Electronic Supplementary Information

Highly-compressed nanosolution restricted in cylindrical carbon nanospaces

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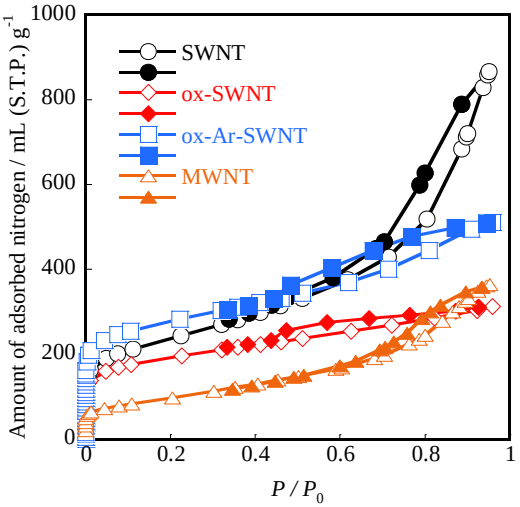

Fig. S1 Adsorption and desorption isotherms of nitrogen on SWNT, ox-SWNT, ox-Ar-SWNT, and MWNT at 77 K.

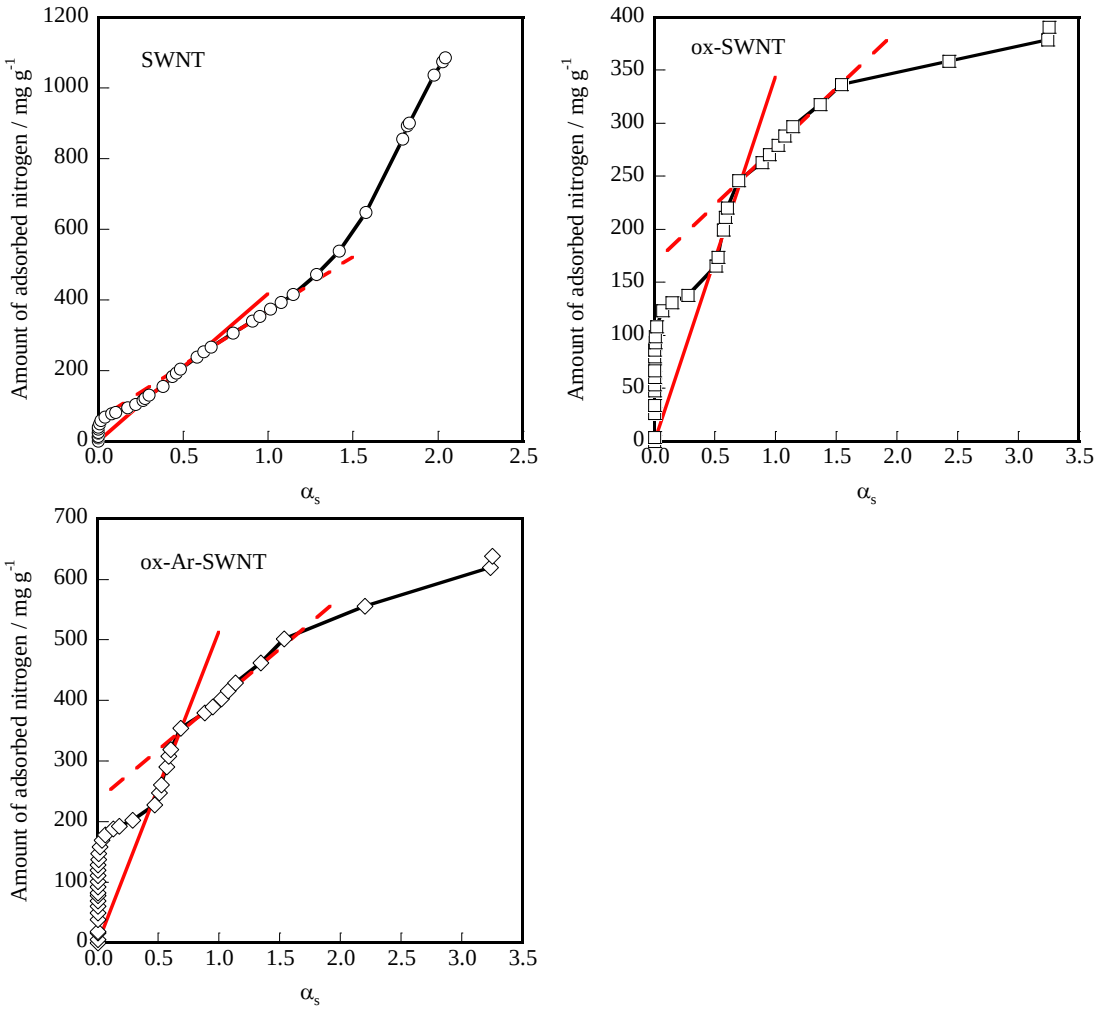

Fig. S2 α_s-plots of the nitrogen adsorption isotherms on SWNT, ox-SWNT, and ox-Ar-SWNT at 77 K.

In the present study, we used the simulated isotherm onto inner pore of model SWNT whose diameter was 8.0 nm as a standard data for α_s-plot analysis.[1] The adsorption isotherm of nitrogen at 77 K on the model pore was estimated by the grand canonical Monte Carlo (GCMC) simulation technique.

The intermolecular interaction (φ_{ff}) between nitrogen molecules was modeled using Lennard-Jones potential shown as equation (1).

$$\varphi_{ff}(r_{ij}) = 4\varepsilon_{ff}\left[\left(\frac{\sigma_{ff}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ff}}{r_{ij}}\right)^{6}\right] \quad (1)$$

Here, r_{ij} is the intermolecular distance between nitrogen molecules. Also, ε_{ff} and σ_{ff} are the Lenard-Jones constants of nitrogen molecules. We used 104.2 K and 0.3632 nm as (ε_{ff} /k_B) and σ_{ff}, respectively, where k_B is the Boltzmann constant.[1] The interaction potential of a nitrogen molecule with the inner surface of model SWNT is described by a summation of the interaction potential of a nitrogen molecule with a carbon cylinder defined as equation (2). In this model, interaction potential between a hydrogen molecule and inner surface of the tube (φ_{sf}) was calculated by the equation shown as equations (3) and (4).[2]

