

Supporting Information:

Highly-Efficient Metal-Free Growth of Nitrogen-Doped Single-Walled Carbon Nanotubes on Plasma-Etched Substrates for Oxygen Reduction

Dingshan Yu[†], Qiang Zhang[†], Liming Dai^{*}

*Department of Chemical Engineering, Case Western Reserve University, Cleveland,
OH 44106, USA*

* To whom correspondence should be addressed. Tel: 1-216-368-4151.

E-mail: liming.dai@case.edu.

[†] These authors contributed equally to this work.

Detailed Experimental Section:

Catalyst preparation:

A 30-nm-thick SiO₂ film deposited SiO₂/Si wafer was employed as the substrate. The SiO₂ film deposition was carried out in a reactive d.c.-magnetron sputtering system using single crystal SiO₂ as target material (99.99% purity, purchased from Angstrom Sciences, Incorporated, USA). The plasma treatment was performed using a custom built reactor, powered by a commercial radio-frequency generator. The SiO₂ film deposited SiO₂/Si wafers were first loaded into the plasma reactor, and water plasma etching was conducted at 250 kHz, 30 W, and 0.62 Torr for 20 min. And then the plasma-treated wafer was cleaned by HNO₃ solution (1.0 M), followed by washing with deionized water and acetone under a sonication bath (VWR Model 75 D) prior to use.

Metal-catalyst-free Growth of SWCNTs:

The H₂O-plasma etched SiO₂/Si wafers were first loaded into a small quartz tube (diameter, 10 mm; length, 15 cm). This small tube was then inserted into a reaction quartz tube (diameter, 30 mm; length, 120 cm), which was fixed in a Ceramic Engineering tube furnace (made in Sydney, Australia). Afterwards, the substrate was annealed in air at 900 °C for 10 min and an Ar (1000 sccm) stream was subsequently introduced to exhaust air for 5 min, followed by the introduction of a mixture gas CH₄(100 sccm)/H₂(100 sccm) to initiate the growth of SWCNTs. For nitrogen doped CNTs growth, 50 sccm NH₃ was also introduced. All the gases were controlled by

mass flow controllers (MFCs). The growth duration varied from 1-20 min. After growth, the furnace was cooled naturally down to room temperature under the protection of Ar/H₂ gas mixture (100/100 sccm). The samples were then collected for subsequent ORR reaction test and related characterization.

Characterization:

The morphology of the samples was investigated using a scanning electron microscope (Hitachi S-4500, SEM) operating at 1.0 kV. The surface topology of SiO₂ deposited SiO₂/Si wafer was examined using an AFM microscope (Micro 40, Pacific Technology) in the tapping mode in air. The surface chemistry was analyzed using a PHI Versa Probe X-ray photoelectron spectrometer (XPS). The SWCNT structure was investigated using a transmission electron microscopy (TEM, FEI Tecnai F30). Samples for the TEM measurements were prepared according to previously reported method in literature.^{s1, s2} Poly(methyl methacrylate) (PMMA) was used to transfer the SWCNTs from the substrate to the TEM grid. Briefly, a thin-layer of PMMA film was firstly spin-coated onto the substrate-supported nanotubes, followed by heating in air for about 1 min to ensure a strong adhesion to the as-grown SWCNTs. Afterwards, the substrate was removed by dipping it into 1 M KOH aqueous solution and the released polymer/SWCNT layer was subsequently transferred to a TEM grid. Finally, the TEM grid was immersed into 10 mL acetone for 0.5 hr to remove the PMMA and then dried for use.

Electrochemical Measurements:

Cyclic voltammetry (CV) measurements were performed using a computer-controlled potentiostat (CHI 760 C, CH Instrument) in a standard three-electrode cell. NCNT/GC or CNT/GC electrode was used as working electrode, a Pt wire as counter electrode, and an Ag/AgCl (3 M KCl filled) electrode as reference electrode. Measurements on rotating ring-disk electrode (RRDE) and/or rotating disk electrode (RDE) were carried out on a MSR-X electrode rotator (Pine Instrument) and the CHI 760 C potentiostat. For all CV and RDE measurements, an aqueous solution of H₂SO₄ (0.5 M) was used as the electrolyte. N₂ or O₂ was used to purge the solution to achieve the oxygen-free or oxygen-saturated electrolyte solution. The voltammetric stability test of NCNTs was performed in O₂-saturated 0.5 M H₂SO₄ in the potential range from 0.8 to -0.2 V at a scan rate of 50 mV/s for two days.

