Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Electronic Supplementary Information

Non-nitrogen Doped and Non-metal Oxygen Reduction Electrocatalysts based on Carbon Nanotubes: Mechanism and Origin of ORR Activity

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Double Layer Normalization

All of the data from the electrochemical measurements are normalized to the electrochemical surface area (ECSA) derived from the double layer (dl) capacitance of our sample taken under saturated Ar conditions[1] by assuming the typical dl capacitance of carbon materials as 25 μF cm^{-2}.[2] This allows for the comparison of actual electrochemical-effective surface area. The ORR polarization curves were obtained by subtracting the Ar and O_2 current responses and also normalized to the double layer taken from CV in saturated Ar conditions.

TPD Quantitative Characterization

The quantity of CO and CO_2 gas evolved from temperature programmed desorption (TPD) measurements done by calibrating the sensitivity of the mass spectrometer detector using an H-implanted Si substrate. The amount of oxygen functionalities was also determined quantitatively from data supplied by TPD characterization as shown in Table S1.

Table S1. CO and CO_2 desorption quantization from TPD characterization.

Sample	CO (mol/g)	CO_2 (mol/g)	Total oxygen desorbed (wt%)	Total oxygen desorbed (at%)
Functionalized MWNTs (precursor) (PMWNT)	1.8×10^{-3}	9.0×10^{-4}	5.76	4.38
DMWNT-HNO_3	4.1×10^{-3}	1.8×10^{-3}	12.32	9.53
DMWNT-H_2SO_4	3.4×10^{-3}	4.7×10^{-4}	6.94	5.30

Table S2. I_D/I_G characterization for different MWNTs.