$$\varphi_{sf}(r_{ij}) = 4\rho_C\varepsilon_{sf}\left[{\sigma_{sf}}^{12}I_6 - {\sigma_{sf}}^{6}I_3\right] \quad (2)$$

$$I_6 = \frac{63\pi^2({}^{a}/_{r})^{11}}{128a^{10}\{1-({}^{a}/_{r})^2\}^{10}}F\left(-\frac{9}{2},-\frac{9}{2},1;\left(\frac{a}{r}\right)^2\right) \quad (3)$$

$$I_3 = \frac{3\pi^2({}^{a}/_{r})^{5}}{4a^{4}\{1-({}^{a}/_{r})^2\}^{4}}F\left(-\frac{3}{2},-\frac{3}{2},1;\left(\frac{a}{r}\right)^2\right) \quad (4)$$

Here, ρ_C is a two-dimensional density of carbon atoms (ρ_C =38.2 nm^{-2}), a is a radius of a tube, r is a distance from the centre axis of a tube to a nitrogen molecule, F is a hypergeometric function, and ε_{sf} and σ_{sf} are the energy and size parameters in the Lennard-Jones potential between a nitrogen molecule and a carbon atom calculated by Lorentz-Berthelot rules, in which we used 28.0 K and 0.340 nm for the Lennard-Jones parameters for carbon. The total interaction potential for the system was calculated by the summation of all interactions of each adsorbate. The types of Monte Carlo steps involved in a GCMC simulation are moves, creations, and destructions. In each step, either move, creation, or destruction was attempted with equal probability. For each isotherm point, the system was allowed to equilibrate over 3×10^6 steps followed by the continuous calculation for over 5×10^6 steps to obtain the average number of the adsorbate in the simulation box.