The working electrode was prepared as follows: a drop of Nafion solution (5 %) was cast onto the surface of the *as-synthesized* CNTs or NCNTs on the SiO₂/Si substrate, followed by drying in air. Thereafter, the substrate was removed by immersing it into an aqueous HF solution (1:6 v/v) to produce a free-standing film of carbon nanotubes supported by the Nafion coating. Finally, the resultant nanotube film was attached onto a glassy carbon electrode to fully cover the electroactive circle.

For a more quantitative evaluation of the ORR electrocatalytic activity for NCNTs, rotation-rate-dependent RDE measurements were performed using the Koutecky-Levich equation.^{s3, s4} This equation was used to determine the number of electrons involved in oxygen reduction using NCNTs. This equation is valid for a

first-order process with respect to the diffusion species, and the current density j is related to the rotation rate ω of the electrode according to

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{B\omega^{0.5}} \quad (1)$$

where j_k is the kinetic current and B is Levich slope which is given by

$$B = 0.2nF(D_{O_2})^{2/3}v^{-1/6}C_{O_2} \quad (2)$$

Here n is the number of electrons transferred in the reduction of one O_2 molecule, F is the Faraday constant ($F = 96485 \text{ C/mol}$), D_{O_2} is the diffusion coefficient of O_2 ($D_{O_2} = 1.15 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), v is the kinematics viscosity for sulfuric acid ($v = 1.07 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$) and C_{O_2} is concentration of O_2 in the solution ($C_{O_2} = 1.4 \times 10^{-6} \text{ mol cm}^{-3}$). The constant 0.2 is adopted when the rotation speed is expressed in rpm.

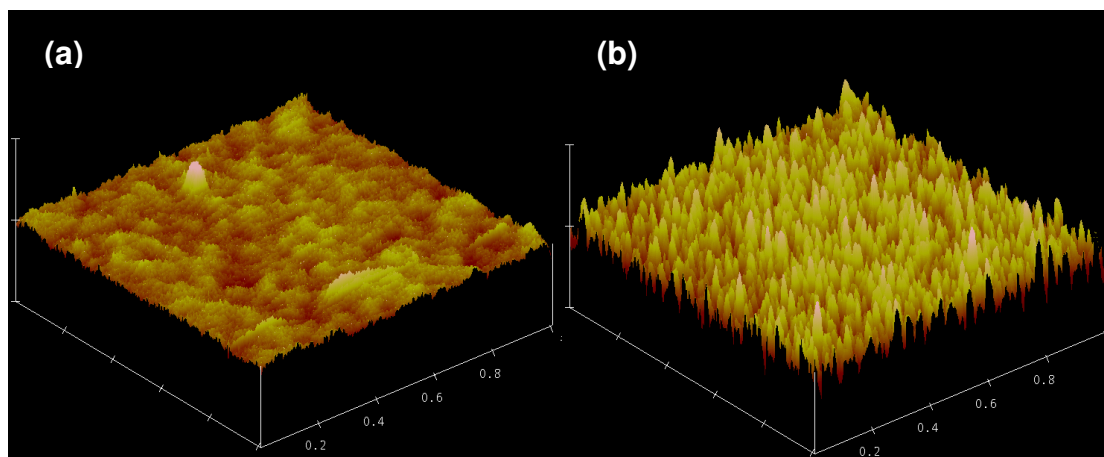


Figure S1. Atomic force microscopy images of the SiO₂/Si wafer (a) before and (b) after the plasma etching.

