially available multiwall carbon nanotubes (MWCNTs, Baytubes C 150 HP, Bayer MaterialScience) were first purified in 1 M HCl at  $60 \text{ }^\circ\text{C}$  for one week to remove the residual metal. The acid treated MWCNTs were then washed thoroughly with deionized water and dried in vacuum. 200 mg MWCNTs were oxidized in 200 mL acid mixture (concentrated  $\text{H}_2\text{SO}_4$  (90 %) /  $\text{HNO}_3$  (70 %) = 3:1) at  $60 \text{ }^\circ\text{C}$  for 3 hours with vigorous stirring. After oxidization, the oxidized MWCNTs (Ox-MWCNTs) were recovered by filtration and purified by deionized water and dialysis for 6 days. The metal-free Ox-MWCNTs suspension were then freeze-dried and annealed in  $\text{NH}_3$  for 3 hours at  $800 \text{ }^\circ\text{C}$  to produce N-CNT.

For the preparation of the N-G-CNT composite, a total of 250 mg GO and Ox-MWCNT (with a weight ratio of 1:1) were stirred in 100 mL deionized water for 2 hours and sonicated for another 1 hour to form a uniform suspension mixture. Then, the GO/Ox-MWCNT suspension was freeze-dried and annealed at  $800 \text{ }^\circ\text{C}$  in  $\text{NH}_3$  for 3 hours. BET surface area of N-G-CNT, N-G and N-CNT after the heat treatment for 3 hours is 422, 432 and  $438 \text{ m}^2 \text{ g}^{-1}$ , respectively.

The transition metal Fe derived control sample (Fe/N/C) was synthesized according to literatures (*Ref.11, Ref.46*). Specifically, we performed ball milling on 100 mg Zeolitic imidazolate frameworks (ZIF8) together with 10 mg tris(1,10-phenanthroline) iron(II) perchlorate ion for one hour, which was subsequently heated in Ar at 1000 °C for 1 hour, and then at 900 °C under NH<sub>3</sub> for 15 minutes.

### ***MEA fabrication and fuel cell tests***

As shown in Fig. 1A, VA-NCNT@Si was electrochemically oxidized in H<sub>2</sub>SO<sub>4</sub> to remove Fe residues, if any (*Ref. 1*). Then, the purified VA-NCNT array was etched off from Si wafer in aqueous 10 wt.% HF, and rinsed with deionized water. The free-standing VA-NCNT array thus prepared was then transferred onto a piece of carbon paper with a preloaded micro-porous layer as gas diffusion layer (GDL) (ElectroChem Inc., Carbon Micro-porous Layer (CMPL)) to support the NCNT array. Thereafter, a predetermined amount of Nafion (Nafion<sup>®</sup> perfluorinated resin, DuPont) solution (0.5 %, 200 mL) was dropped onto the VA-NCNT array and automatically dispersed into the array. After drying at 80 °C for one hour in vacuum with a piece of mirror-like stainless steel covering on the top of the array to prevent it from curling during drying, the cathode (VA-NCNT array catalyst layer with the GDL) was ready for MEA fabrication.

For N-G-CNT based cathodes, catalyst inks were prepared by mixing catalysts with Nafion resin (with or without Ketjenblack<sup>®</sup> EC-600JD, primary particle radius 34 nm, BET surface area 1270 m<sup>2</sup> g<sup>-1</sup>, Akzo Nobel Surface Chemistry LLC.) at ionomer/(catalyst+KB) ratio = 1/1, and painted onto the GDL as the cathode. For

example, 2.5 mg N-G-CNT was mixed with 10 mg Ketjenblack and 375 mg Nafion solution (5 %) in 1.5 mL deionized water and isopropanol mixture (volume ratio = 1 : 2). The ink was sonicated for 10 minutes and stirred overnight, and then painted onto 5 cm<sup>2</sup> GDL as the cathode. The metal-free nature of the N-CNT and N-G-CNT was clearly evident by the XPS and TGA measurements shown in Figs. S1 and S15.

The anode was Pt/C (20 %) with an excessive Pt loading of 0.4 mg cm<sup>-2</sup> to ensure sufficient proton supply from the anode. A pair of cathode and anode was hot pressed onto two sides of a N211 (Nafion<sup>®</sup>, Du Pont) membrane at 130 °C for 0.5 min under pressure 20 lb cm<sup>-2</sup> firstly, then under pressure 60 lb cm<sup>-2</sup> for another 1.5 min (figs. S4 & S6). The membrane electrode assemble (MEA) thus produced was tested in a 5 cm<sup>2</sup> PEM fuel cell (Scribner Inc.) at 80 °C with 100 % relative humidity (RH) and back pressure 2 bars. Pure H<sub>2</sub> (300 mL min<sup>-1</sup>) and O<sub>2</sub> (500 mL min<sup>-1</sup>) were used as anode and cathode fuels, respectively. Durability was measured at a constant voltage mode at 0.5 V or 0.4 V, or a scanning voltage model from OCV to 0.1 V at a rate of 10 mV s<sup>-1</sup> with H<sub>2</sub> (100 mL min<sup>-1</sup>) and O<sub>2</sub> (100 mL min<sup>-1</sup>).

