Electronic Supplementary Information

Experimental Determination of Diameter-Dependent Wettability of Carbon Nanotubes as Studied Using Atomic Force Microscopy

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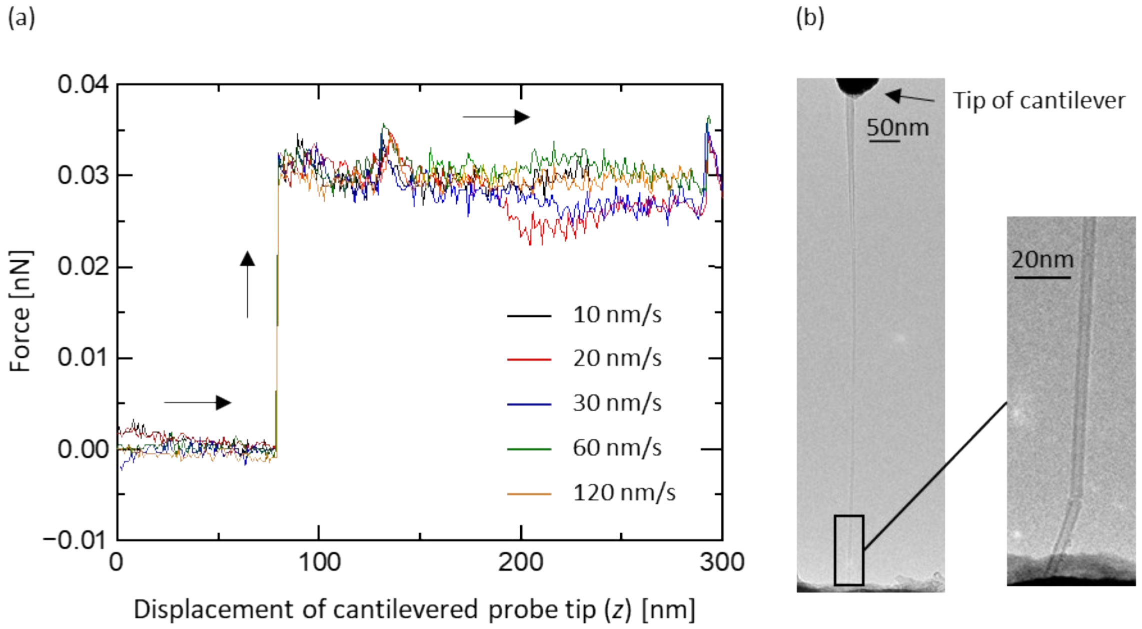
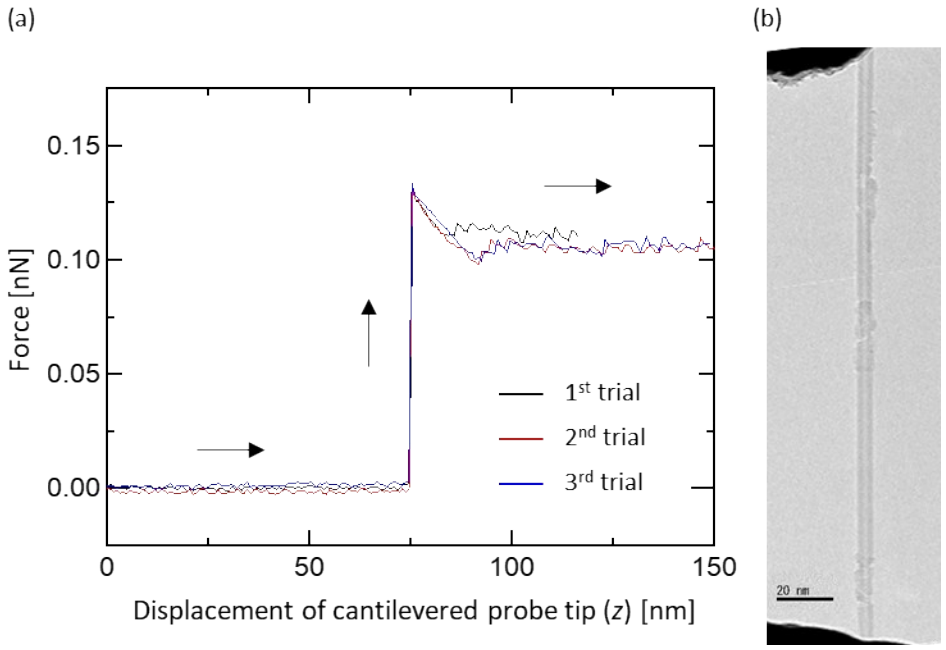
S1. Effect of insertion speed on the collection of force curves (Figure S1).