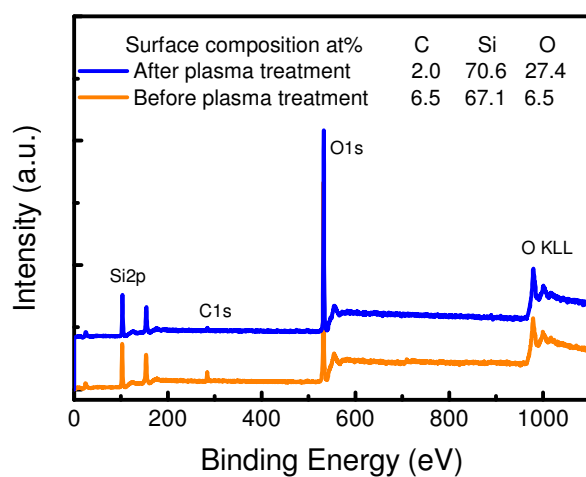


Figure S2. XPS spectra of the SiO₂/Si wafer before and after the water plasma etching.

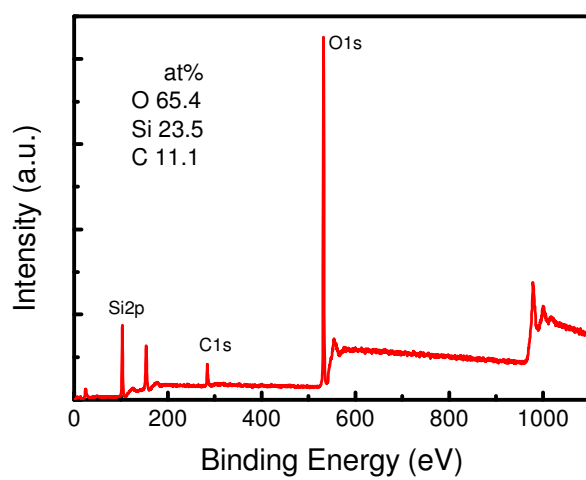


Figure S3. XPS spectra of the as-grown CNTs on the SiO₂/Si wafer pre-etched by the water plasma.

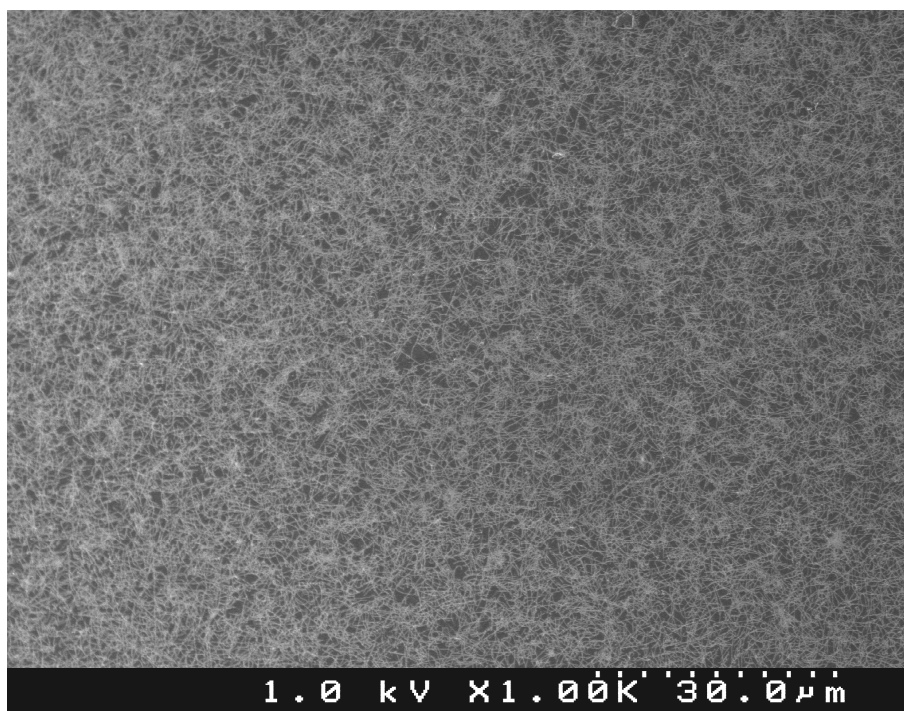


Figure S4. SEM image of high-density SWCNTs grown on a SiO₂/Si wafer pre-etched by the water-plasma for 1 hr. No post-treatment with HNO₃ solution was taken before the SWCNT growth.