Also, the average micropore width (w) of a cylindrical pore can be evaluated from both the surface area of micropore and the micropore volume using the simple geometrical relation.

$$w = \frac{2W_{\mathrm{micro}}}{a_{\mathrm{micro}}} \quad (5)$$

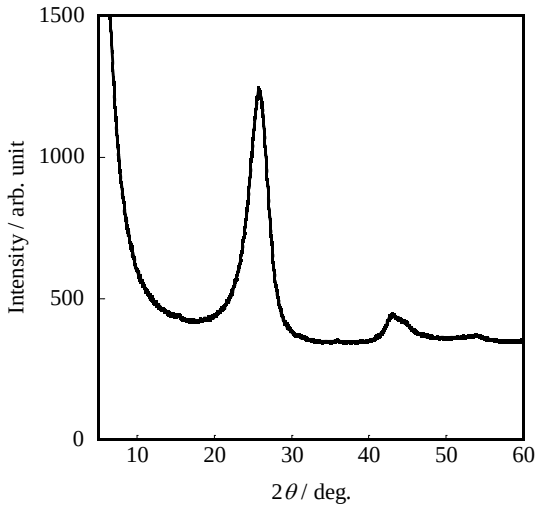

Fig. S3 Powder XRD profile of MWNT (λ=0.154 nm).

The average number of carbon layers constructing MWNT was about 10 when we used Scherrer equation to determine the crystalline size of layering direction obtained from 002 reflection (2θ=25.8 deg.). Here, we assumed the interlayer distance as 0.3354 nm which is the ideal distance for graphite. Therefore, we could calculate the GCMC-simulated adsorption isotherms on model MWNTs having different inner pore sizes whose number of the carbon layers could be assumed as 10. We could calculate the theoretical isotherms of nitrogen on MWNTs as shown in Fig. S4, just applying the potential model for the calculation of SWNT. The interaction potential between a nitrogen molecule and the pore wall of MWNT could be simply calculated by the summation of the potential for SWNT shown in equations (2), (3), and (4), because we can assume the structure of MWNT as an integrated one of SWNT having different diameters.

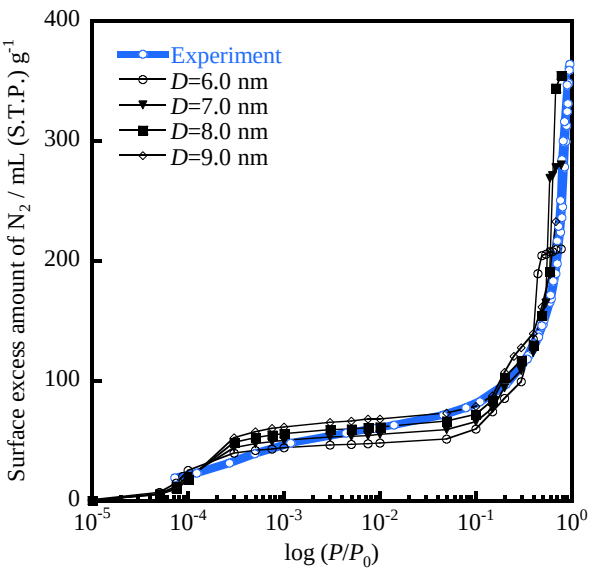

Fig. S4 GCMC-simulated adsorption isotherms of nitrogen on MWNTs (10 carbon layers) at 77 K as a function of pore width.

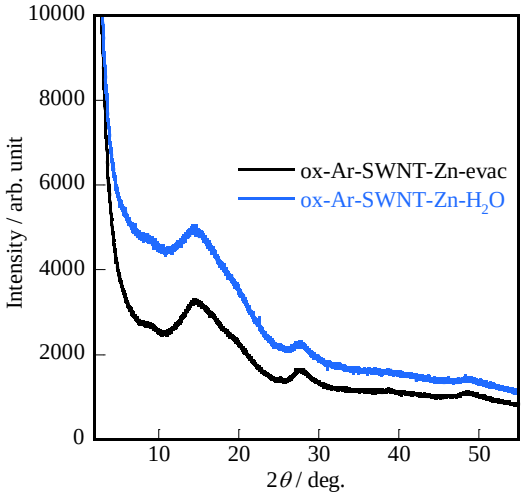

Fig. S5 Powder XRD profiles of ox-Ar-SWNT-Zn-evac and ox-Ar-SWNT-Zn-H_2O (λ=0.100 nm).