#### ***Characterization of the N-G-CNT on rotating disc electrode***

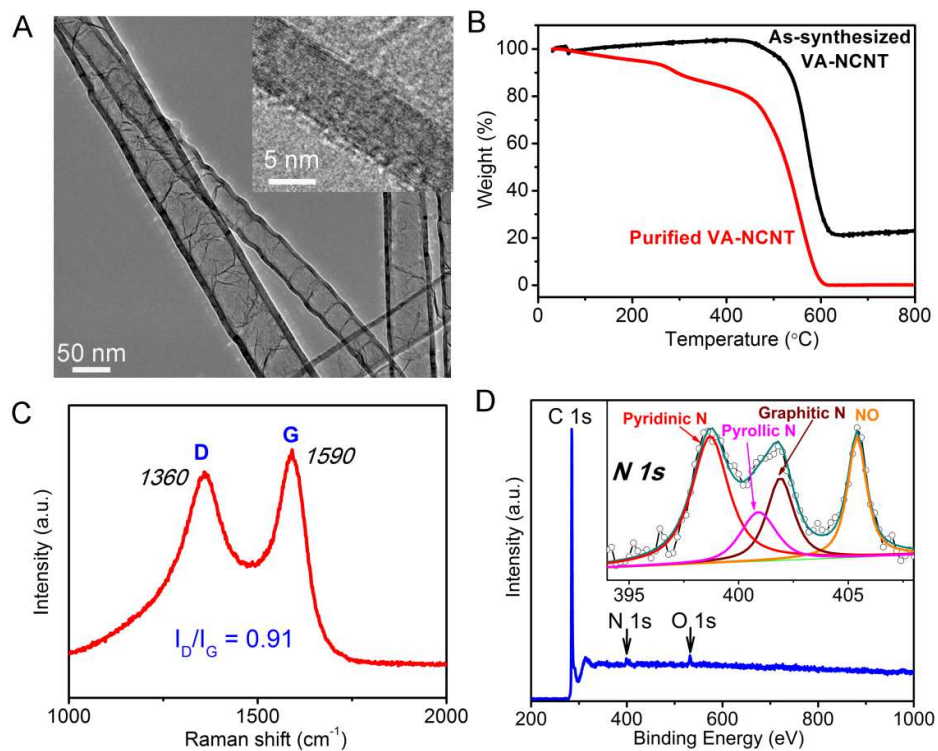
The measurements were performed using a potentiostat (CHI 760D, CH Instrument) with a typical three-electrode cell at room temperature (~25 °C). A platinum wire was used as counter electrode. A silver/silver chloride electrode (Ag/AgCl) and saturated calomel electrode (SCE) were used as reference electrodes in O<sub>2</sub> saturated 0.1 M HClO<sub>4</sub> and 0.1 M KOH electrolytes, respectively. For working electrode, special attention was paid to make sure that the N-G-CNT foam was not

broken into fine powder in order to make a porous catalyst layer. In order to do so, 1 mg electrocatalysts was dispersed in 0.4 mL water/isopropanol (1:1) with mild sonicating for 30 seconds to make a uniform ink. 15  $\mu$ L ink was loaded on a glass-carbon electrode, and 10  $\mu$ L Nafion solution (0.05 %) was then loaded on the electrode. The ORR activity of the electrocatalysts was evaluated by the linear sweep voltammetry (LSV) technique on a rotating disk electrode (RDE) and rotating ring-disk electrode (RRDE) test. Methanol, CO tolerance test and durability test (50000 s) on N-G-CNT and Pt/C were conducted by the chronoamperometric technique at -0.3 V (vs. SCE) in O<sub>2</sub> saturated 0.1 M KOH.

#### ***Morphology, composition characterization***

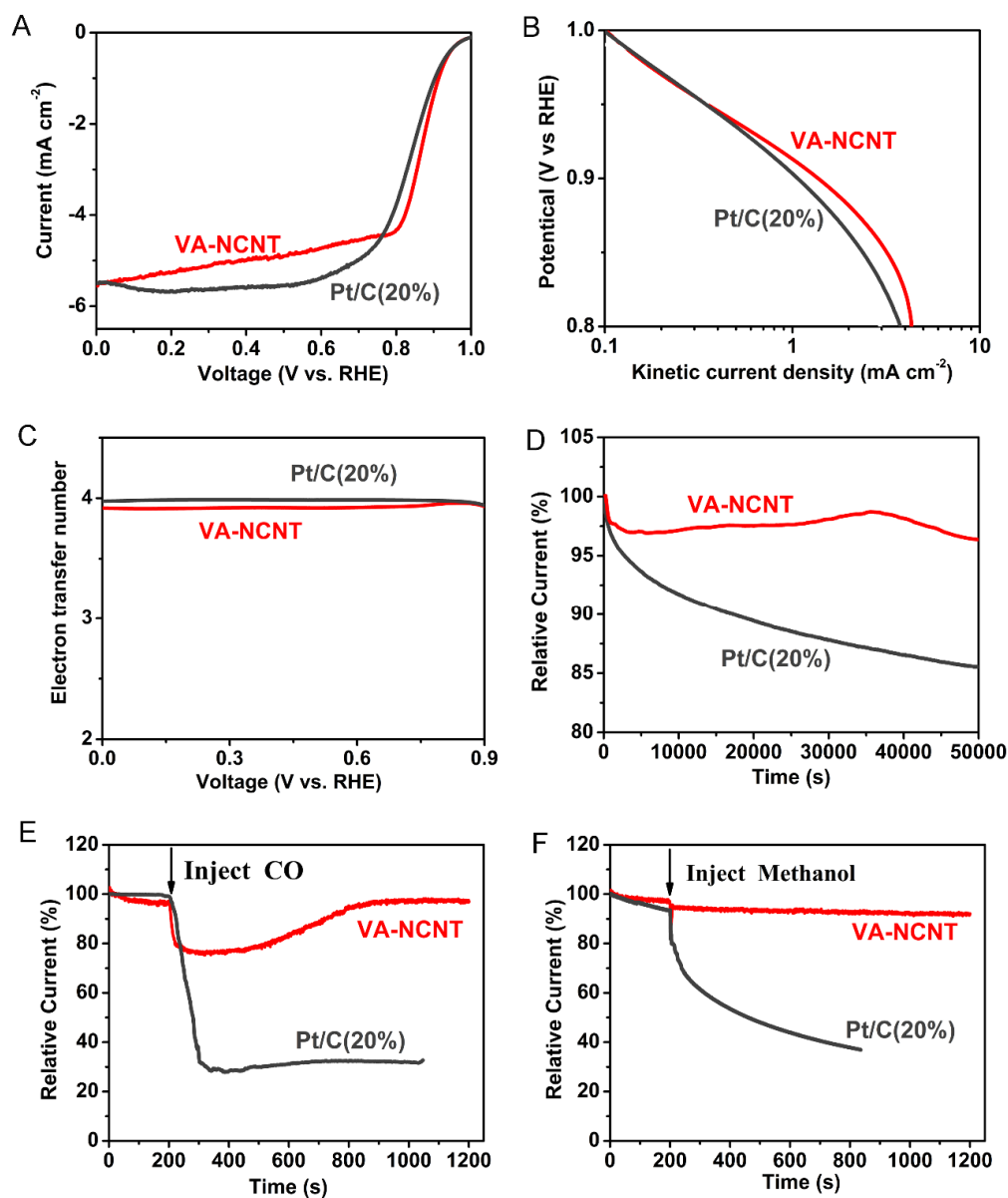
The morphology of VA-NCNT, N-G, N-CNT and N-G-CNT with and without the addition of Ketjenblack<sup>®</sup> EC-600JD were investigated by scanning electron microscopy (Tescan Vega3) and transmission electron microscopy (FEI Tecnai TF20 FEG). Brunauer, Emmett and Teller (BET) surface area and pore size distribution were measured by a TriStar II, Micromeritics<sup>®</sup>. For the blank GDL sample, a piece of 5 cm<sup>2</sup> GDL was brushed with 250 mg Nafion solution (1%) to mimic the real electrode where GDL would be immersed by Nafion solution during brushing catalyst inks onto the GDL. To mimic the real electrode porosity in the MEAs, all the electrode samples, including blank GDL, were hot pressed at the same condition as hot pressing a MEA except without the Nafion membrane and the anode. Raman spectra were measured on a Renishaw Raman spectrometer using 514 nm laser. Thermogravimetric analysis was performed on a thermogravimetric analyzer (TGA,

TA instrument, Q50) in air condition with a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ . X-ray photoelectron spectroscopic (XPS) measurements were performed on a VG Microtech ESCA 2000.