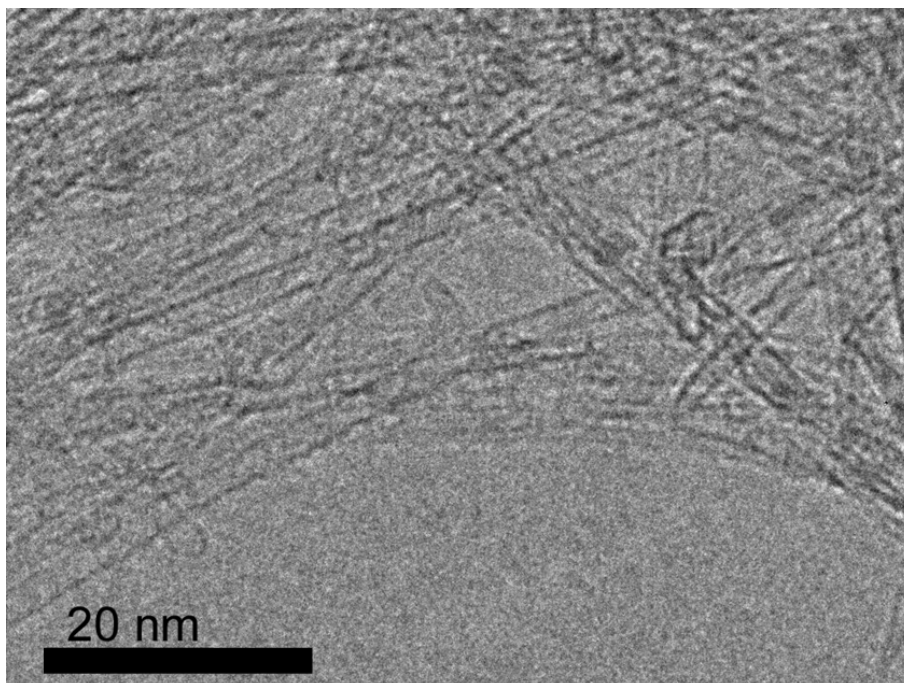


Figure S5. TEM image of SWCNTs grown on a water-plasma etched SiO₂/Si wafer.

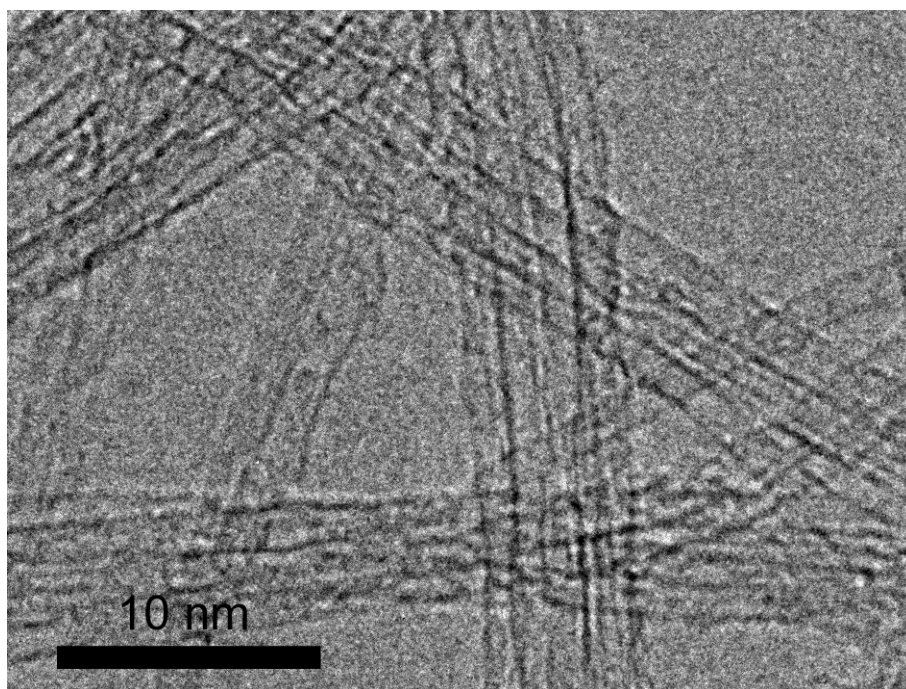


Figure S6. TEM image of N-doped SWCNTs grown on a water-plasma etched SiO_2/Si wafer.

