Supplementary Material (ESI) for Chemical Communications
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Supplementary information

Carbon-nanotube-supported graphene-rich non-precious metal oxygen reduction catalyst with enhanced performance durability

Gang Wu,[a,*] Karren L. More,[b] Ping Xu,[c] Hsing-Lin Wang,[c] Magali Ferrandon,[d] Arthur J. Kropf,[d] Deborah J. Myers,[d] Shuguo Ma,[e] Christina M. Johnston,[a] and Piotr Zelenay[a,*]

[a] *Materials Physics and Applications Division and* [c] *Chemistry Division*
Los Alamos National Laboratory, Los Alamos, NM 87545, USA

[b] *Materials Science and Technology Division, Oak Ridge National Laboratory*
Oak Ridge, Tennessee 37831, USA

[d] *Chemical Sciences and Engineering Division, Argonne National Laboratory*
Lemont, IL 60439, USA

[e] *Department of Chemical Engineering, University of South Carolina*
Columbia, SC 29208, USA

[*] Corresponding authors:

E-mails: wugang@lanl.gov; zelenay@lanl.gov

Tel: +1 505-665-0659; +1 505-667-0197

1. Experimental

1.1 Materials synthesis

Commercially available multi-walled carbon nanotubes (MWNTs) with a Brunauer-Emmet-Teller (BET) surface area of ~ 230 $m^2 g^{-1}$ were first treated in 1.0 M HCl solution to remove impurities, followed by oxidation in mixed $HNO_3 + H_2SO_4$ solution. Except for using MWNTs in place of carbon black, the detailed catalyst synthesis procedures were described in our previous reports. The product was labeled as PANI-Fe-MWNT. In order to explore the roles of MWNT as an NMPC support, catalysts supported on traditional carbon blacks (KJ, Vulcan XC-72, and Black Pearl® 2000) were synthesized and subjected to identical treatment.

1.2 Electrochemical characterization

The ORR activity was electrochemically evaluated by rotating disk electrode (RDE). Selectivity for the four-electron reduction of oxygen was determined by a rotating ring-disk electrode (RRDE). RDE and RRDE data reported in this paper were acquired using a total catalyst loading of 0.6 mg cm^{-2} in 0.5 M H_2SO_4 at a rotating disk speed of 900 rpm and room temperature. These NPMCs were further tested in a hydrogen/air fuel cell to evaluate their activity and durability under practical polymer electrolyte fuel cell (PEFC) operating conditions. Cathode catalyst loading was 4.0 mg cm^{-2}. A commercially available Pt-catalyzed cloth gas diffusion electrode (E-TEK, 0.25 mg_{Pt} cm^{-2}) and Nafion® 1135 were used as the fuel cell anode and membrane, respectively.

1.3 Physical characterization

High-resolution transmission electron microscopy (HR-TEM) images were taken on a Hitachi Model HF 3300 microscope operated at 300 kV at Oak Ridge National Laboratory. X-ray absorption spectroscopy (XAS) measurements at the Fe *K*-edge were carried out using either transmission or fluorescent mode at the 12-BM beam lines at the Advance Photon Source at Argonne National Laboratory. The near-edge region of the X-ray absorption fine structure (XAFS) spectra (7105 to 7170 eV) was fit using the linear combination algorithm of the *Athena* software (version 0.8.054) based on the *IFEFFIT* code to the spectra for a suite of Fe-containing standards. The total Fe loading in the sample was measured using the XAFS edge-step height in transmission mode.

The crystallinity of various samples was determined by X-ray diffraction (XRD) using a Bruker AXS D8 Advance diffractometer with Cu Kα radiation. The patterns were obtained at a scan rate of 5°/min with a step of 0.02°. Elemental quantification and specie analysis using X-ray photoelectron spectroscopy (XPS) were performed on an ESCA 210 and MICROLAB 310D spectrometer. All Raman spectra were obtained using a Kaiser Holospec Raman system at 514 nm excitation. Samples were prepared as powders on a glass surface, with the excitation laser focused through at 100× microscope objective for a total interrogation spot size of 1 micron. Excitation power was held constant at 150 μW for all samples. Scattered light was collected in backscatter configuration into an optical fiber, then dispersed through the Kaiser spectrometer and projected onto a CCD camera. Four individual 30 s spectra were summed for a total integration time of 120 s. Spectra were fit using 4 Lorentzians.

2. XRD analysis

XRD patterns for the PANI-Fe catalysts supported by MWNTs and KJ-300J are shown in **Fig. S1**. The results indicate that heat treatment results in a dominant formation of FeS in the PANI-derived catalysts. The sulfur source in the catalyst system derives from the use of ammonium persulfate, $(NH_4)_2S_2O_8$, for polymerizing aniline.