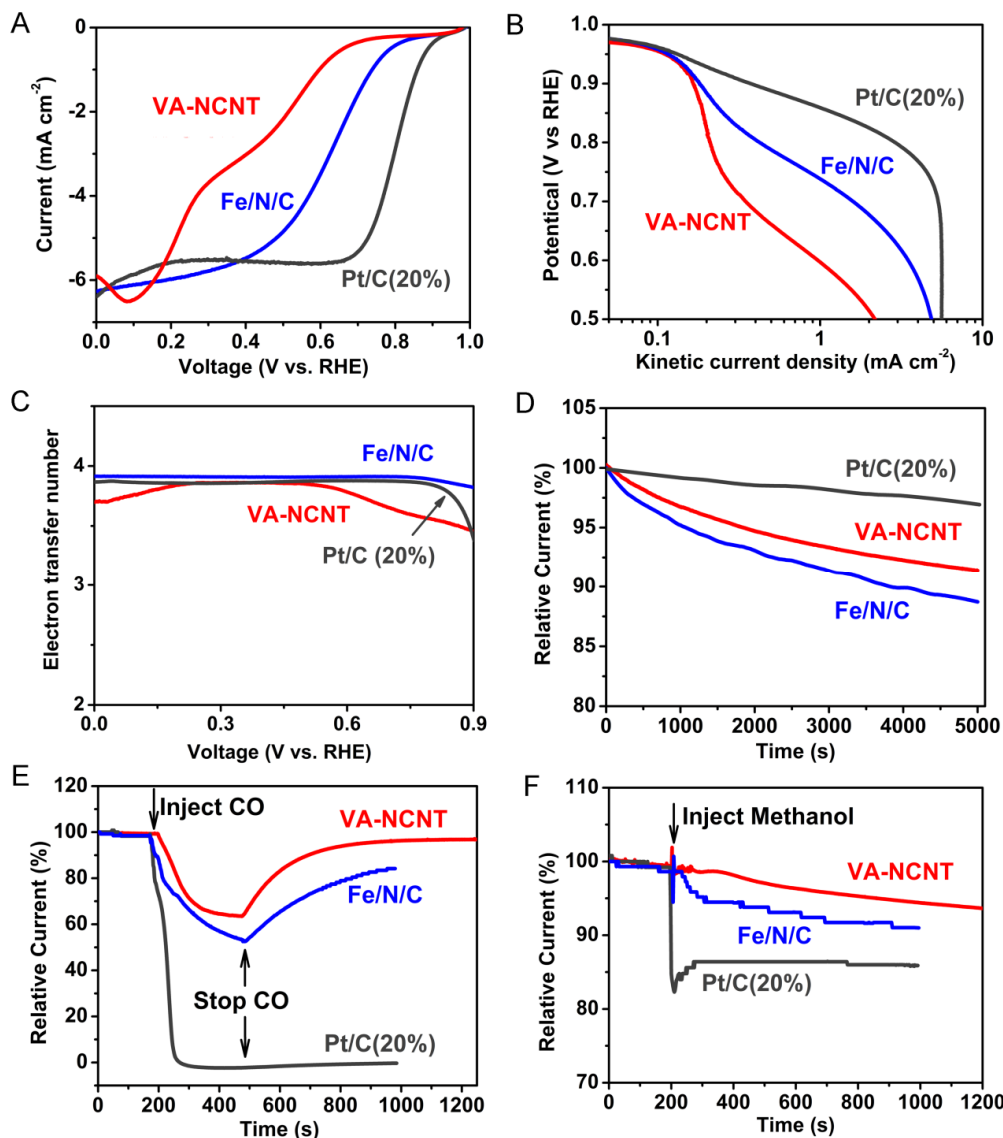
**Figure S1.** Characterization of VA-NCNTs. (A) A TEM image of purified individual CNTs. (B) TGA of the *as-synthesized* VA-NCNT, showing increased weights on two plateaus over  $50 - 500\text{ }^{\circ}\text{C}$  due to the residual Fe being oxidized on the surface and in the inner part of the CNTs, respectively, as well as about 20 wt.% residue over  $600\text{ }^{\circ}\text{C}$ . The purified NCNTs gradually lost 20% weight up to  $500\text{ }^{\circ}\text{C}$  due to the loss of adsorbed acidic groups generated during the purification process. Above  $600\text{ }^{\circ}\text{C}$ , the purified NCNT material was completely burned off, indicating no metal residue left. (C) Raman spectrum showing highly graphitic character with  $I_D/I_G = 0.91$ . (D) XPS spectrum indicating 2.9% N content in the purified VA-NCNTs, including 45% pyridinic-N, 15% pyrrolic-N, 21% graphitic-N, and 19% from NO.