Sample	I_D/I_G
PMWNT	1.14
DMWNT-HNO_3	1.56
DMWNT-H_2SO_4	1.43
DMWNT-H_2SO_4-Ar900	1.46

Supplementary Figures

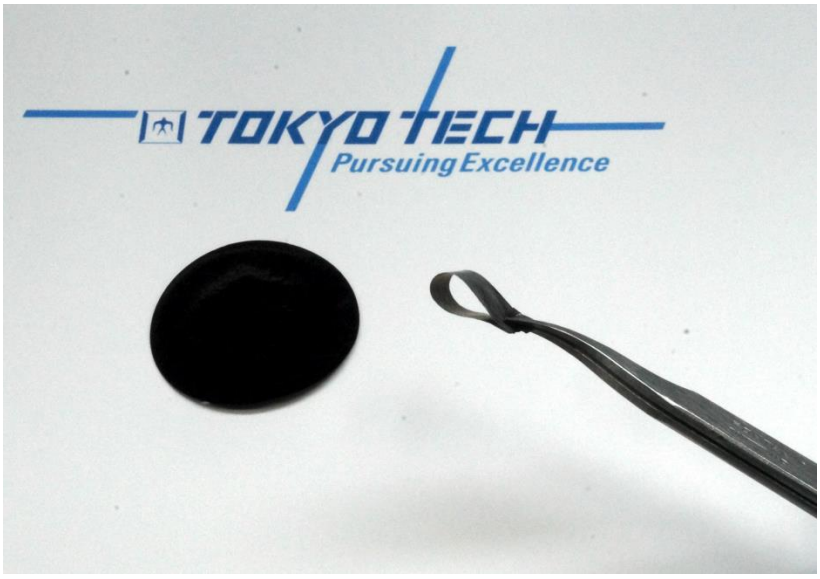

Figure S1. Digital photograph of typical as-prepared buckypaper

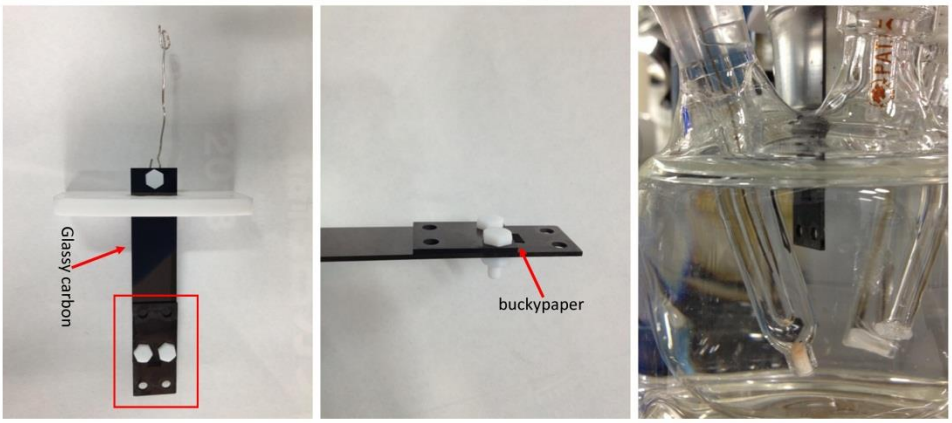

Figure S2. Digital photographs of the working electrode setup

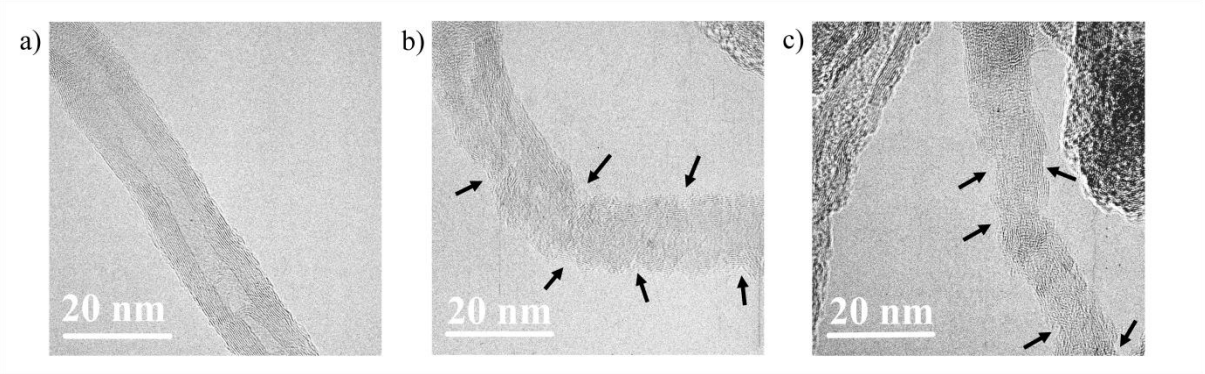

Figure S3. TEM micrographs of typical as-prepared (a) functionalized precursor to chemical drilling (PMWNT), (b) DMWNT-HNO_3, and (c) DMWNT-H_2SO_4 showing the effects of the chemically drilled holes and defects on the MWNTs. The TEM images were obtained using FE-TEM (JEOL, JEM-2010F) operated at 200 kV.

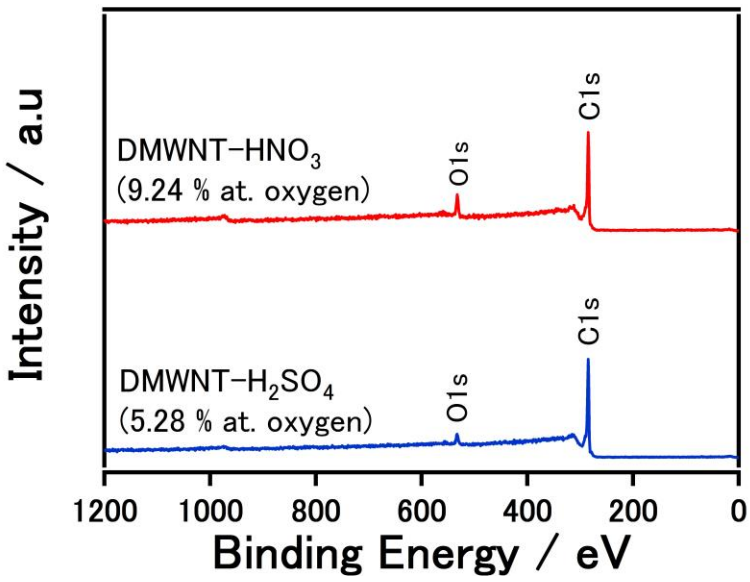

Figure S4. XPS survey scan for DMWNT-HNO_3 and DMWNT-H_2SO_4. X-ray photoelectron spectroscopy (XPS) measurements were carried out using Perkin-Elmer XPS model 5500MT, with a monochromatized Al Kα X-ray source.