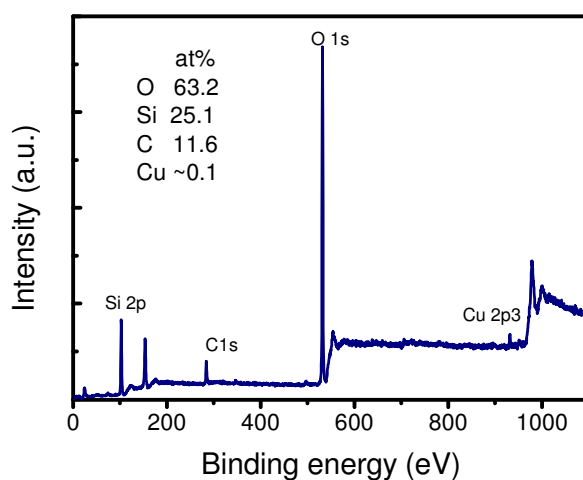


Figure S7. XPS spectra of the CNTs grown on a SiO₂/Si wafer pretreated by water-plasma etching for 1 hr. Slight Cu contamination from the Cu electrodes used in the plasma reactor can be found on the surface, and the water-plasma etched SiO₂/Si wafer supported a high-yield growth of SWCNTs, as shown in Figure S4. If the plasma etched wafer was cleaned by HNO₃ solution (1.0 M), followed by washing with deionized water and acetone under sonication before the SWCNT growth, the Cu can be almost fully removed (as indicated by Figure S2). The plasma etched metal-free SiO₂/Si wafer is still very effective and efficient for the high-density nanotube growth.

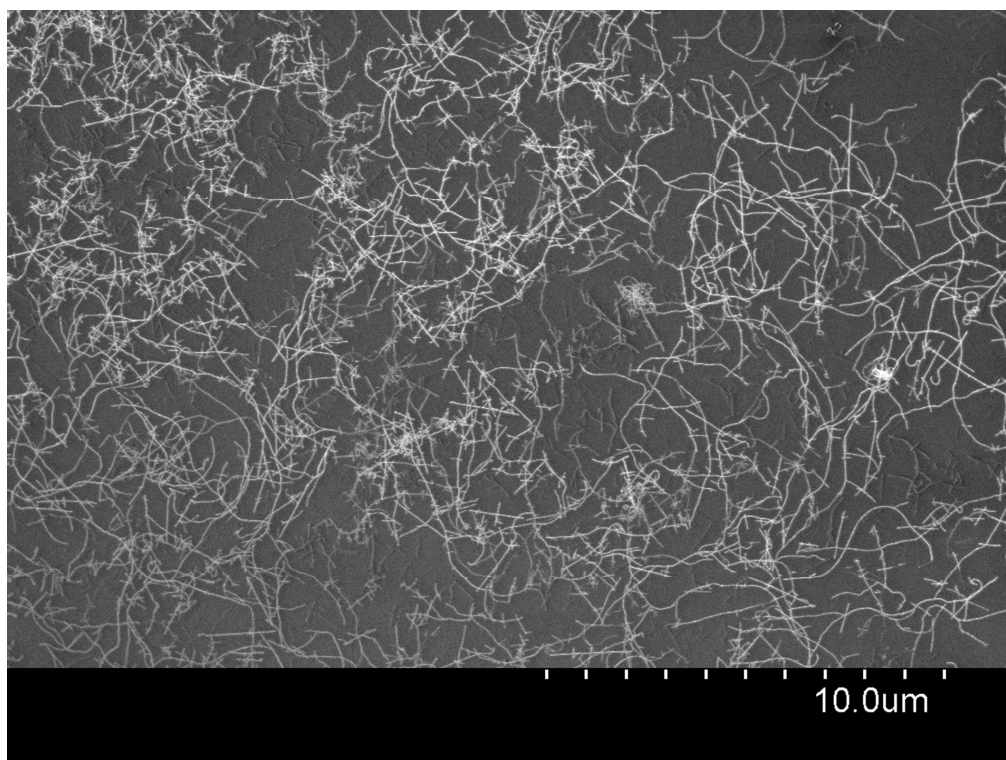


Figure S8. Typical SEM image of SWCNTs grown on a water-plasma etched quartz.

