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Supporting Information

Janus Structured Pt-FeNC Nanoparticles as Catalyst for the Oxygen Reduction Reaction

Kurian A. Kuttiyiel,[a, b] Kotaro Sasaki,[a] Gu-Gon Park,[a, d] Miomir B. Vukmirovic,[a] Lijun Wu,[c] Yimei Zhu,[c] Jingguang G. Chen[a, b] and Radoslav R. Adzic*[a]

[a]Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA
[b]Department of Chemical Engineering, Columbia University, New York, NY 10027, USA
[c]Department of Condensed Matter Physics and Materials Science, Brookhaven National Laboratory, Upton, NY 11973, USA
[d]Fuel Cell Laboratory, Korea Institute of Energy Research, Daejeon 305-343, South Korea

*Corresponding author: R. R. Adzic (adzic@bnl.gov)

Synthesis. Graphene encapsulated FeNC nanoparticles was prepared by sonicating 5 wt. % of Fe tetra(4-pyridyl) porphyrin chloride salt with high surface area graphene in ethylene glycol. Later, the mixture was washed and rinsed with Millipore water, and then dried. The dried sample was annealed at 700°C in NH_3 stream for 30 minutes in a tube furnace. The as-obtained FeNC catalyst was acid washing in 0.1M H_2SO_4 to eliminate the inactive Fe species.

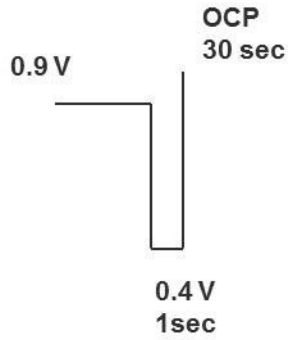
Electrochemical deposition of Pt was carried out in a three-electrode test cell by using a Bio-logic potentiostat. Initially, the catalyst ink of as-prepared FeNC catalyst was prepared by

ultrasonic mixing of 4 mg of catalyst with 1 ml MilliQ water, 1 ml iso-propanol and 5 µl 5wt% Nafion solution until a uniform aqueous dispersion was obtained. A thin film of the catalyst was prepared on a glassy carbon rotating disk electrode (RDE) by placing 20 µl of the obtained dispersion, and then dried in air at room temperature. The RDE was then immersed in a three-electrode test cell containing 1.0 mM K_2PtCl_4 / 50 mM H_2SO_4 solution. Pulse deposition was applied using chronoamperometry from 0.9V to 0.4V with a pulse width of 1 second and 30 sec dwell time at open circuit potential (OCP). A Pt foil and Ag/AgCl (3M NaCl) electrode served as the counter electrode and reference electrode, respectively. The oxygen reduction reaction (ORR) measurements were performed in an O_2-saturated 0.1 M $HClO_4$ solution at the scan rate of 10 mV s^{-1}. The accelerate durability tests were carried out in air-saturated 0.1 M $HClO_4$ solution using potential cycling between 0.6 V and 1.0 V with the sweep rate of 50 mV s^{-1} at room temperature. For comparison, commercial Pt/C (Tanaka Kikinzoku International Inc., 46.6 wt% Pt, Pt particle size 2.6 nm) was used as the baseline catalyst under the same measuring conditions. The electrochemical measurements were all performed at room temperature, and the potential were referenced to that of the reversible hydrogen electrode (RHE). The electrolytes were prepared from Optima sulfuric acid and perchloric acid (Fisher), and MilliQ UV-plus water. The geometric electrode surface area (0.196 cm^2) was used in expressing current densities in all CV plots.

Characterization. HAADF-STEM images were performed using the double aberration-corrected JEOL-ARM200F microscope with a cold-field emission gun and operated at 200 kV. The microscope is equipped with JEOL and Gatan HAADF detectors for incoherent HAADF (Z-contrast) imaging and Oxford Instruments SDD detector for EDS.

For the X-ray absorption spectroscopy (XAS) measurements, the electrocatalyst were pressed and sealed in an electrochemical cell as described in the references.[1,2] All the XAS measurements

were carried out at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory using Beam Line X19A. The data were processed and analyzed by Athena and Artemis software.[3]



Schematic S1. Pulse deposition potentials for Pt- Fe-N-C Janus structures using chronoamperometry.