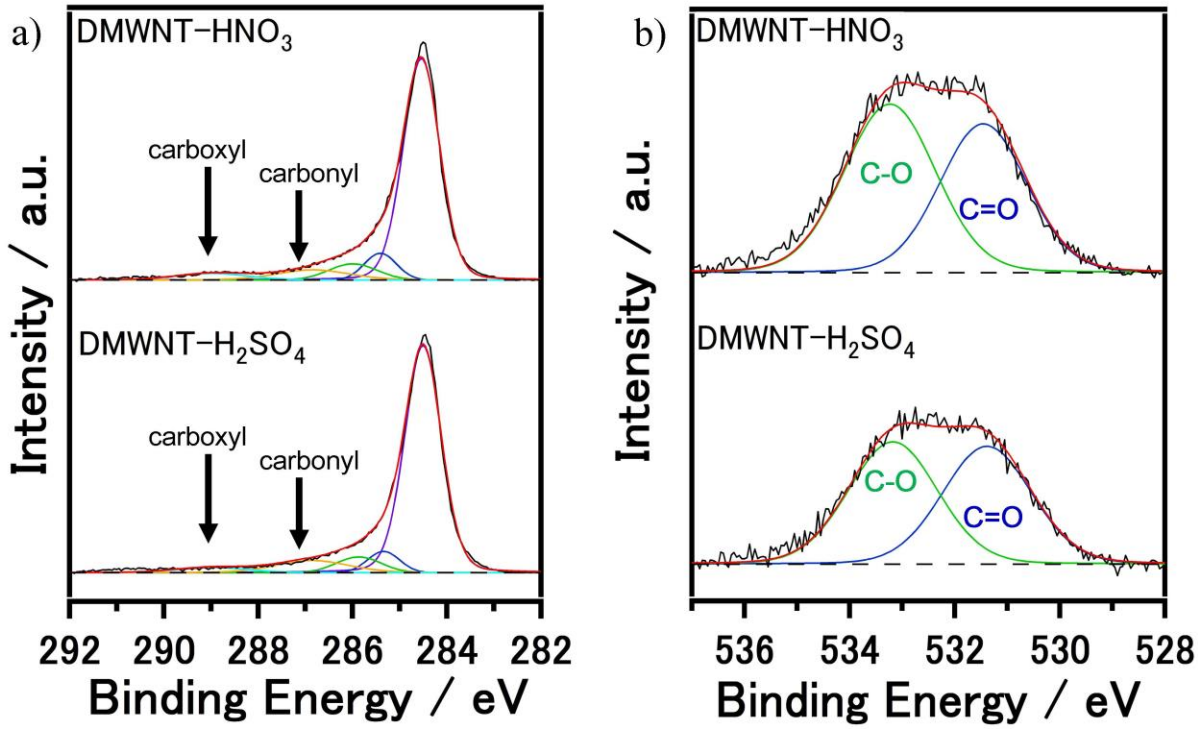

Figure S5. (a) XPS C1s spectrum and (c) XPS O1s spectrum of the corresponding samples.

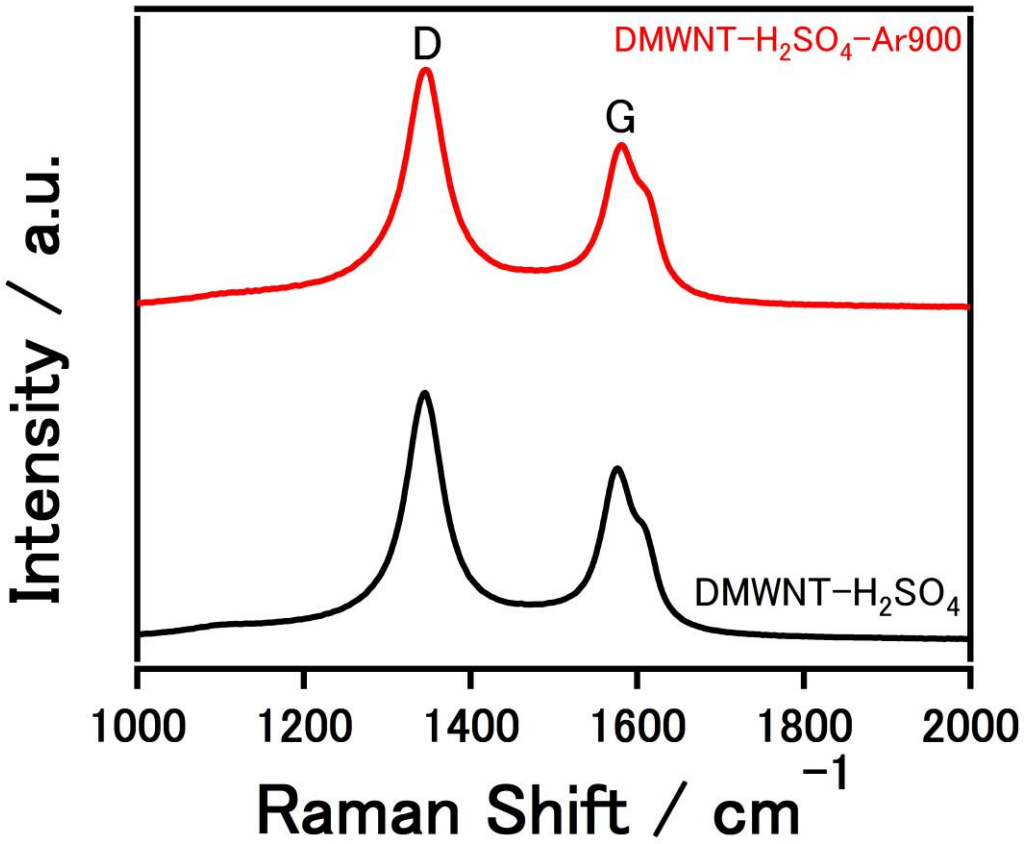

Figure S6. Raman spectra for DMWNT-H_2SO_4 before (black) and after annealing in Ar at 900 ˚C DMWNT-H_2SO_4-Ar900 (red). Raman spectra were taken under ambient condition using an NRS-3100 Series (JASCO) with and Ar-ion laser beam at an excitation wavelength of 532 nm.