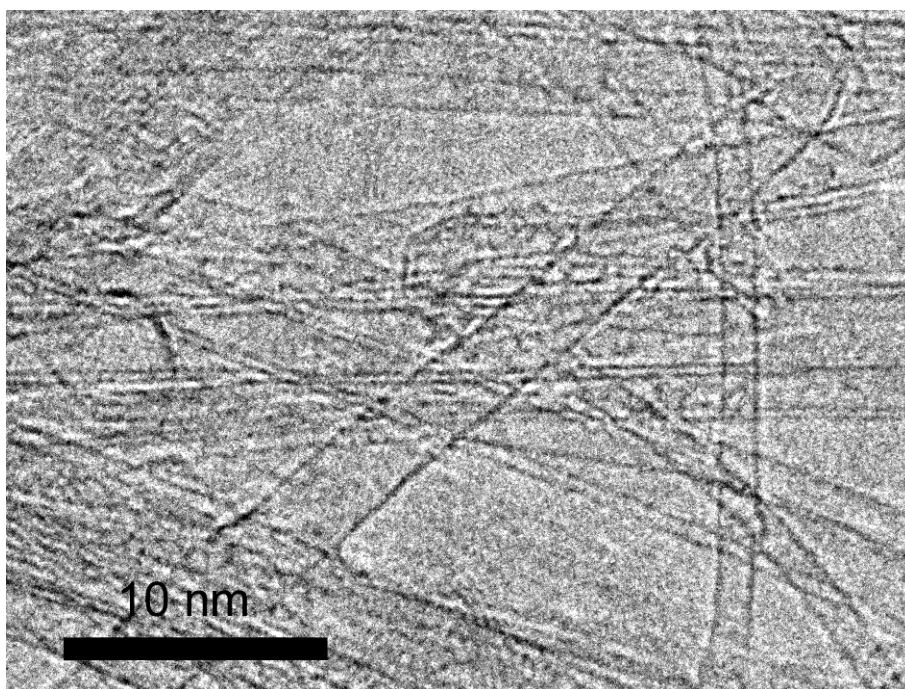


Figure S9 TEM image of SWCNTs grown on a water-plasma etched quartz.

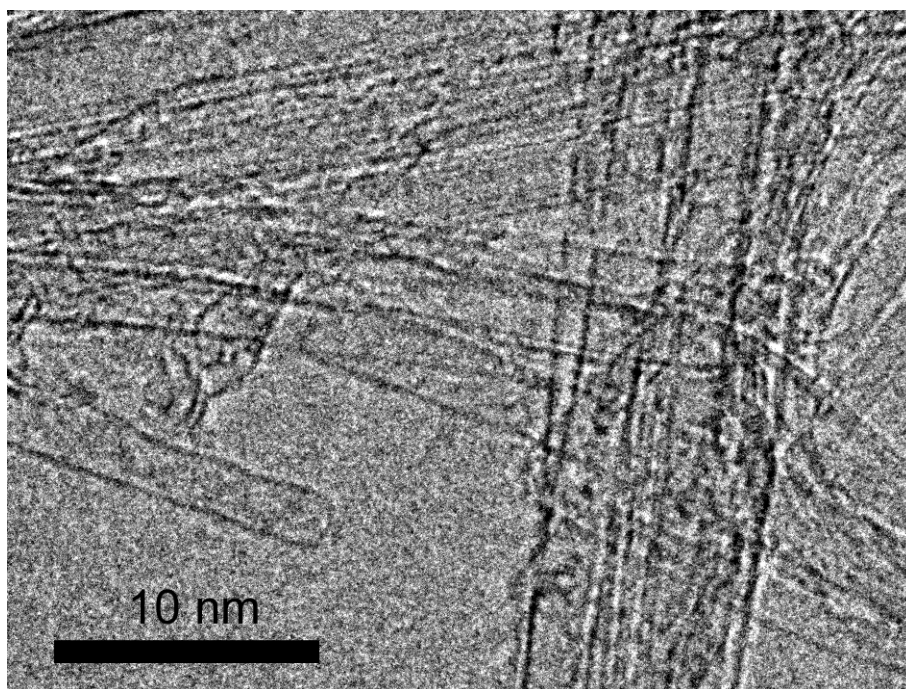


Figure S10 Typical TEM image of N-doped SWCNTs grown on a water-plasma etched quartz.