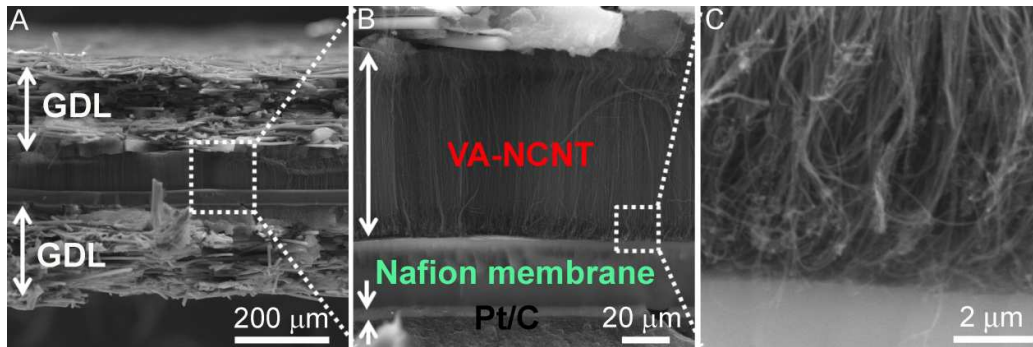


**Figure S2. Electrocatalytic activities of the VA-NCNT catalyst in alkaline electrolyte ( $\text{O}_2$ -saturated 0.1 M KOH) by half-cell tests. (A) LSV curves, (B) Tafel plot and (C) electron-transfer number of the VA-NCNT compared with Pt/C(20%) electrocatalyst by RRDE at scan rate of  $10 \text{ mV s}^{-1}$  and a rotation speed of  $1600 \text{ rpm}$ . (D) Long time stability, and tolerance to (E) carbon monoxide and (F) methanol of metal-free catalyst VA-NCNT compared with Pt/C(20%) electrocatalyst at  $0.5 \text{ V}$  (vs. RHE). CO ( flow  $100 \text{ mL s}^{-1}$ ) was injected into the electrolytes (100 mL) at the time of 200 s and stopped at the 500 s. Methanol (10 mL) was injected into the electrolytes**

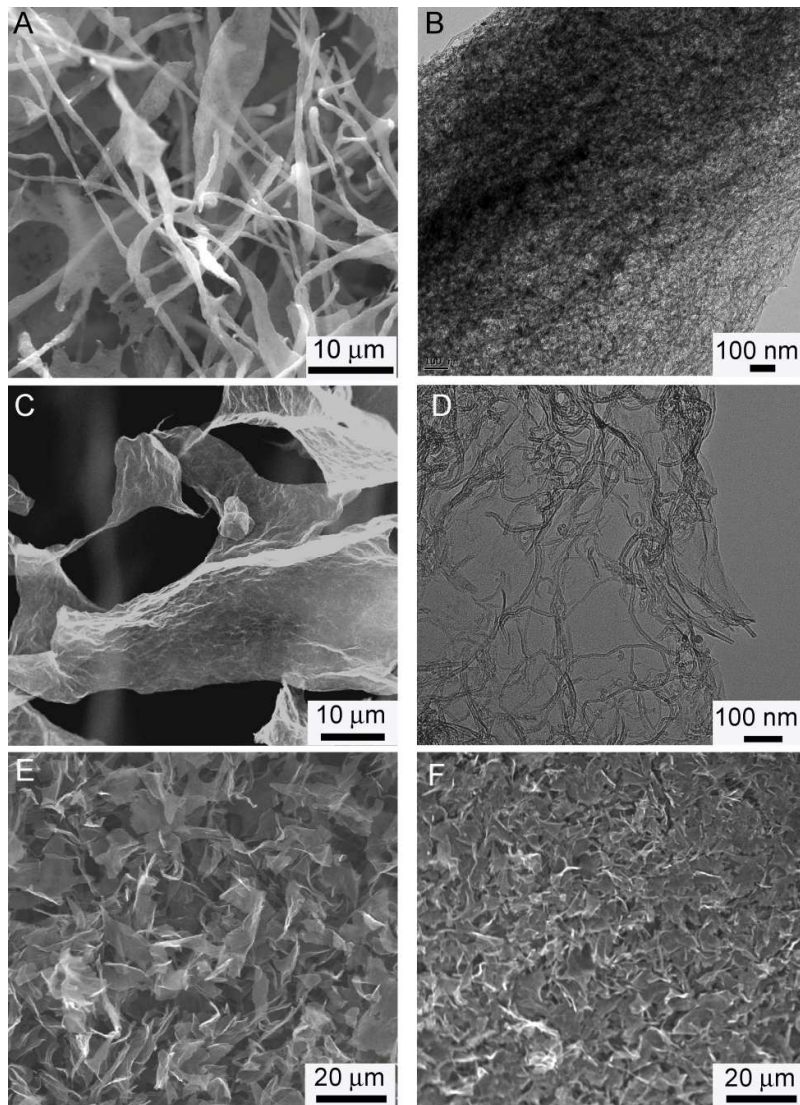
(100 mL) at the time of 200 s.



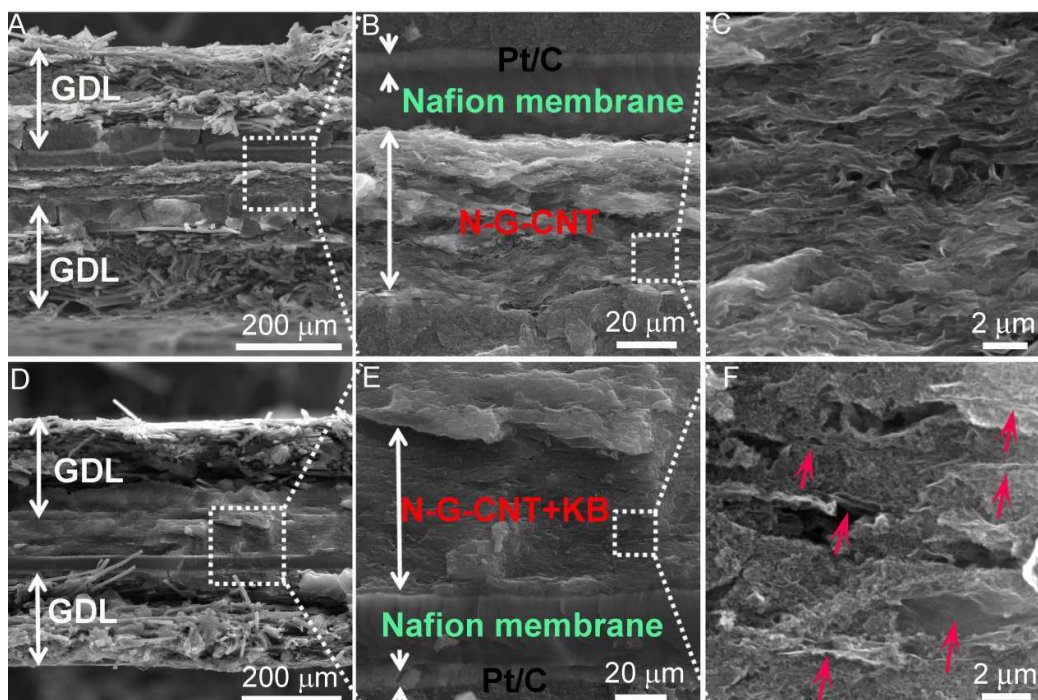
**Figure S3. Electrocatalytic activities of the VA-NCNT catalyst in acidic electrolyte ( $\text{O}_2$ -saturated 0.1 M  $\text{HClO}_4$ ) by half-cell tests. (A)** LSV curves, **(B)** Tafel plot and **(C)** electron-transfer number of the VA-NCNT compared with Fe/N/C and Pt/C(20%) electrocatalysts by RRDE at scan rate of  $10 \text{ mV s}^{-1}$  and a rotation speed of 1600 rpm. **(D)** Long time stability, and tolerance to **(E)** carbon monoxide and **(F)** methanol of metal-free catalyst VA-NCNT compared with Fe/N/C and Pt/C(20%) electrocatalysts at 0.5 V (vs. RHE). CO ( flow  $100 \text{ mL s}^{-1}$ ) was injected into the electrolytes (100 mL) at the time of 200 s and stopped at the 500 s. Methanol (10 mL) was injected into the electrolytes (100 mL) at the time of 200 s.