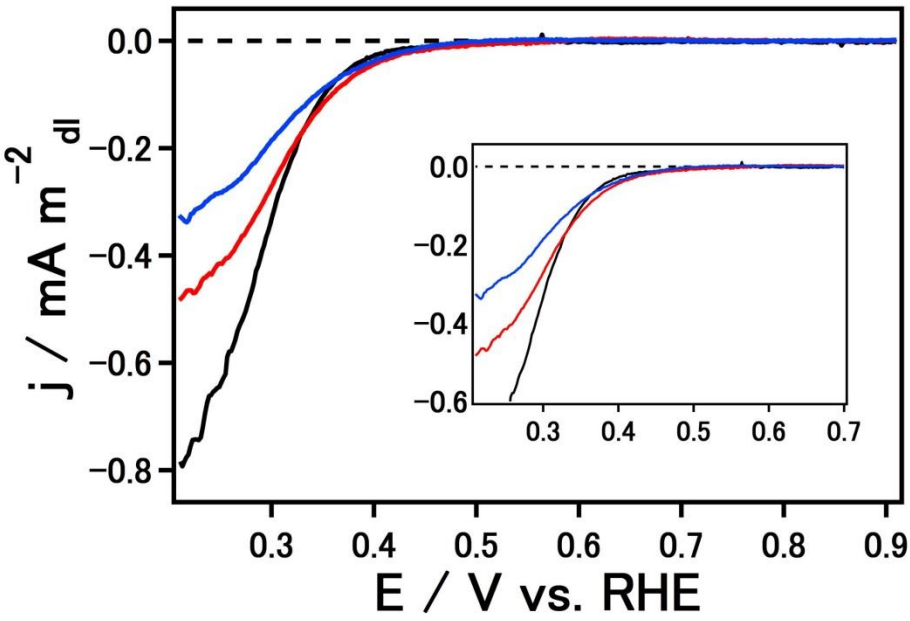

Figure S7. ORR polarization curve showing as-prepared (red) DMWNT-H_2SO_4, (black) DMWNT-HNO_3, and (blue) DMWNT-HNO_3 after annealing at 300°C in Ar taken in 0.1 M $HClO_4$ with scan rate of 1 mV/s. The inset shows a reduced current density and potential window.

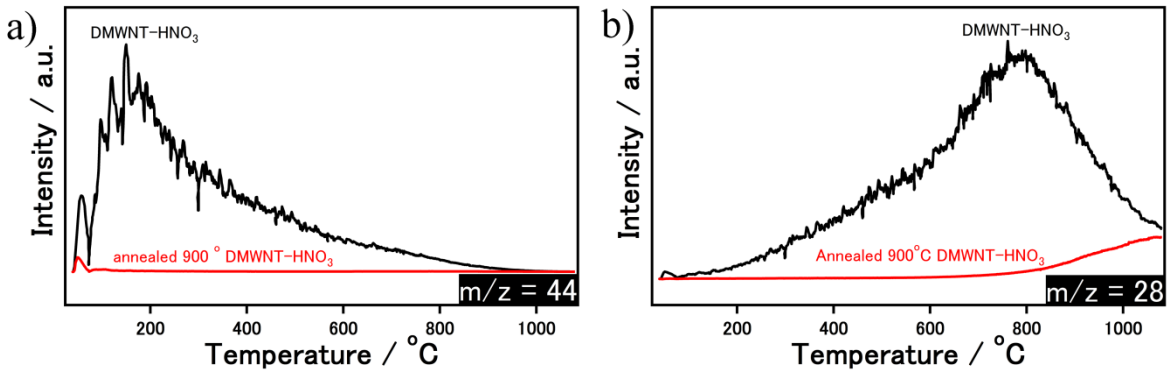

Figure S8. Temperature programmed desorption (TPD) (a) CO_2 and (b) CO spectra of (black) as-prepared DMWNT-HNO_3 and (red) DMWNT-HNO_3 following annealing in Ar at 900°C showing the effects of oxygen recombination