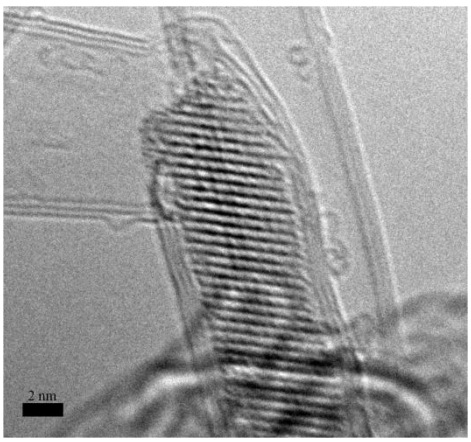

Fig. S6 TEM image of $Zn(OAc)_2$ crystal formed in MWNT involved in ox-Ar-SWNT.

Here, the interlayer distance of the crystal was 0.322 nm which can be assigned to 311 plane of $Zn(OAc)_2$ crystal (PDF No. 33-1464).

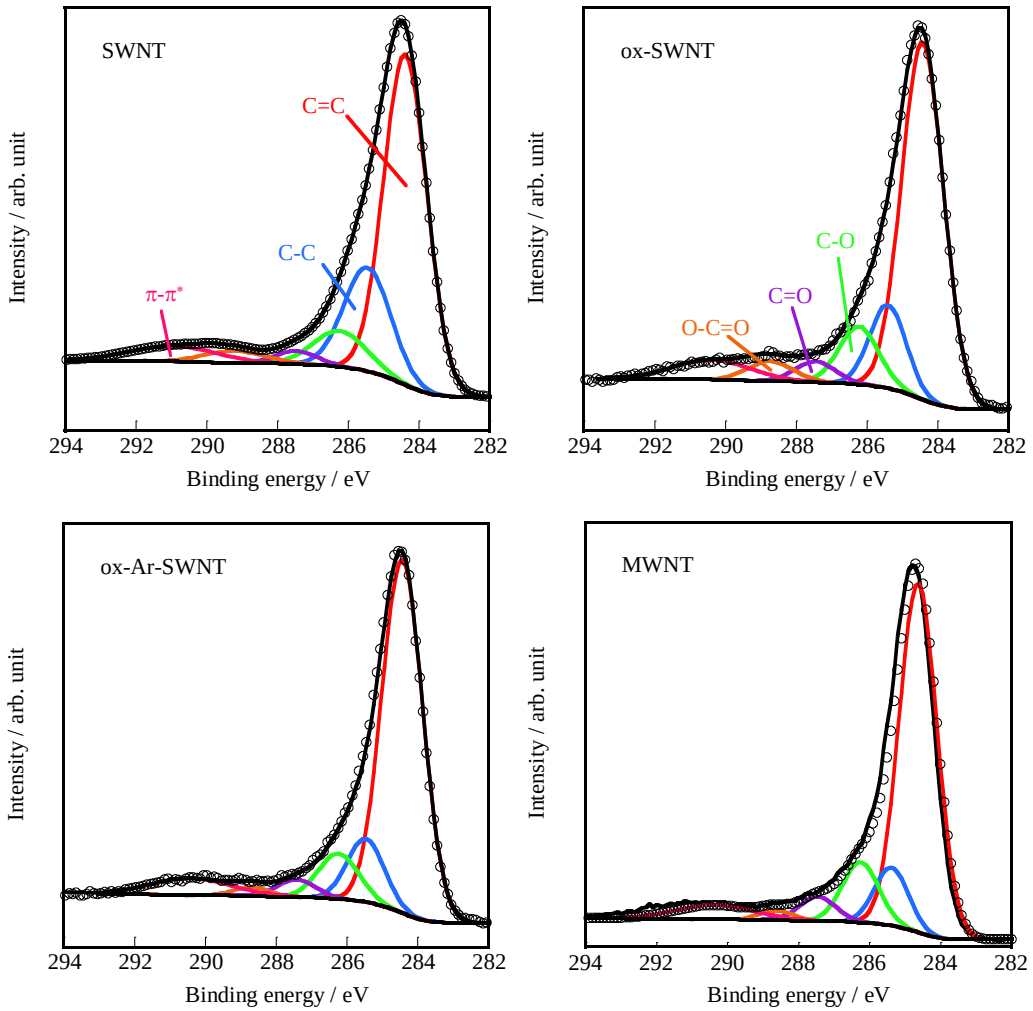

Fig. S7 C1s XPS spectra of SWNT, ox-SWNT, ox-Ar-SWNT, and MWNT and deconvoluting results.