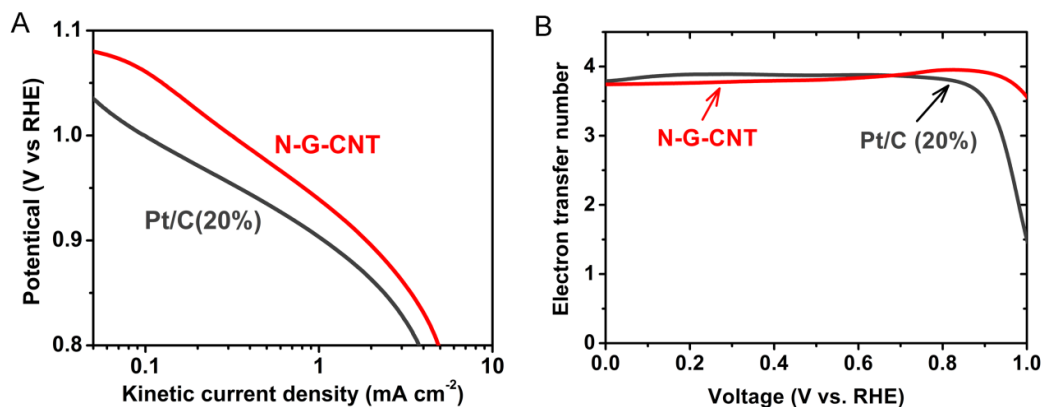
**Figure S4.** Typical cross-section SEM images of the GDL with the MEA of VA-NCNTs as the cathode catalyst layer, Nafion membrane (N211) as the separator, and Pt/C as the anode. A piece of carbon paper with a carbon black layer (ElectroChem Inc, Carbon Micro-porous Layer (CMPL)) was used as the gas diffusion layer (GDL).



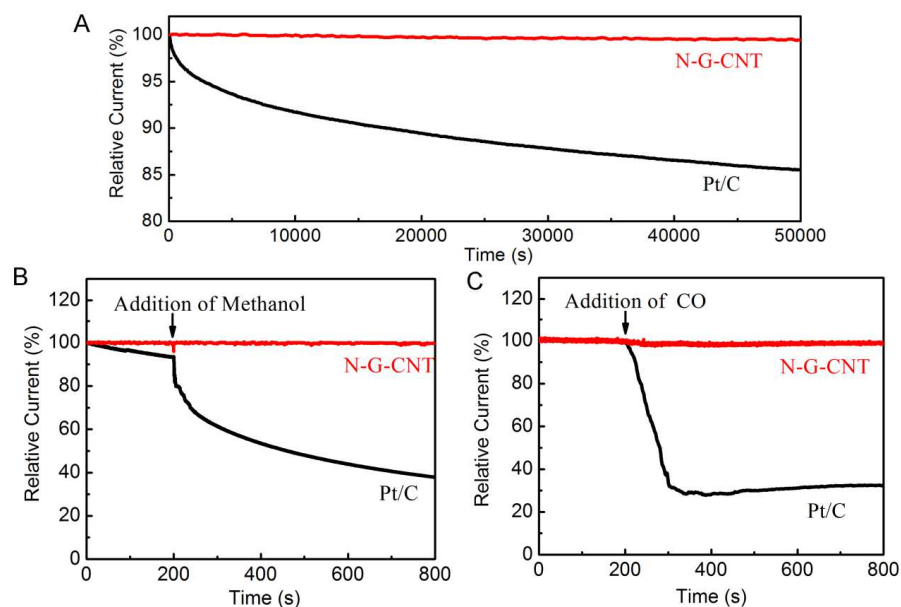
**Figure S5.** (A) SEM and (B) TEM images of N-CNT bundles. (C) SEM and (D) TEM images of the N-G-CNT sheets. Top view of (E) the N-G-CNT and (F) the N-G films made by dispersing the materials in isopropanol uniformly, dropping the dispersions onto two Al foils and then drying the films. The N-G-CNT sheets are more rigid and against restacking better than the N-G sheets.



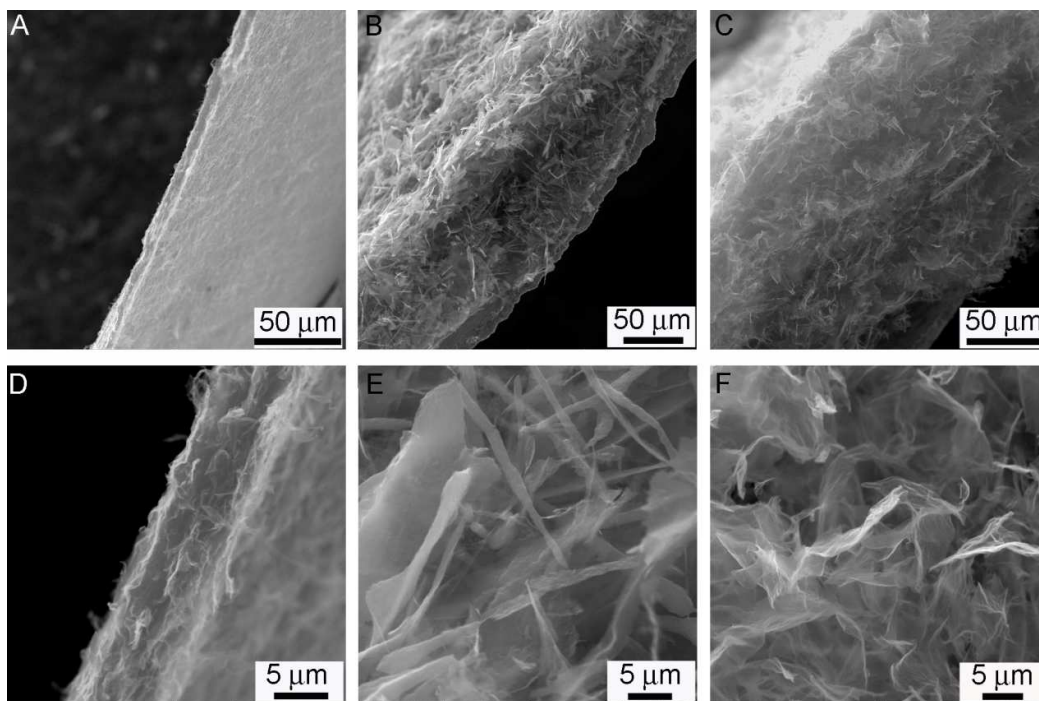
**Figure S6.** Typical cross-section SEM images of the GDLs with the MEAs of (A-C) N-G-CNT ( $2 \text{ mg cm}^{-2}$ ) and (D-F) N-G-CNT + KB ( $0.5 + 2 \text{ mg cm}^{-2}$ ) as the cathode catalyst layers, respectively. Arrows point several N-G-CNT sheets separated by KB agglomerates in (F). Nafion membrane (N211) as the separator, and Pt/C as the anode. A piece of carbon paper with a carbon black layer (ElectroChem Inc, Carbon Micro-porous Layer (CMPL)) was used as the gas diffusion layer (GDL).