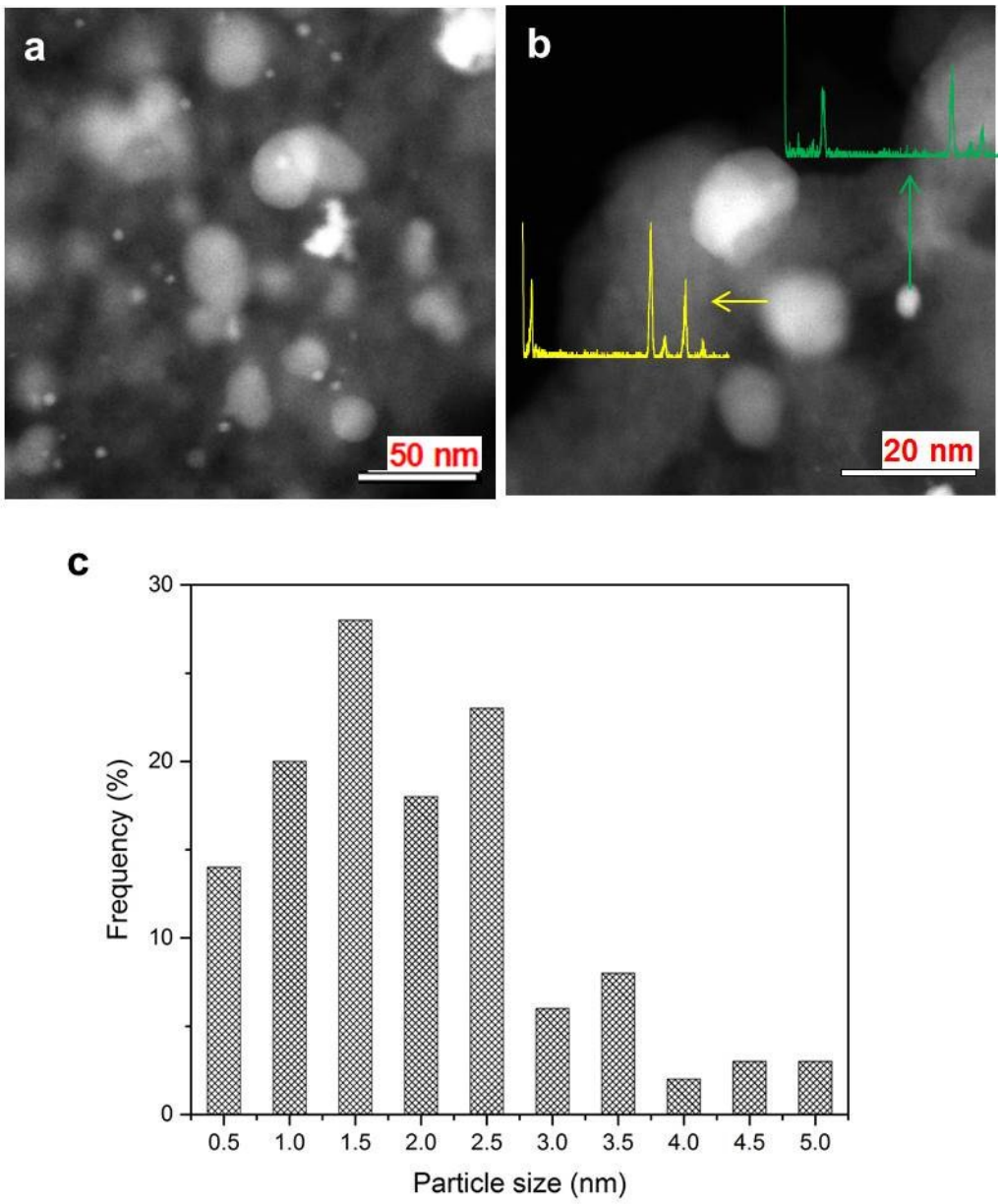


Figure S1. (a) HAADF-STEM image of pulse deposited Pt-FeNC Janus structured nanoparticles. (b) STEM-HAADF image and EDS show independent large and small particles are Fe and Pt, respectively (yellow has Fe and green has Pt). (c) Particle size distribution of Pt nanoparticles (sample size=125).

