Supporting Information

Atomically Isolated Iron Atom Anchored on Carbon Nanotubes for Oxygen Reduction Reaction

Dong Liu, † *Jin-Cheng Li,* *† *Qiurong Shi,* † *Shuo Feng,* † *Zhaoyuan Lyu,* † *Shichao Ding,* † *Leiduan Hao,* ‡ *Qiang Zhang,* ‡ *Chenhui Wang,* † *Mingjie Xu,*§ *Tao Li,*#, ‖ *Erik Sarnello,*‖ *Dan Du* † *and Yuehe Lin**†

† School of Mechanical and Materials Engineering, Washington State University, Pullman, WA, 99164, USA

‡ Department of Chemistry, Washington State University, Pullman WA, 99164, USA

§ Irvine Materials Research Institute (IMRI), University of California, Irvine, CA, 92697, USA

Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, IL, 60115, USA

‖ X-ray Science Division, Argonne National Laboratory, Lemont, IL, 60439, USA

E-mail: yuehe.lin@wsu.edu; jin-cheng.li@wsu.edu

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Experimental Section

Characterization of the SAICN catalysts

The materials were characterized using were characterized using scanning electron microscopy (SEM, FEI Sirion 200, operated at 30 kV), transmission electron microscopy (TEM, Tecnai G2 T20, 200 kV; JEOM Grand ARM300F, 300 kV), X-ray photoelectron spectroscopy (XPS, Escalab 250, Al Kα), X-ray diffraction (XRD, Rigaku Miniflex 600, 40 kV). The specific surface area and pore structure of the samples were investigated with an automatic volumetric sorption analyzer (ASAP 2020 M) which N_2 acts as the adsorbate at -196 °C. The Fe content of the catalyst was evaluated with an Agilent inductively coupled plasma mass spectrometer (ICP-MS). The X-ray absorption spectroscopy measurement at Fe K-edge was performed at the Advanced Photon Source (APS) on the bending-magnet beamline 12-BM and 20-BM with electron energy of 7 GeV and average current of 100 mA. The radiation was monochromatized by a Si (111) double-crystal monochromator. Harmomic rejection was accomplished with Harmonic rejection mirror. All spectra were collected in fluorescence mode by vortex four-element silicon drift detector.

Electrochemical measurements

2.5 mg as prepared catalysts were ultrasonically dispersed in a mixture which consisting of 990 μL ethanol and 10 μL 1 wt% Nafion solution to form a concentration of 2.5 mg/ml catalyst ink. Followed by pipetting the certain volume of catalyst ink onto the surface of the glassy carbon electrode (GCE, geometric area: 0.247 cm^2) disk and air dried, calculating to electrode loadings of 0.1 mg/cm^2 in alkaline condition and 0.2

mg/cm^2 in acidic condition. Pt/C (20 wt%, Alfa Aesar) with a loading of 0.1 mg/cm^2 were used as reference sample. The durability of the products can be evaluated by potential cycling measurements in O_2-saturated 0.1 M KOH (0.6-1.0 V at 50 mV) and 0.1 M $HClO_4$ (0.5-0.9 V at 50 mV/s). Electrochemical measurements for ORR of all the catalyst samples were characterized with a standard three-electrode cell by CHI660E electrochemical workstation (CH Instruments). RDE and RRDE coated with the catalysts acted as the working electrode, respectively. A graphite rod and a saturated calomel electrode (SCE) were used as the counter electrodes and reference electrode, respectively. The O_2/N_2 was bubbled into the electrolyte for 30 min before tests. The measure potential values *vs.* SCE were converted to that of a reversible hydrogen electrode (RHE) scale according to the Nernst equation:

$$E_{RHE} = E_{SCE} + 0.059pH + 0.241. \quad (1)$$

All LSV tests were measured at rotating speed range from 400 to 2500 rpm at the scan rate of 10 mV/s. Kouteckey-Levich (K-L) plots presenting the linear relation between j^{-1} and $\omega^{-1/2}$ were obtained based on the following equations:

$$j^{-1} = j_L^{-1} + j_k^{-1} = B^{-1}\omega^{-1/2} + j_K^{-1} \quad (2)$$

$$B = 0.62nFC_0D_0^{2/3}\vartheta^{-1/6} \quad (3)$$

$$j_K = \frac{j * j_L}{j_L - j} \quad (4)$$

where j means the measured current density, j_L is the diffusion-limiting current density, j_K corresponded to the kinetic current density, ω is the rotation rate (rpm), and n is the number of electron transfer. B^{-1} means the slope of K-L plots, F is the Faraday constant (96485 C/mol), C_0 is bulk concentration of O_2 (1.2×10^{-3} mol/L in both 0.1 M KOH and

0.1 M $HClO_4$), D_0 is the diffusion coefficient of O_2 (1.9×10^{-5} cm^2/S in 0.1 M KOH and 1.93×10^{-5} cm^2/S in 0.1 M $HClO_4$), and υ is the kinematic viscosity of the electrolyte (0.01 cm^2/S in both 0.1 M KOH and 0.1 M $HClO_4$).

The number of electron transfer (n) and the peroxide yield (H_2O_2 %) can also be precisely evaluated by RRDE, as the following equation:

$$n = \frac{4I_D}{I_D + I_R/N} \quad (5)$$

$$\%H_2O_2 = 100 \times \frac{2I_R/N}{I_D + I_R/N} \quad (6)$$

where I_D is the Faradaic current at the disk, I_R means the Faradaic current at the ring, and N is the H_2O_2 collection coefficient at the ring.

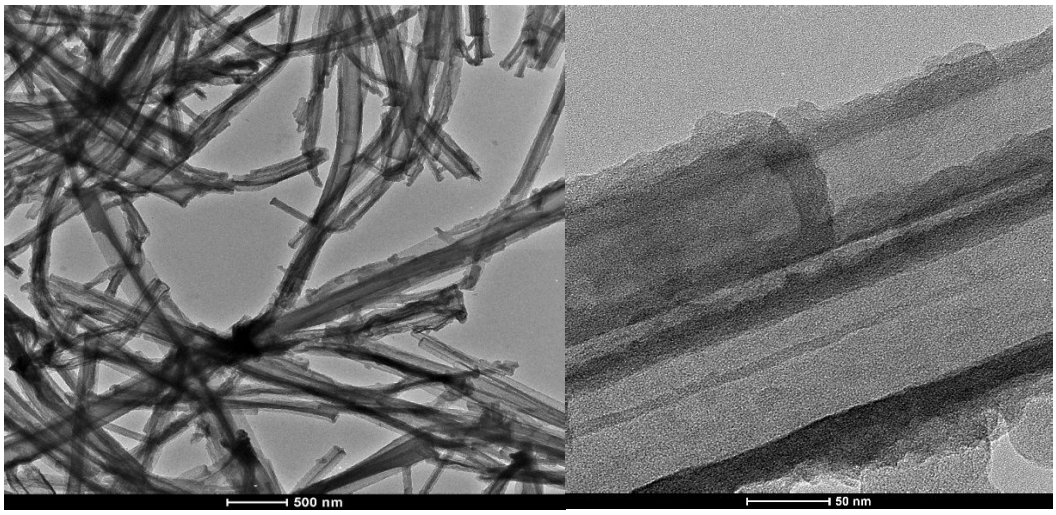


Figure S1. TEM image of the PPy precursor at different resolution.