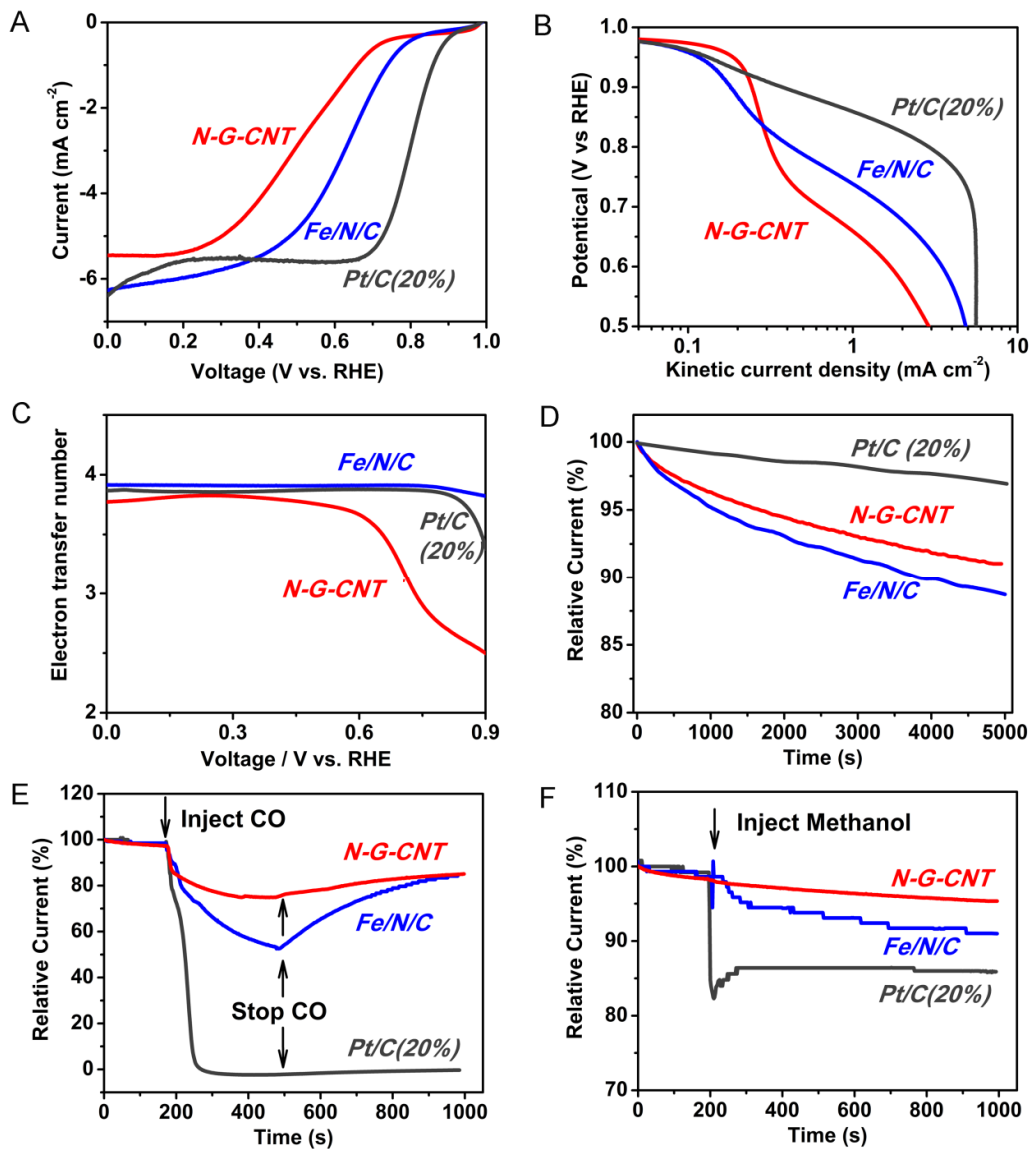
**Figure S7.** (A) Tafel plot and (B) Electron-transfer number for the N-G-CNT and Pt/C(20%) as the function of electrode potential by RRDE in oxygen-saturated 0.1 M KOH solution at scan speed of 5 mV s<sup>-1</sup> and a rotation speed of 1600 rpm.



**Figure S8.** Long time stability and tolerance to methanol/carbon monoxide of metal-free catalyst N-G-CNT. (A) The normalized ORR cathodic current-time response of the N-G-CNT and 20% Pt/C in O<sub>2</sub>-saturated 0.1 M KOH for 50000 s. The relative ORR cathodic current as the function of time for the N-G-CNT and 20%Pt/C before and after adding (B) 3 M methanol, and (C) CO into the O<sub>2</sub>-saturated 0.1 M KOH.