During the collection of force curves in this study, the CNT tip moves against a liquid surface; specifically, the force measurement is conducted dynamically and the viscosity of the ionic liquid may affect the measurement. Therefore, we investigated the effect of the dipping and withdrawing speeds in advance. Fig. S1(a) shows force curves (dipping processes only) recorded for different dipping speeds (10–120 nm s^{-1}), when a CNT probe tip was brought in contact with the ionic-liquid surface. The CNT probe that was depicted in Fig. S1(b) was used to obtain these data in which the tip of the CNT was attached to the Si substrate to avoid thermal fluctuation of the CNT as the TEM image was being captured. The force used for calculating the $F/(\pi d)$ value for this force curve was the averaged force measured from z = 150 to 280 nm. The difference in the averaged force for each dipping speed was ~3% at maximum. Similarly, a smaller difference was confirmed for the force curves corresponding to the withdrawing process and for other series of force curves collected using different CNT probes. Accordingly, we deduced that the effect of viscosity on the measurement of force curves is negligibly small.

S2. Effect of repetition on the measurement of force curves (Figure S2).



We repeatedly measured the force curves using same CNT tips. For example, Fig. S2 (a) shows three force curves (dipping process only) obtained by repeatedly bringing the CNT probe tip into contact with an ionic liquid. The TEM image of the CNT probe is exhibited in Fig. S2 (b) in which the tip was also attached to the Si substrate to avoid thermal fluctuation of the CNTs while capturing the images. The value of force used for calculating the $F/(\pi d)$

value for this force curve was the averaged one measured from $z = 100$ to 150 nm. The difference between the averaged force for the first trial and those for the second and third trials was ~5% at maximum, which is smaller than the error bar (shown in Fig. 5). These results suggested that the CNT was neither extensively damaged nor contaminated by several repetitions of acquiring force curves.

S3. Origin of the errors in AFM force measurement during the present study.

The magnitude of the error bar in Fig. 5 corresponds to the accumulated inaccuracy of the force values that are obtained by AFM in this study. In the following section, the method that is used to estimate the error based on the detailed experimental procedure is described.

First, while performing the measurement using AFM, the force, $F_{m,}$ is detected as the bending of a cantilevered tip and is obtained according to Hooke's law using the measured deflection of the cantilever, x, and the spring constant of the cantilever, k_{set}.

$$F_m = k_{set}\, x \qquad \text{(S3-1)}$$

In the actual measurement, $k_{set} = 0.03$ N/m is provided as input into the instrument, which is the standard value for the CSG01/Pt (NT-MDT) cantilever. However, the actual spring constant varies for each product, even in case of two products that are produced in the same lot. Therefore, we have rectified the spring constant of each cantilever used in the experiments by individually measuring the resonance frequency as well as the three-dimensional shape of the cantilever (length, width, and height). The force, $F_{m,}$ is further rectified using the corrected spring constant, k_m; the experimental value of the force due to wetting F_wet can further be expressed as

$$F_\mathrm{wet} = k_\mathrm{m}\frac{F_\mathrm{m}}{k_\mathrm{set}}, \tag{S3-2}$$

where k_m is obtained from the resonant frequency in the following manner based on the fundamental material mechanics. The relation between the deflection x and the force acting at the tip of cantilever F can also be expressed as

$$F = \frac{3EI}{l^3}x, \tag{S3-3}$$

where E, I, and l are the Young's modulus, area moment of inertia, and the length of the cantilever, respectively. From equation (S3-3), we can understand that the spring constant of the cantilever k is

$$k = \frac{3EI}{l^3} \tag{S3-4}$$

However, the n-th resonant frequency f_n of the cantilever can be expressed as

$$f_\mathrm{n} = \frac{\beta_\mathrm{n}^2}{(2\pi)l^2}\sqrt{\frac{EI}{\rho wt}} \tag{S3-5}$$

where n, β_n, ρ, w, and t are the resonant mode, the coefficient of the resonant mode, and the density, width, and thickness of the cantilever, respectively. With this relation, Eq. (S3-4) at the first resonant mode ($\beta_1 = 1.875$) becomes

$$k = \frac{3 \times (2\pi)^2}{1.875^2} \times \rho A l f_1^2 \tag{S3-6}$$

Accordingly, we estimate the experimental value of F_wet as

$$F_\mathrm{wet} = \frac{3 \times (2\pi)^2}{1.875^2} \times \rho w t l f_1^2 \times \frac{F_\mathrm{m}}{k_\mathrm{set}} \tag{S3-7}$$

, and the parameters are specified in the following table.

Table. Values of the parameters used for the estimation of F_wet.