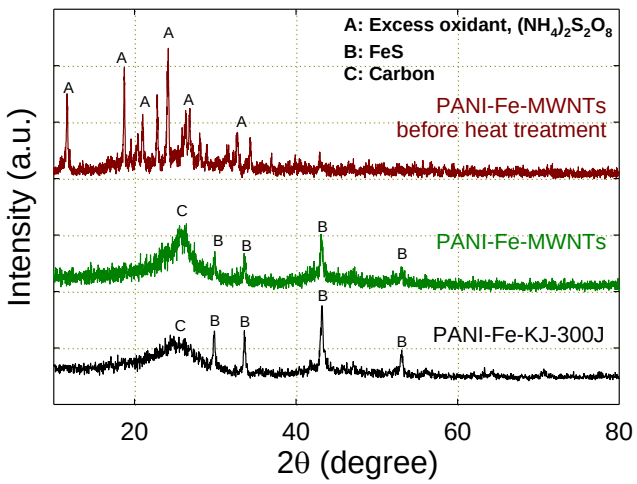

Fig. S1. XRD patterns for PANI-Fe catalysts supported by MWNTs and Ketjenblack-EC300J (KJ-300J)

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3. XPS analysis

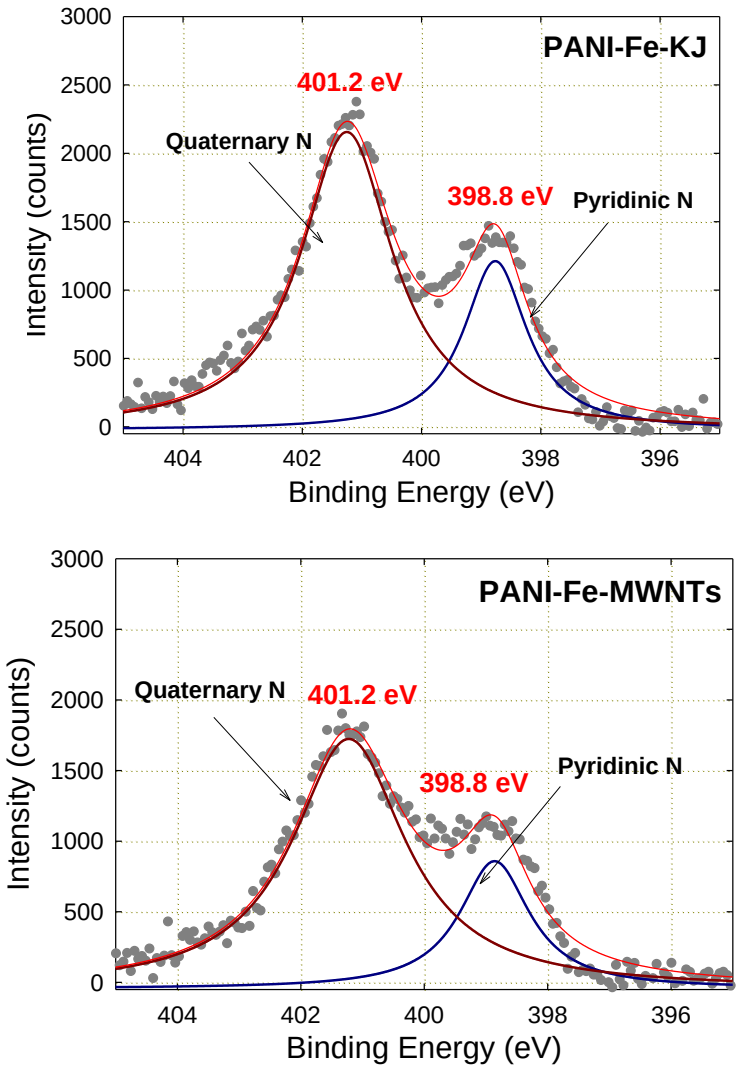

Fig. S2. N 1s XPS spectra of PANI-Fe-KJ and PANI-Fe-MWNT catalysts.