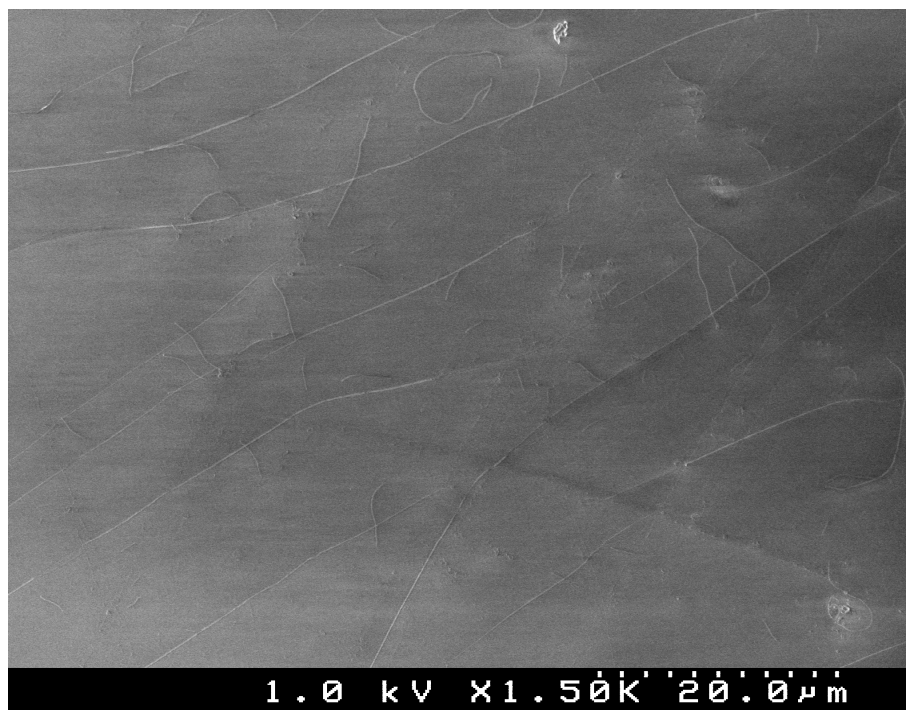


Figure S11. Typical SEM image of SWCNTs grown on a water-plasma etched mica.

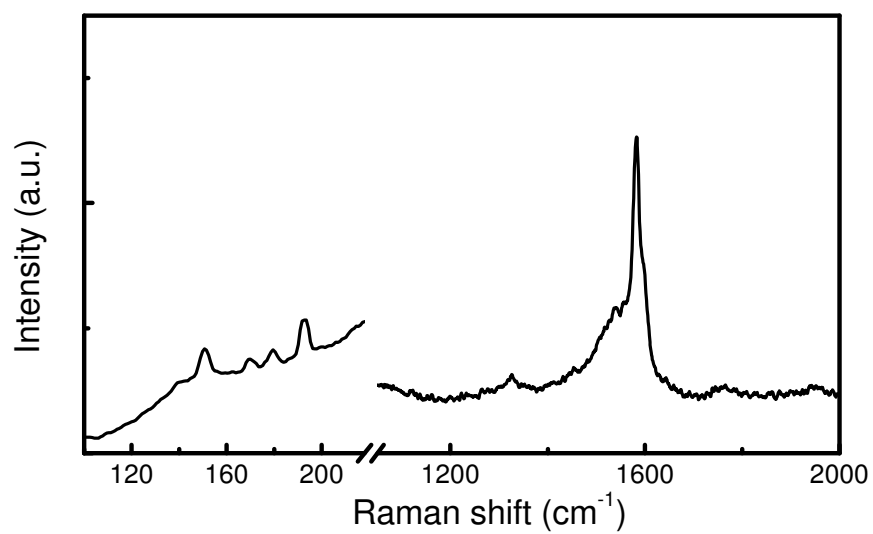


Figure S12. Typical Raman spectrum collected from SWCNTs grown on a SiO₂/Si wafer pretreated by water-plasma etching.