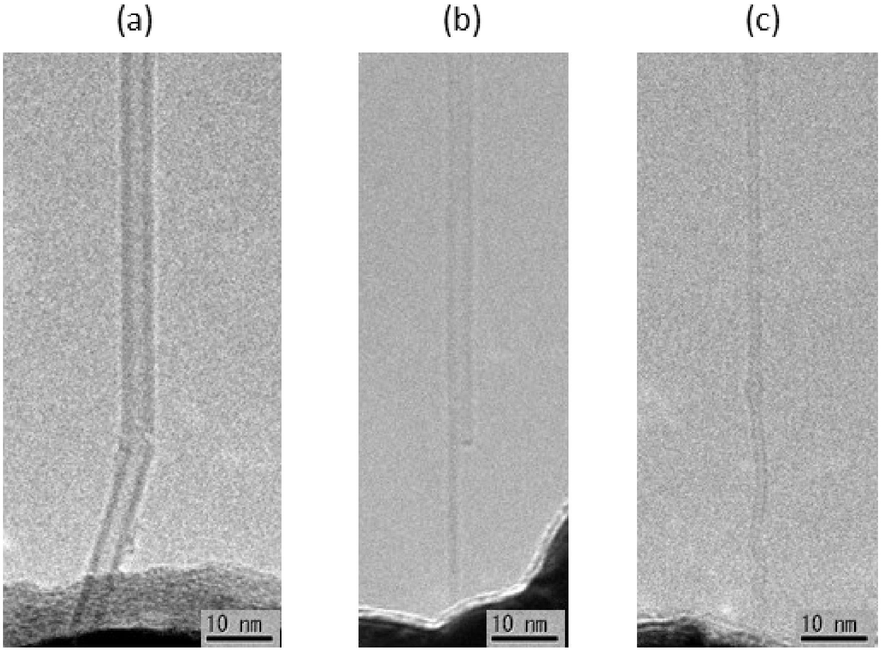
ρ	2330 [kg/m^3] for silicon.
w	30 ± 3 [μm]: catalog value.
t	Measured individually by scanning electron microscopy. Error: ± 0.01 [μm].
l	350 ± 5 [μm]: catalog value.
f_1	Measured individually by AFM. Error: ± 0.01 [kHz].
F_m	Measured value, initially obtained by automatic calculation using the AFM instrument during the force curve measurement, with the inputted spring constant of k_set = 0.03 [N/m]. Error: ± 0.01 [nN].

In case of this calculation, the accumulated error, σ_{F_wet}, is given in accordance with the law of error propagation as

$$\sigma_{F_{\mathrm{wet}}} = \pm F_{\mathrm{wet}} \times \sqrt{\left(\frac{\sigma_w}{w}\right)^2 + \left(\frac{\sigma_t}{t}\right)^2 + \left(\frac{\sigma_l}{l}\right)^2 + \left(2\sigma_{f_1}\right)^2 + \left(\frac{\sigma_{F\mathrm{m}}}{F_{\mathrm{m}}}\right)^2}, \qquad \text{(S3-8)}$$

where σ_w, σ_t, σ_l, σ_{f_1}, $\sigma_{F\mathrm{m}}$ are the errors for w, t, l, f_1, and F_{m}, respectively, as summarized in the table. The errors, σ_w and $\sigma_{l'}$ are given by the catalog. The error, σ_t, is obtained from the resolution of an SEM image. The error, σ_{f_1}, is the error from the average value of f_1, and $\sigma_{F\mathrm{m}}$ is the fluctuation of the force that is obtained during the measurement. In this calculation, t strongly affects $\sigma_{F_{\mathrm{wet}}}$ such that it is necessary to measure each t by SEM for each measurement. Finally, $\sigma_{F_{\mathrm{wet}}}$ for each experiment is calculated using these error values.

S4. Effect of the number of CNT graphene layers on the CNTs' wettability (Figure S3)



d = 4.5 nm
layer: 5-6
$F/(\pi d)$: 1.98 [mN/m]

d = 4.05 nm
layer: 4
$F/(\pi d)$: 1.78 [mN/m]

d = 1.95 nm
layer: 3-4
$F/(\pi d)$: 8.82 [mN/m]

To investigate whether the number of layers affects the wetting characteristics of individual CNTs, we estimated their number of layers. Figure S3 shows the TEM images of three different CNTs (a)–(c) used for measuring the pulling force owing to wetting. These images are blurred possibly because of thermal oscillations at room temperature although these images are recorded by attaching their tips to the Si substrate to reduce the vibration; nonetheless, the number of layers composing individual CNTs can be deduced from the thickness of the walls considering the defocus. The diameter, estimated number of layers, and the measured $F/(\pi d)$ value of each CNT are summarized in the figure. CNTs (a) and (b) have similar diameters (4.8 and 4.05 nm, respectively) but different numbers of layers (5–6 and 4, respectively). In addition, the $F/(\pi d)$ values, which are not affected by the numbers of layers, differ by ca. 0.2 nN. By contrast, CNTs (b) and (c) have similar numbers of layers (4 and 3–4, respectively) but different diameters (4.05 and 1.95 nm, respectively). The $F/(\pi d)$ values, which are strongly affected by the diameters of the CNTs, differ by a factor of five. These results suggest that the diameter of CNTs rather than the number of CNT layers is the dominant factor influencing the CNTs' wettability.