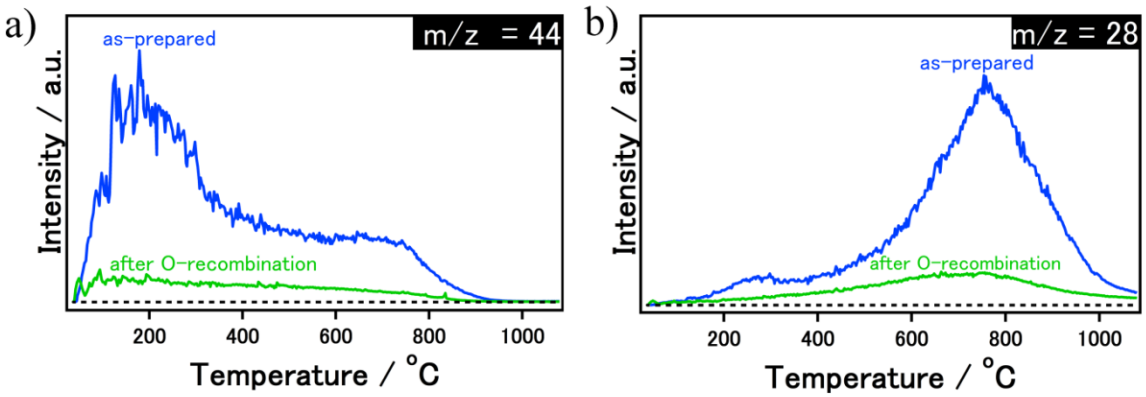

Figure S9. (a) CO_2 (b) CO, TPD spectra showing "as prepared" DMWNT-H_2SO_4 (blue). The flat dotted line shows the measurement taken directly afterwards. The sample was then exposed to air and subsquently characterized with TPD again, labeled as "after O-recombination" (green) showing the partial recombination of oxygen functional groups

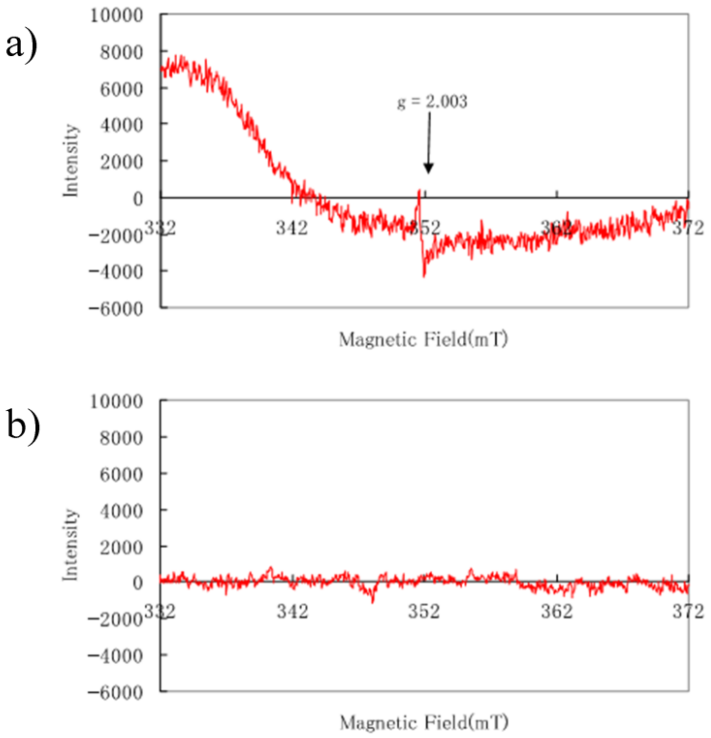

Figure S10. Electron spin resonance (ESR) spectra for (a) as-prepared precursor containing functionalized MWNTs (PMWNT) and (b) PMWNT following annealing in Ar at 900°C

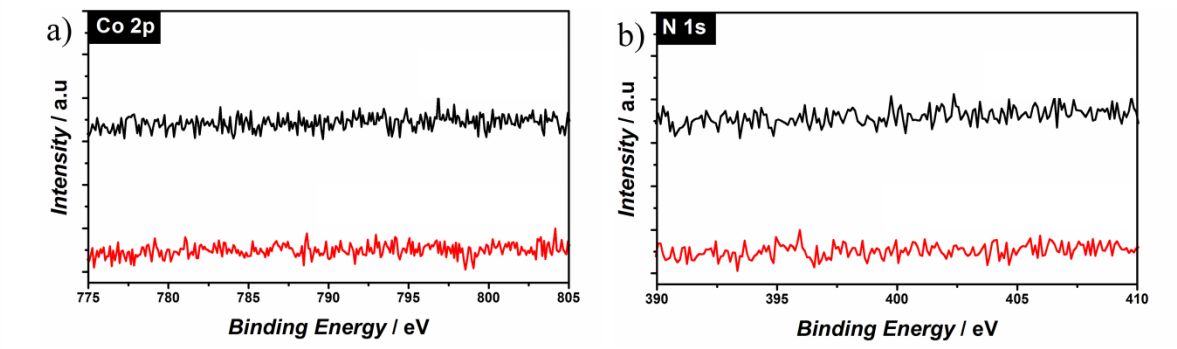

Figure S11. XPS spectra containing Co 2p and N 1s regions of the (black) precursor functionalized MWNTs and (red) DMWNT-H_2SO_4 following annealing in Ar at 900˚C.