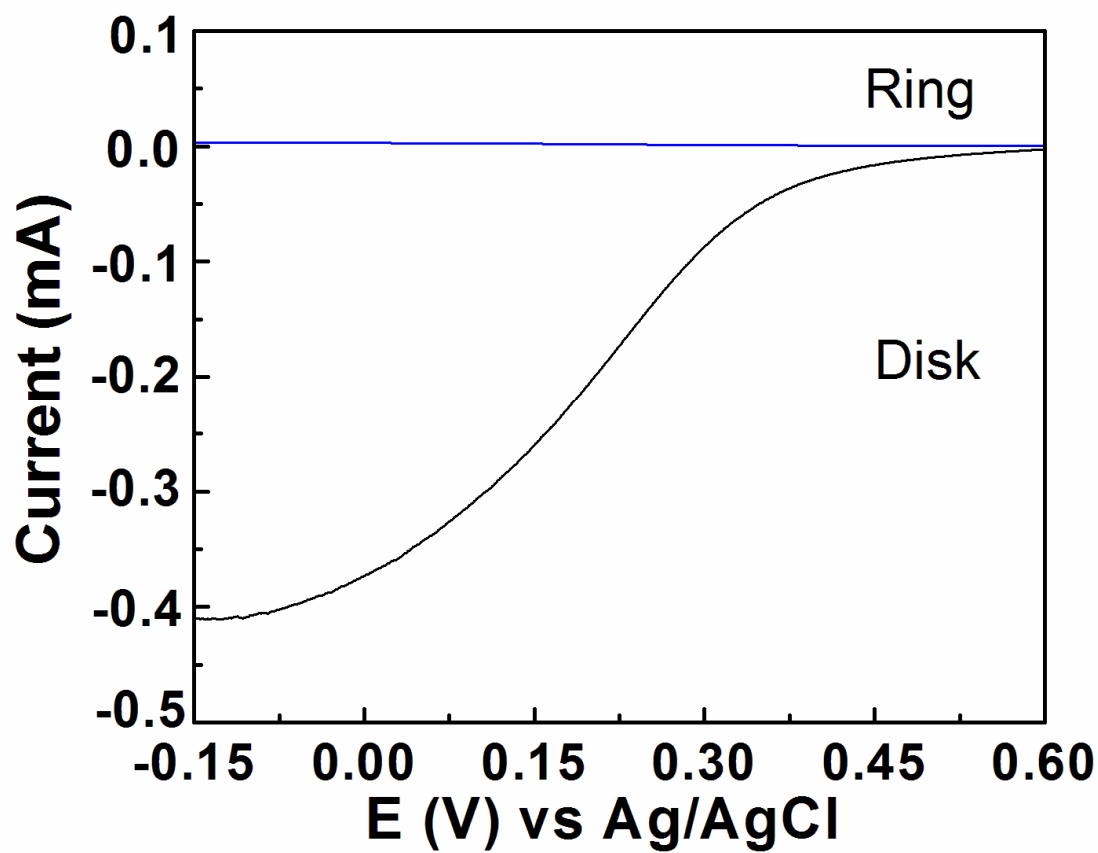


Figure S13. RRDE voltammogram of N-doped metal-free SWCNTs in 0.5 M H₂SO₄ solution saturated with O₂ at 1200 rpm. The ring electrode was polarized at 1.0 V.

References:

- S1. Jiao, L. Y.; Fan, B.; Xian, X. J.; Wu, Z. Y.; Zhang, J.; Liu, Z. F. *J. Am. Chem. Soc.* **2008**, 130, (38), 12612-12613.
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- S3. Chen, J.; Zhang, W. M.; Officer, D.; Swiegers, G. F.; Wallace, G. G. *Chem. Commun.* **2007**, (32), 3353-3355.
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