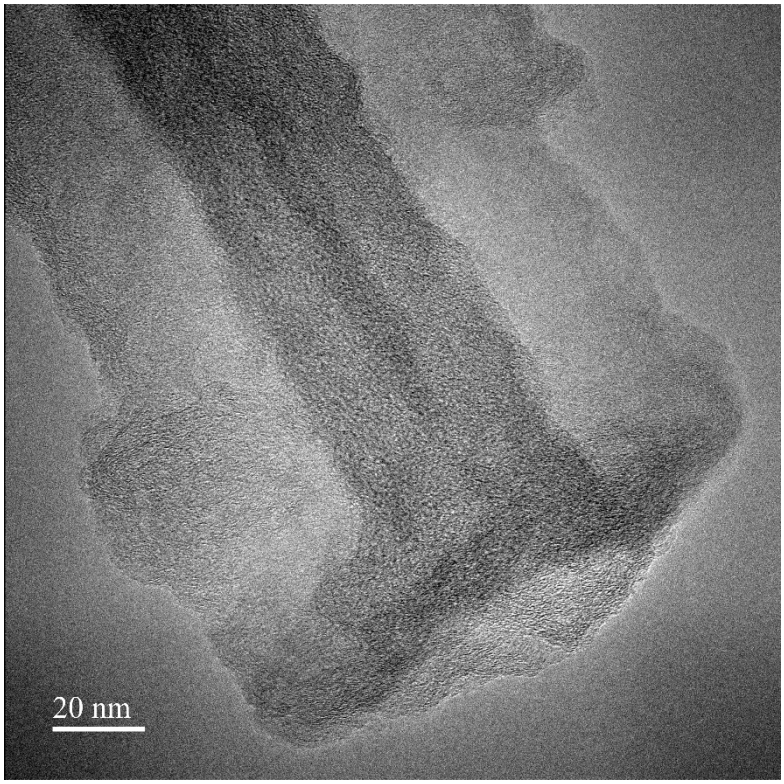


Figure S2. High-resolution BF-STEM image of SAICNT-900.

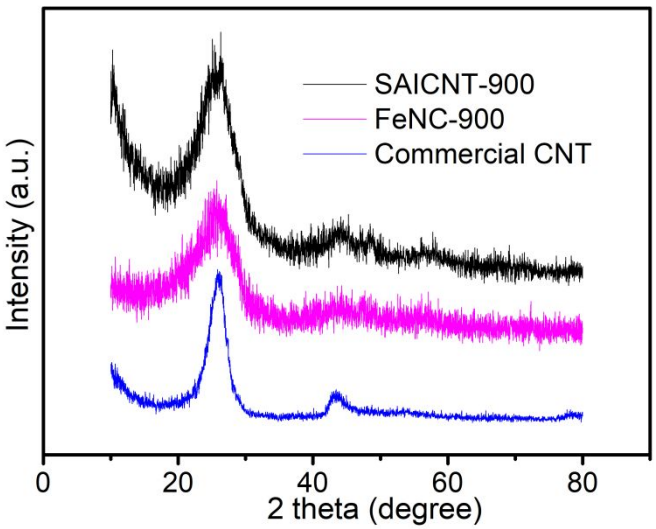
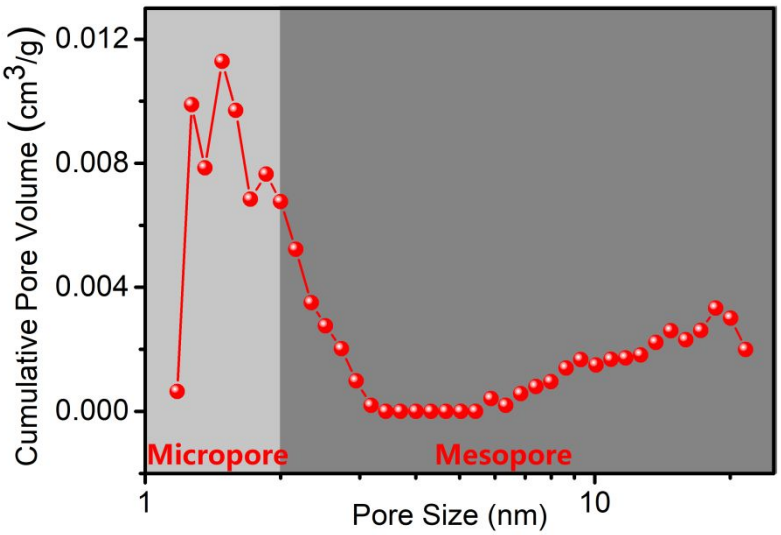


Figure S3. XRD patterns of SAICNT-900, FeCN-900 and commercial CNT.