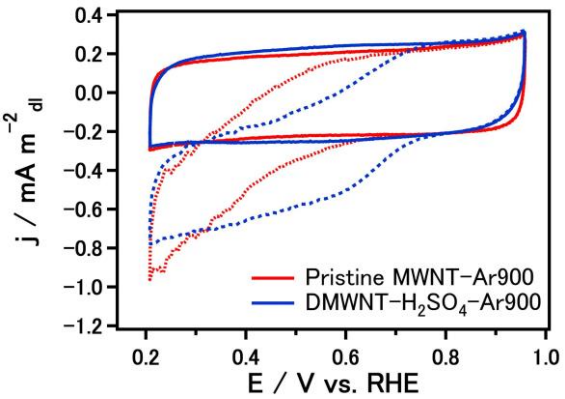

Figure S12. Cyclic voltammetry (CV) curves of buckypaper fabricated from Pristine MWNT-Ar900 (red) and DMWNT-H_2SO_4-Ar900 (blue). CV was taken in 0.1 M $HClO_4$ with scan rate of 1 mV/s in Ar (solid) and O_2 (dotted)

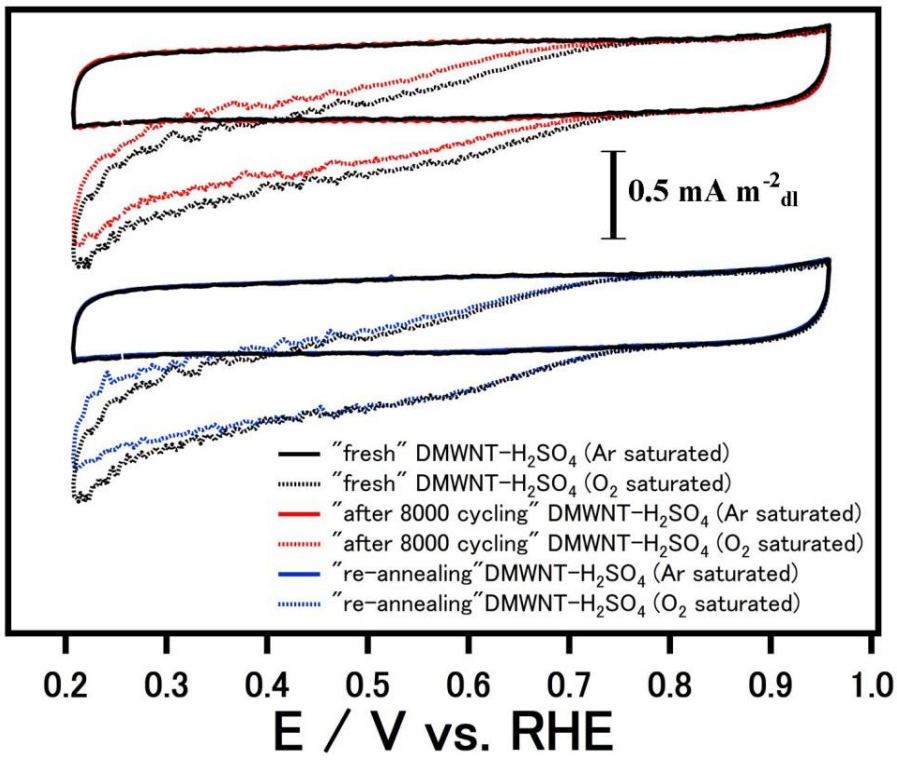

Figure S13. Cyclic voltammetry (CV) showing DMWNT-H_2SO_4-Ar900 (DMWNT-H_2SO_4 annealed at 900^{o}C in Ar) **initial (fresh catalyst)**, **after 8000 cycles (for durability test)** and **re-annealing (after proceeding durability test)** at 900^{o}C under Ar atmosphere. CV was taken in 0.1 M $HClO_4$ with scan rate of 1 mV/s. Meanwhile, durability test was conducted by cycling under O_2 with a scan rate of 50 mV/s, voltage window [0.2 - 0.6] V vs. Ag/AgCl.