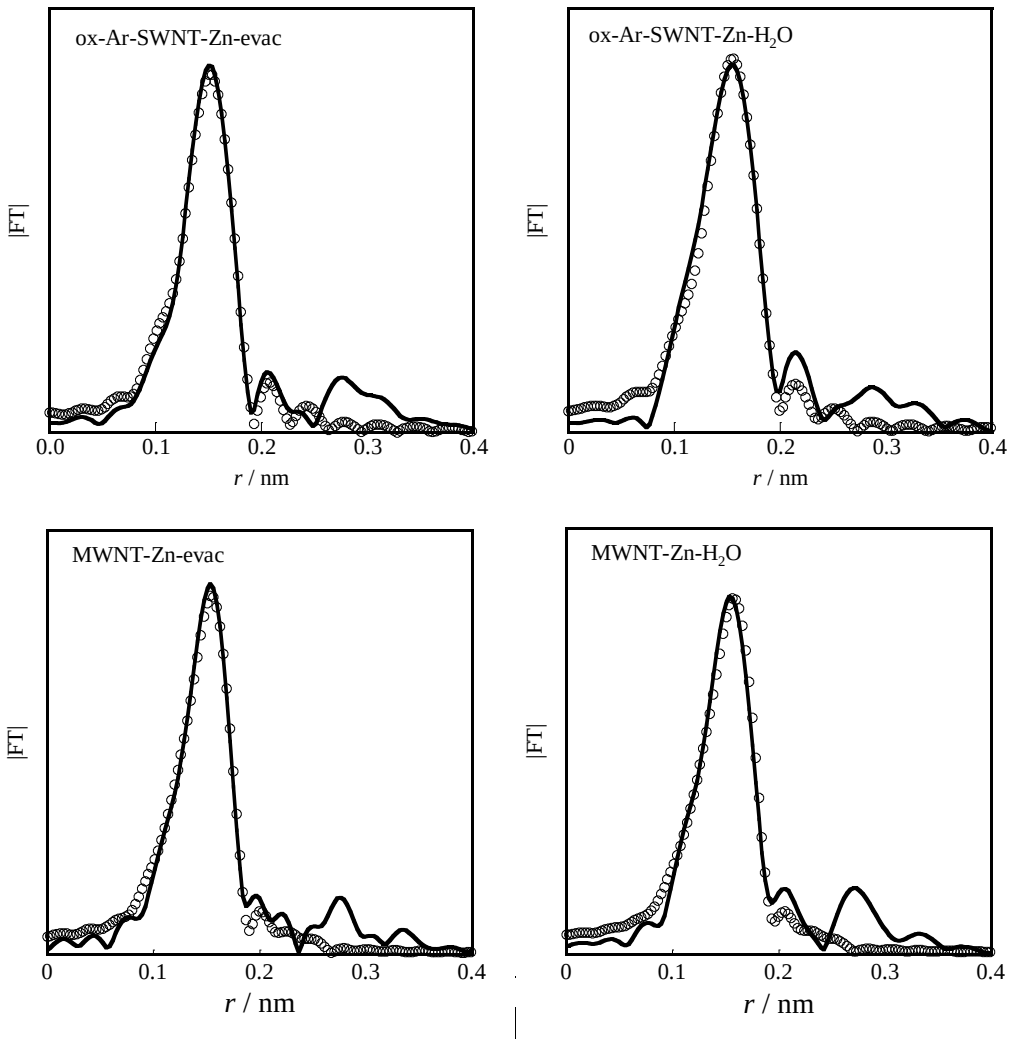

Fig. S8 Fourier transforms of Zn *K*-edge EXAFS spectra of ox-Ar-SWNT-Zn-evac, ox-Ar-SWNT-Zn-H_2O, MWNT-Zn-evac, and MWNT-Zn-H_2O. The spectra obtained by the experiment and the theoretical calculations are plotted by solid line and white circles, respectively.

1 T. Ohba and K. Kaneko, *J. Phys. Chem. B*, 2002, **106**, 7171-7176.
2 W. A. Steele and M. J. Bojan, *Adv. Colloid Interface Sci.*, 1998, **76-77**, 153-178.