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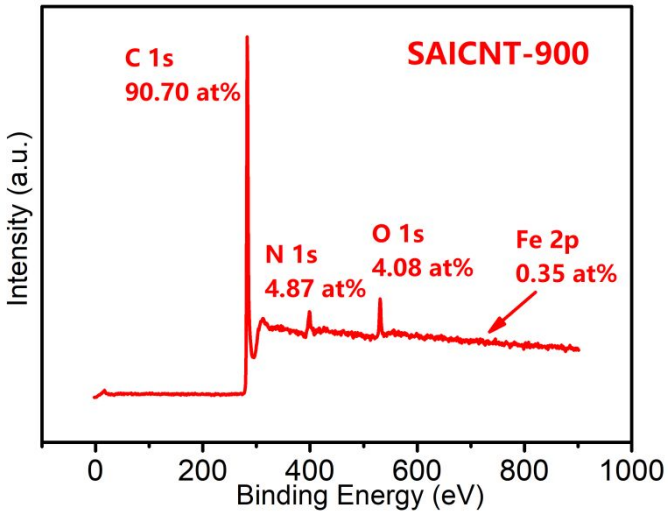
61 **Figure** S4. Pore size distribution of the SAICNT-900 catalyst.



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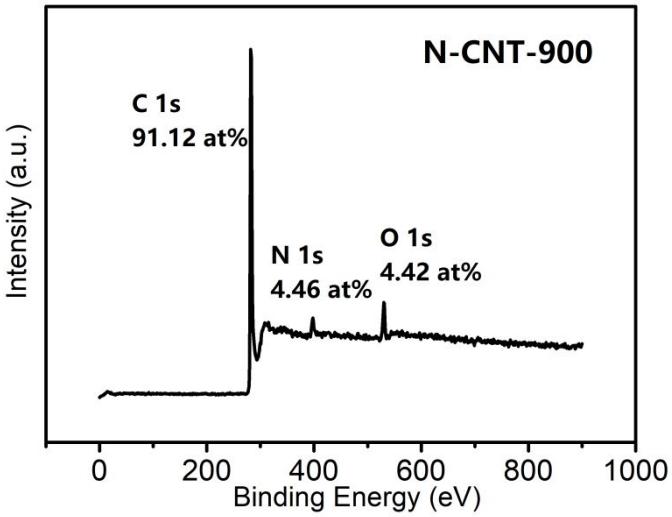
63 **Figure** S5. XPS spectrum of SAICNT-900.



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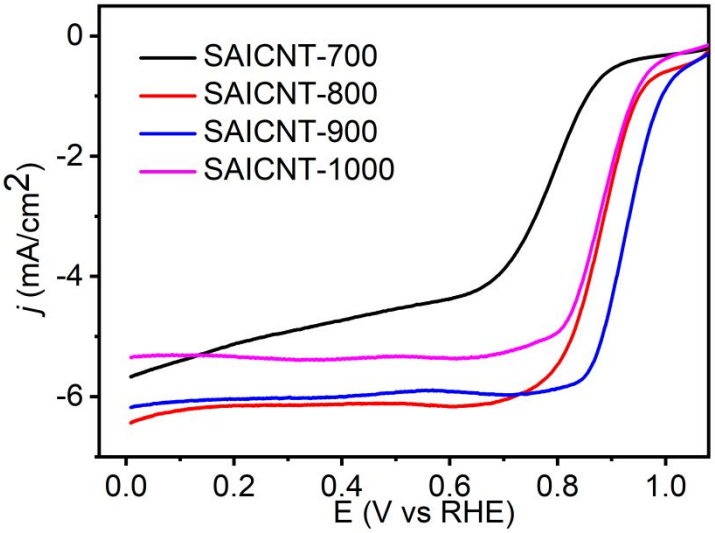
65 *Figure* S6. XPS spectrum of N-CNT-900.