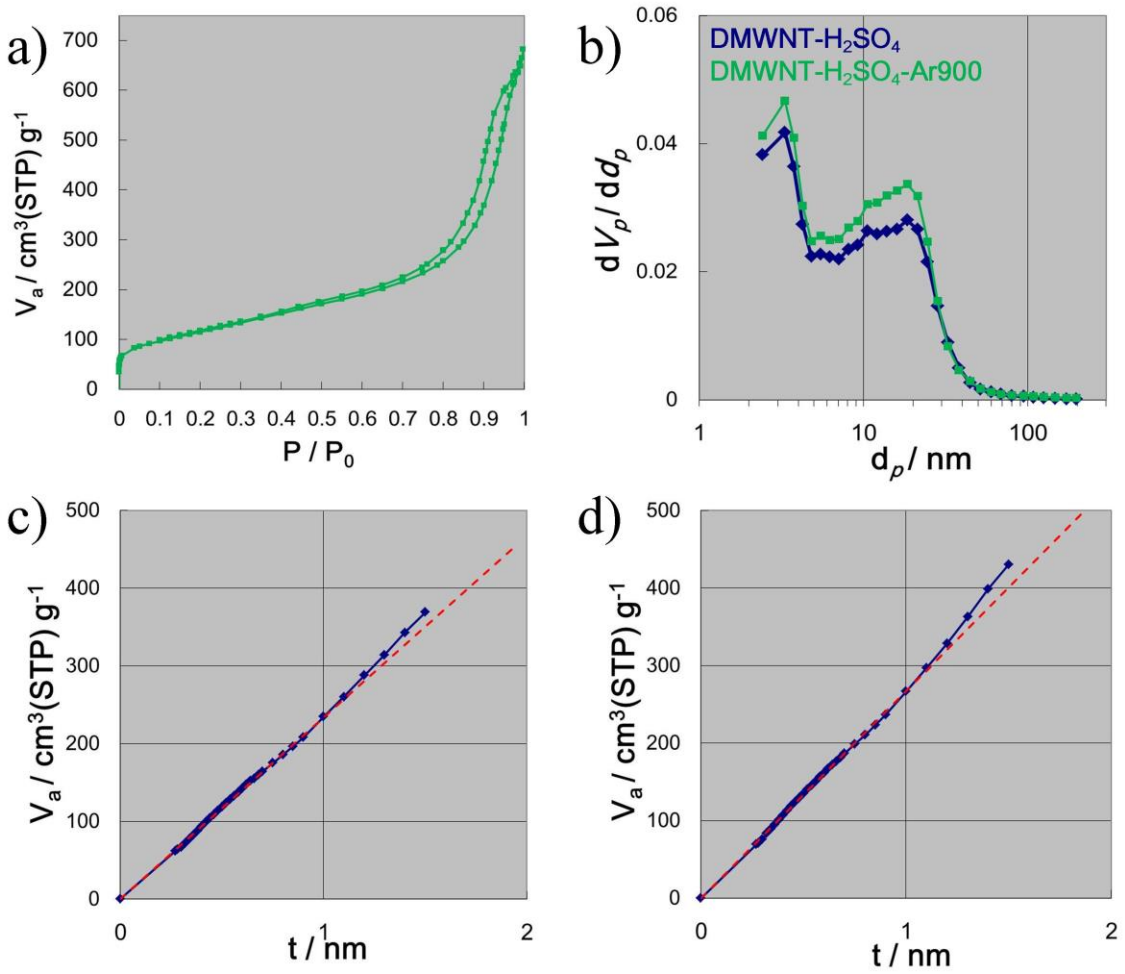

Figure S14. N_2 adsorption-desorption isotherm of (a) DMWNT-H_2SO_4-Ar900, (b) BJH plot for corresponding samples-confirming their microporosity characteristics, equipped with t-plot analysis for DMWNT-H_2SO_4 (c) as-prepared and (d) after annealing under Ar at 900 ^oC.