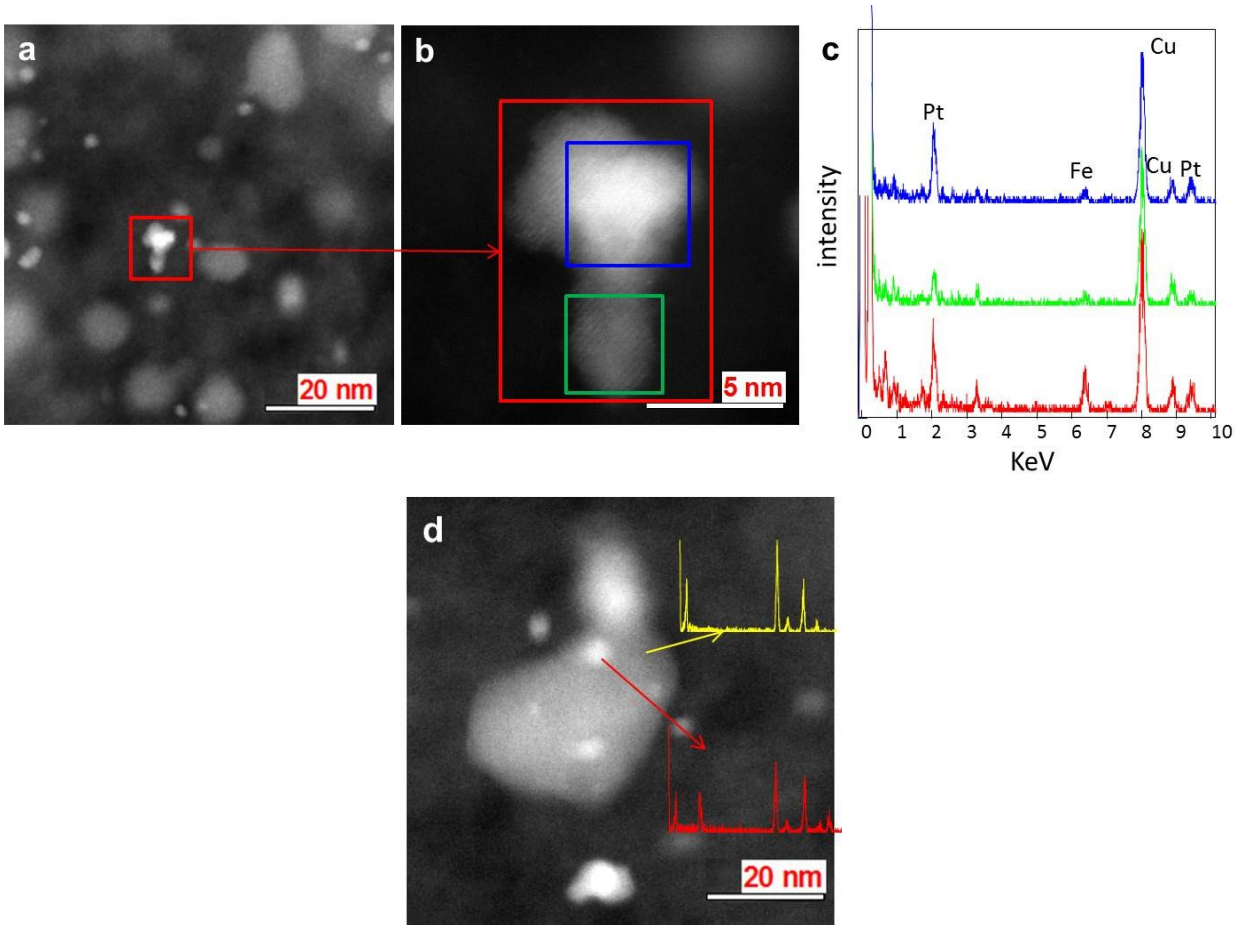


Figure S2. (a - c) HAADF-STEM images of Pt-FeNC Janus structured nanoparticles after 25,000 potential cycles along with its corresponding EDS showing the bonding of Pt and Fe. (d) HAADF-STEM image of several Pt nanoparticles bonded with FeNC nanoparticle after 25,000 potential cycles along with the EDS. Red has both Fe and Pt while yellow has only Fe.