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67 **Figure** S7. RDE polarization curves of SAICNT-700, SAICNT-800, SAICNT-900, and

68 SAICNT-1000 at rotating speed of 1600 rpm in O_2-saturated 0.1 M KOH solution.

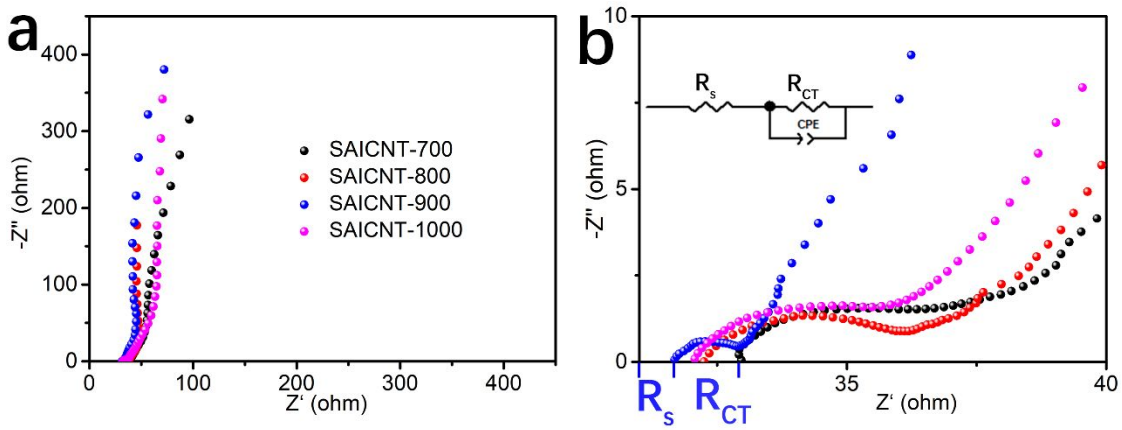

Figure S8. (a) Nyquist plots of SAICNT-700, SAICNT-800, SAICNT-900, and SAICNT-1000, (b) the magnified view of high frequency region of the impedance spectra and the equivalent circuit.

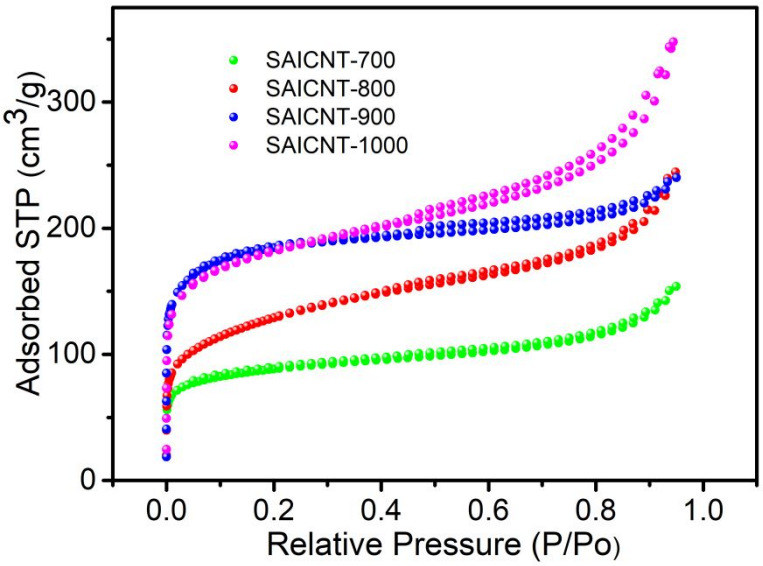

Figure S9. N_2 adsorption–desorption isotherms of SAICNT-700, SAICNT-800, SAICNT-900 and SAICNT-1000.