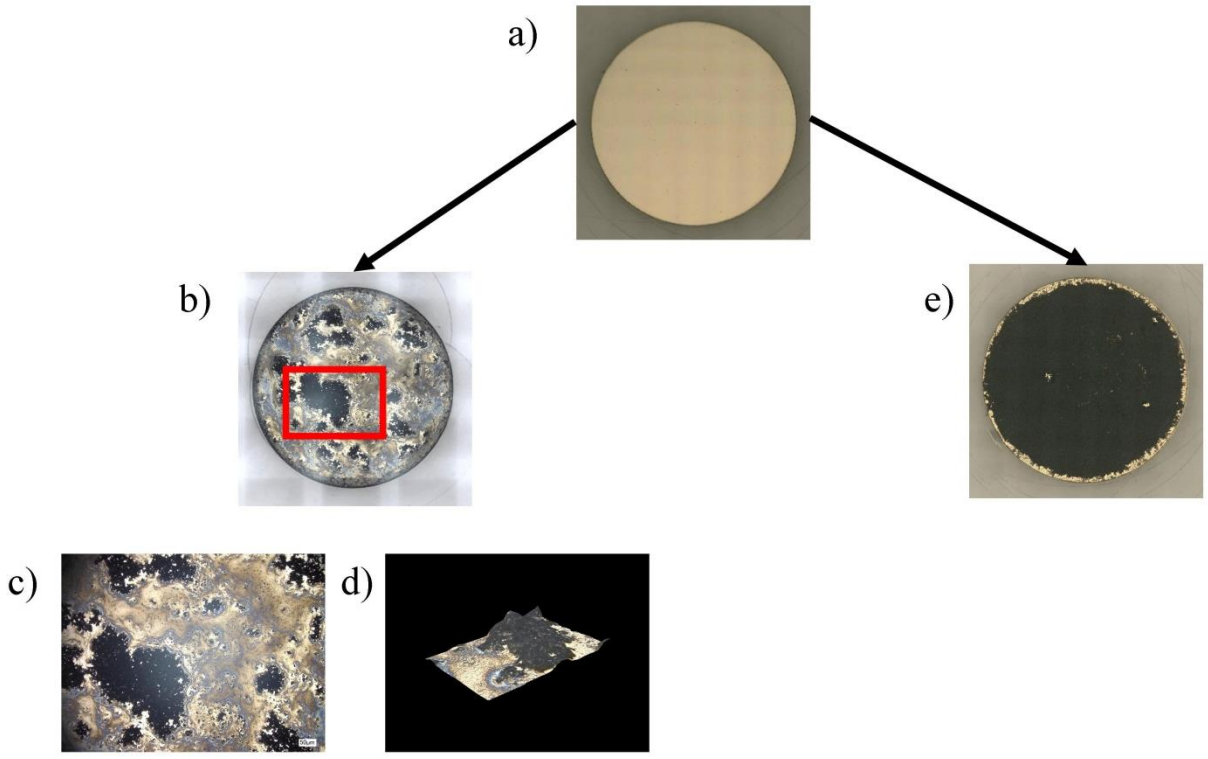

Figure S15. Digital photograph taken from microscope (Keyence VHX-2000) of typical (a) clean RDE electrode (diameter: 5 mm) (b) RDE drop-casted with sample DMWNT-H_2SO_4 that was heat treated in Ar at 900°C, followed with ink preparation and drop-casting on glassy carbon (GC) electrode (c) close up of DMWNT-H_2SO_4 prepared RDE electrode of the red rectangle (d) 3D topology of close up area showing the uneven catalyst coating and (e) RDE drop-casted with an alternative technique, instead of removing O-functionalities by Ar treatment, DMWNT-H_2SO_4 ink (containing functionalities) directly drop casted on a detachable GC. The drop-casted GC disk then annealed under Ar atmosphere at 900°C. For these microscope photographs, the ink procedures is as follows: 4 mg carbon sample (Ar treated or not), 0.8 mL water, 0.2 mL ethanol and 10 μL of 5 wt% Nafion, followed by vigorous sonication for at least 30 minutes. The multicolored tint is caused by Nafion.

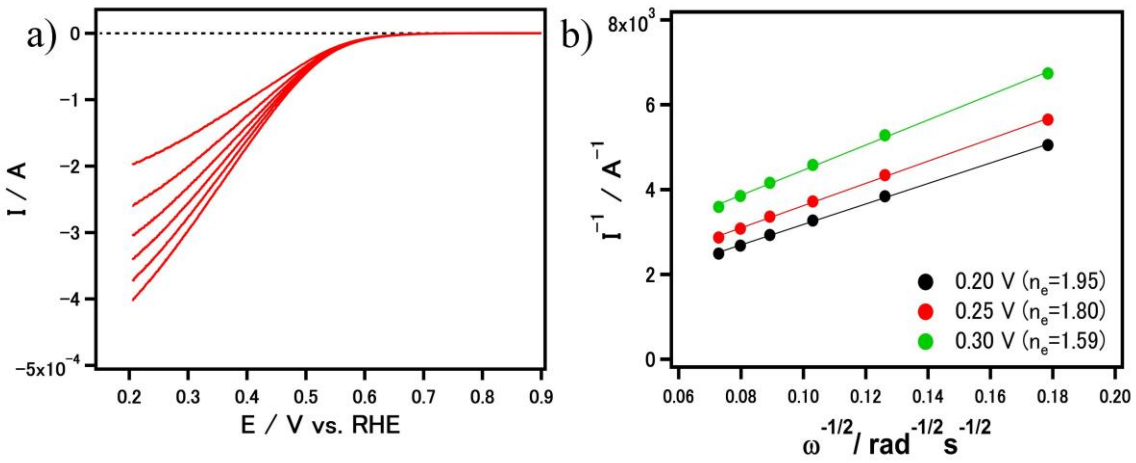

Figure S16. a) ORR polarization and b) Koutecky-Levich plots showing the electron number at different potentials of DMWNT-H_2SO_4-Ar900. ORR polarization was derived by linear scan voltammetry (LSV) sweep in Ar and O_2 atmosphere at a scan speed of 5 mV/s, under various rotating speed 300-1800 rpm (interval 300 rpm)

References

(1) Trasatti, S.; Petrii, O. A. *Pure Appl. Chem*., **1991**, 63, 711-734.

(2) Conway, B. E. *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*.; Kulwer: New York, **1997**.

(3) Kundu, S.; Wang Y.; Xia W.; Muhler M. *J. Phys. Chem. C*, **2008**, 112, 16869-16878.

(4) Serp P.; Corrias M.; Kalck P. *Appl. Catal. A*, **2003**, 253, 337-358.