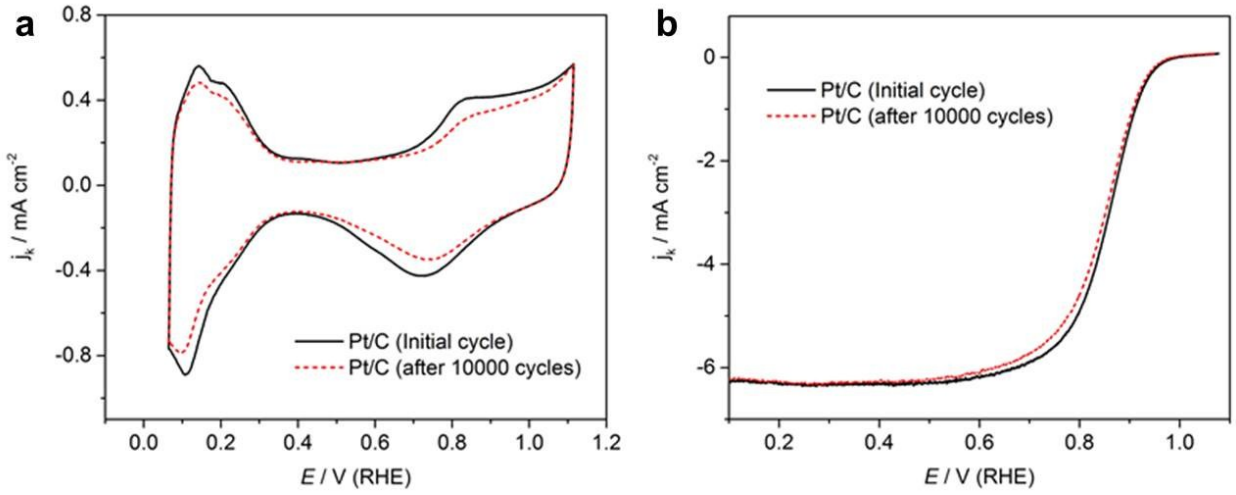


Figure S3 (a) Cyclic voltammetry at a scan rate of 20mV s^{-1} and (b) ORR polarization curves at 1600rpm at a scan rate of 10mV s^{-1} for commercial Pt/C in 0.1 M $HClO_4$. Black line is the initial cycle and the red dotted line is after 10,000 potential cycles. Pt loading was 9.7μg cm^{-2}.

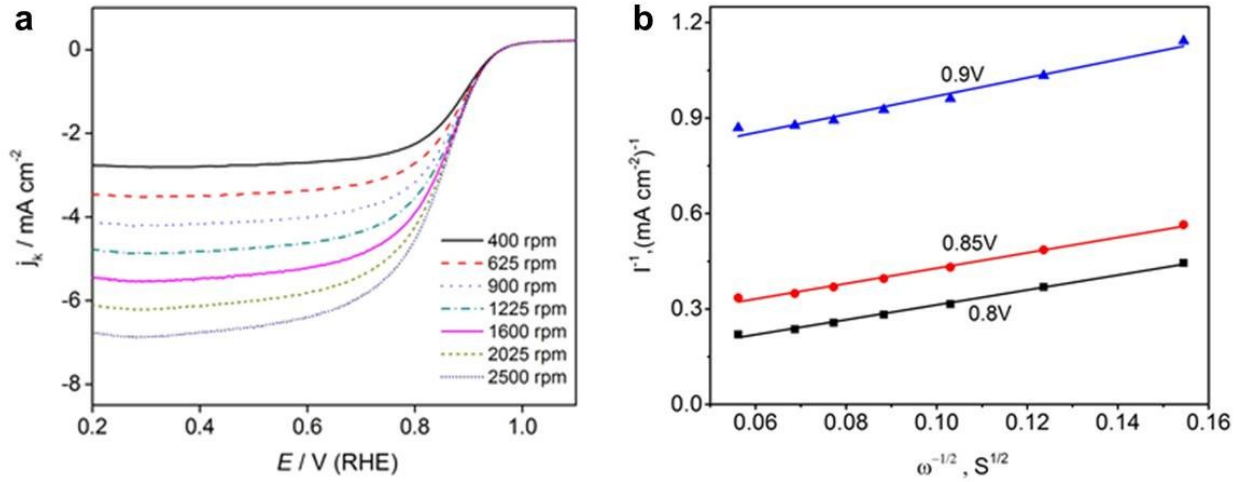


Figure S4 (a) ORR Polarization curves for Pt-FeNC Janus structured catalyst at various rpm in O_2-saturated 0.1 M $HClO_4$ at a scan rate of 10 mV s^{-1}. b) Koutecky-Levich plots at various potentials for the Janus catalyst obtained from the ORR polarization curves as shown in (a).

Half Wave Potential (mV)		Mass Activity A/mg_{Pt}
Pt/C	860	0.22
Pt/C after 10,000 cycles	848	0.18
FeNC/G	633	
Pt-FeNC/G	838	0.69
Pt-FeNC/G after 5,000 cycles	853	0.73
Pt-FeNC/G after 10,000 cycles	858	0.75
Pt-FeNC/G after 25,000 cycles	869	0.85

Table S1. Half wave potential and Pt mass activity of commercial Pt/C, FeNC/G and Pt-FeNC/G Janus structured catalyst. Pt loading for Pt-FeNC/G and commercial Pt/C catalysts were 2.1 and 9.7 μg cm^{-2} respectively.

References

(1) Sasaki, K.; Wang, J. X.; Naohara, H.; Marinkovic, N.; More, K.; Inada, H.; Adzic, R. R. *Electrochim Acta* **2010**, *55*, 2645.

(2) Mcbreen, J.; Ogrady, W. E.; Pandya, K. I.; Hoffman, R. W.; Sayers, D. E. *Langmuir* **1987**, *3*, 428.

(3) Ravel, B.; Newville, M. *J Synchrotron Radiat* **2005**, *12*, 537.