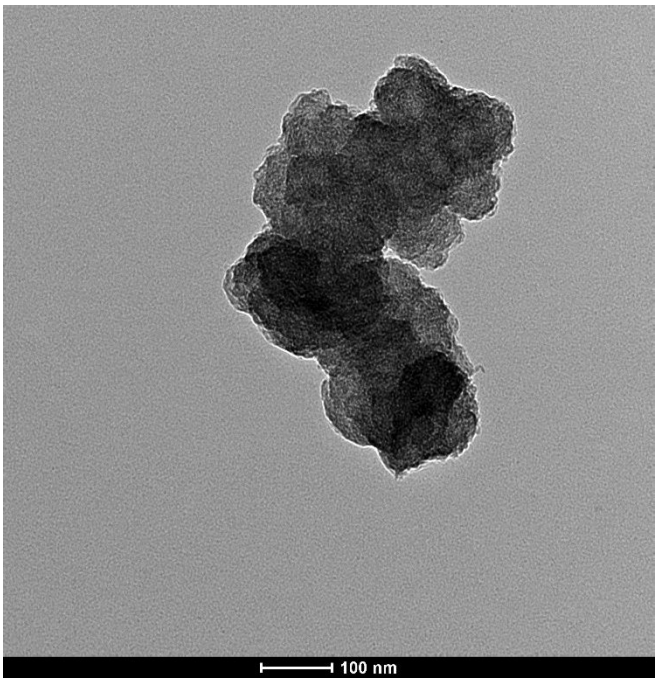

Figure S10. TEM image of FeNC-900.

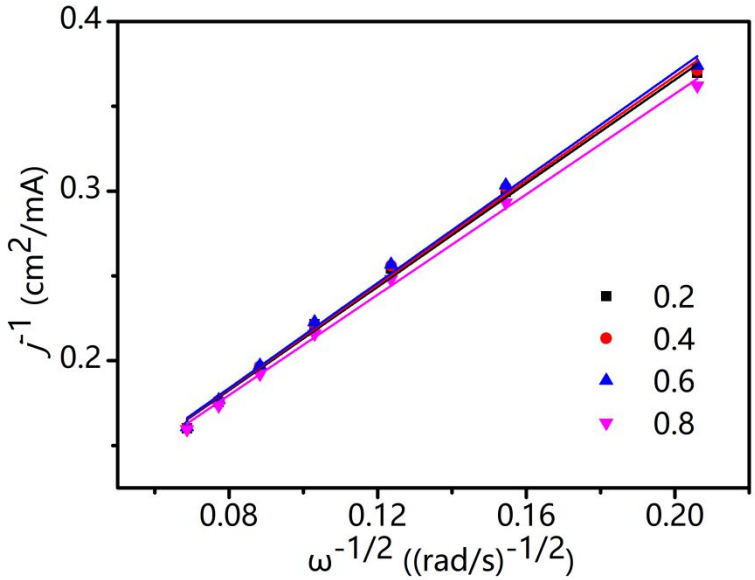

Figure S11. K–L plot of J^{-1}versus ω^{-1} based on the LSV curves on SAICNT-900 at different rotation rates in alkaline solution.

Table S1. The Fe content obtained from ICP-MS and the SSA calculated from BET method of the catalysts pyrolyzed at different temperatures.

	SAICNT-700	SAICNT-800	SAICNT-900	SAICNT-1000
Fe content (wt.%)	0.170	0.460	0.497	0.390
SSA (m^2/g)	331.29	476.13	691.90	648.16