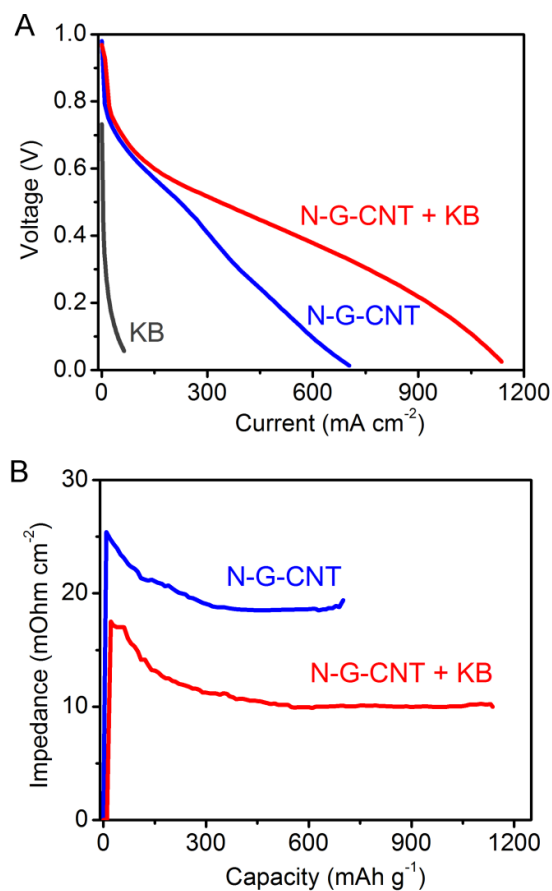
**Figure S9.** SEM images of catalyst layer cross-sections used in RDE measurements. (A, D) N-G; (B, E) N-CNT; and (C, F) N-G-CNT. Catalyst layers contain 5 wt.% Nafion binder loaded on the glass carbon electrode.



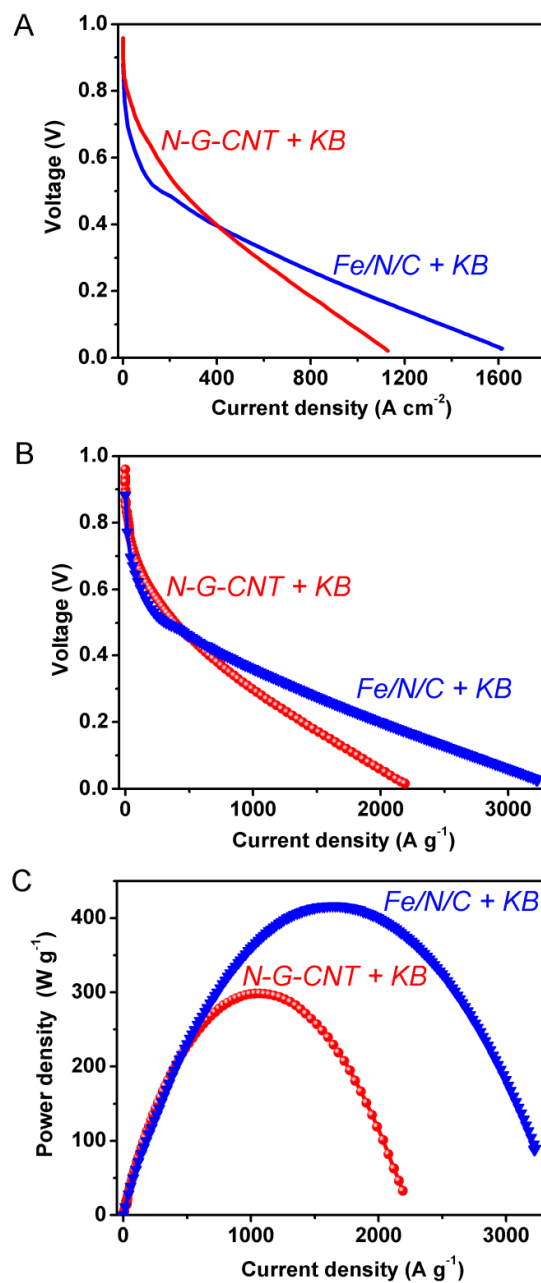
**Figure S10. Electrocatalytic activities of the carbon-based metal-free N-G-CNT catalysts in acidic electrolyte (O<sub>2</sub>-saturated 0.1 M HClO<sub>4</sub>) by half-cell tests. (A) LSV curves. (B) Tafel plot and (C) electron-transfer number of the N-G-CNT compared with Fe/N/C and Pt/C(20%) electrocatalysts by RDE at scan rate of 10 mV s<sup>-1</sup> and a rotation speed of 1600 rpm. (D) Long time stability, and tolerance to (E) carbon monoxide and (F) methanol of metal-free catalyst N-G-CNT compared with Fe/N/C and Pt/C(20%) electrocatalysts at 0.5 V (vs. RHE). CO ( flow 100 mL s<sup>-1</sup>) was injected into the electrolytes (100 mL) at the time of 200 s and stopped at the 500 s. Methanol (10 mL) was injected into the electrolytes (100 mL) at the time of 200 s.**



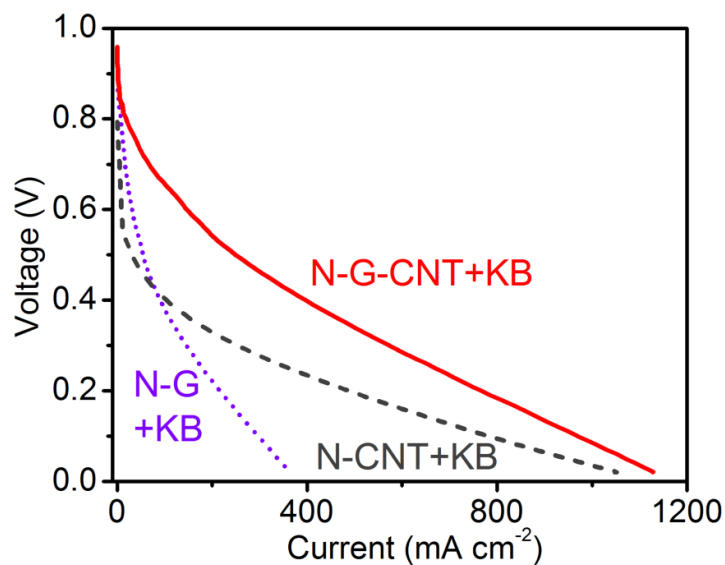
Prior to the single cell performance evaluation, we carried out the RDE test for the newly-developed N-G-CNT metal-free catalyst in a three-electrode electrochemical cell in acidic media (fig. S10). Although electrocatalytically less active (onset potential 0.8 V and half-wave potential 0.5 V, electron transfer number 3.7) than Pt/C and Fe/N/C catalysts based on the LSV curves (fig. S10A&C), N-G-CNT presents a better durability than Fe/N/C in the acidic environment with 9% current decay in 5000 s at 0.5 V (vs. RHE) (fig. S10D). More importantly, metal-free catalyst N-G-CNT shows better tolerances to CO than Fe/N/C that had 30% current decay in 200 s with the presence of CO, and Pt/C that lost all the activity and could not revive even after the removal of CO (fig. S10E). In addition, N-G-CNT is almost inert to methanol while Fe/N/C and Pt/C were seriously deactivated with the presence of methanol in the acidic electrolyte (fig. S10F), indicating a very promising utilization of metal-free catalysts as the cathode in alcohol fuel cells.