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4. Raman analysis

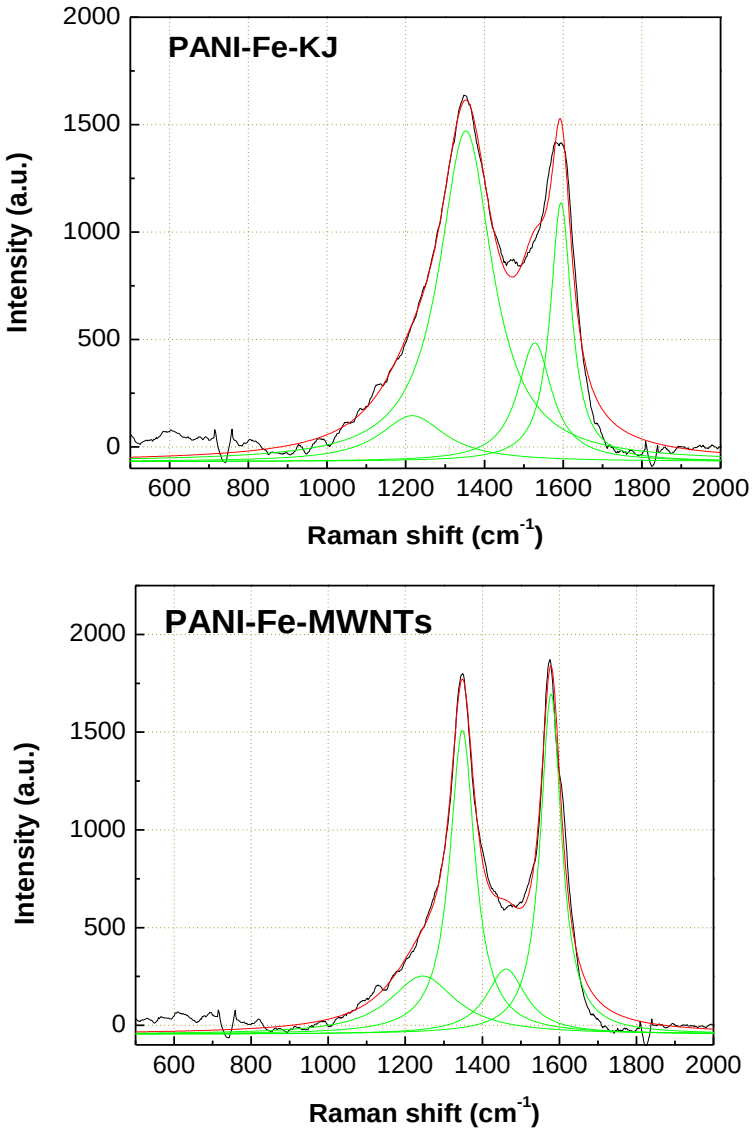

Fig. S3. Raman spectra for PANI-Fe-KJ and PANI-Fe-MWNT catalysts.

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5. High-resolution TEM images

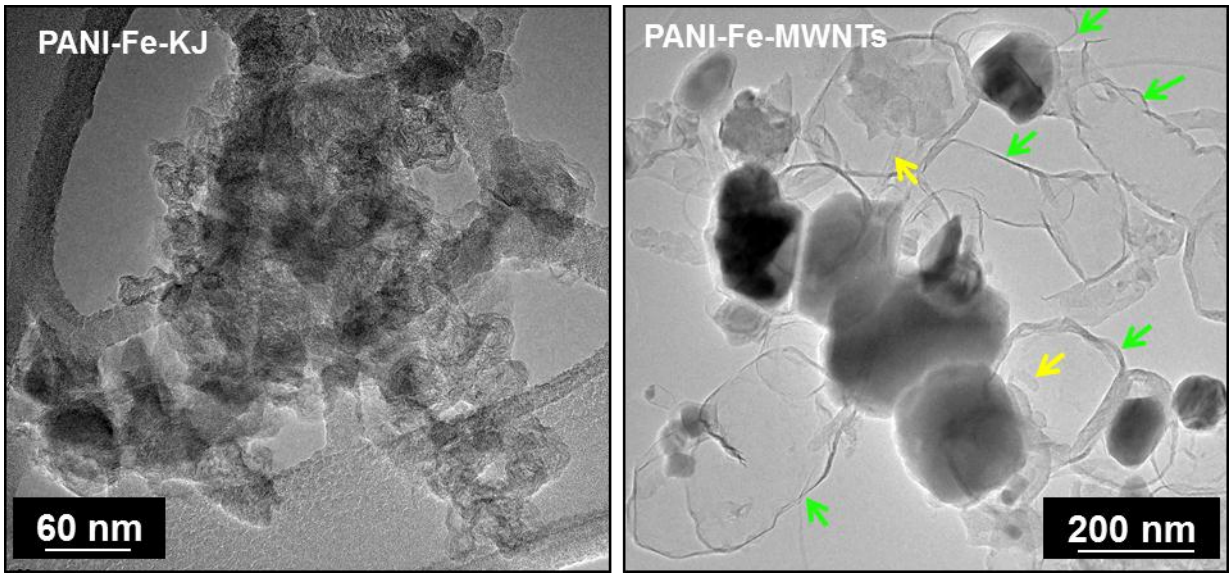

Fig. S4. Morphology comparison between KJ- and MWNT-supported PANI-Fe catalysts (graphene marked by green arrows; nanotube marked by yellow arrows).