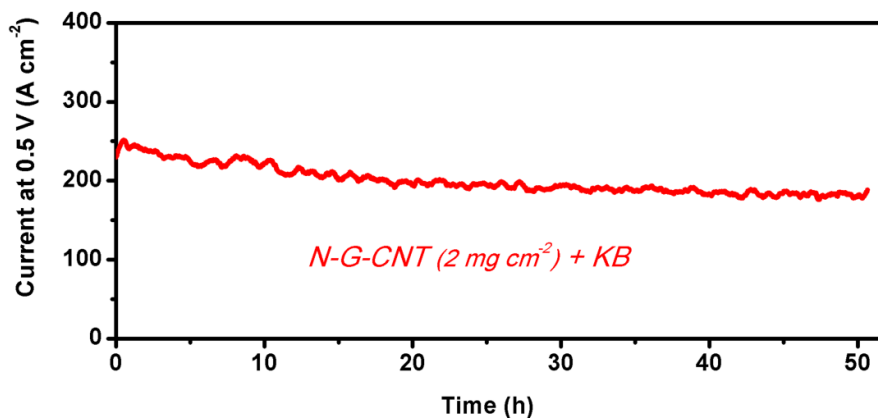
**Figure S11.** Optimization of cathode catalyst layer composition. (A) Polarization curve of the N-G-CNT with or without carbon black (KB) at the loading of  $2 \text{ mg cm}^{-2}$  for each catalyst layer composition. The weight ratio of Carbon (N-G-CNT+KB) / Nafion = 1 / 1. (B) The corresponding cell resistances of N-G-CNT and N-G-CNT+KB based catalyst layers. Testing condition for all MEAs are fueled with pure  $\text{H}_2/\text{O}_2$ , under back pressures 2 bar, at  $80 \text{ }^\circ\text{C}$  and 100% RH.



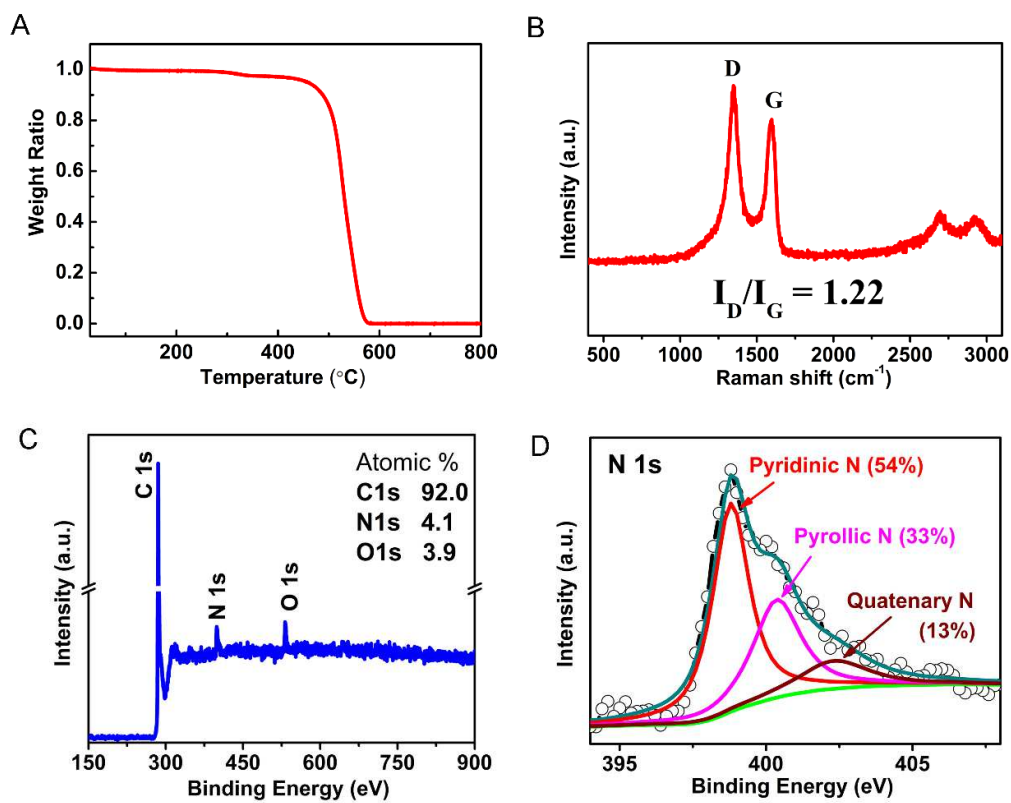
**Figure S12.** Single cell performance comparison between N-G-CNT and Fe/N/C catalysts at the same catalyst layer composition: catalyst 0.5 mg cm<sup>-2</sup> / KB 2 mg cm<sup>-2</sup> / Nafion 2.5 mg cm<sup>-2</sup>. (A) Polarization curves as the function of areal current. (B) Polarization curves as the function of gravimetric current. (C) Power density as the function of gravimetric current. Test condition: H<sub>2</sub>/O<sub>2</sub>, 80 °C, 100% RH, back pressures 2 bar.



**Figure S13.** Polarization curves of the N-G-CNT and individual components of N-G or N-CNT. Catalyst loadings were  $(0.5 \text{ mg catalyst} + 2 \text{ mg KB}) \text{ cm}^{-2}$ . Testing condition for all MEAs are fueled with pure  $\text{H}_2/\text{O}_2$ , under back pressures 2 bar, at 80 °C and 100% RH.



**Figure S14.** Durability of the catalyst layer composed of metal-free N-G-CNT ( $2 \text{ mg cm}^{-2}$ ) + KB ( $2 \text{ mg cm}^{-2}$ ) in a PEM fuel cell measured at 0.5 V. Test condition:  $\text{H}_2/\text{O}_2$ , 80 °C, 100% RH, back pressures 2 bar.



**Figure S15** The metal-free character of N-G-CNT catalyst. (A) TGA curve of the N-G-CNT in air, showing no residue above 600 °C. (B) Raman spectrum showing  $I_D/I_G = 0.91$ . (C) XPS spectrum of the N-G-CNT with no detectable Fe. (D) N 1s XPS of N-G-CNT.