Wettability of the outer and inner surfaces of carbon nanotubes evaluated by single-nanotube-level force measurements and in-situ observations

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Nanometer-scale morphology of a solid surface often affects its wetting characteristics [1]. It is interesting to understand how a carbon nanotube (CNT) surface is wetted by a liquid, since its surface comprises a highly-curved graphene sheet due to its cylindrical feature with nanometer scale diameter. Furthermore, it is interesting to investigate how the CNT interior wall is wetted when liquid enters the interior hollow space of a CNT. In addition to the curvature effect by negative curvature, the packing of liquid molecules may also affect to the wetting since they are geometrically restricted at the nanometer-scale. Previous research has demonstrated that the wettability of CNTs with diameters >10 nm is independent of the diameter [2]. In this study, we have experimentally evaluated the wettability of both the exterior and interior CNT surfaces.

To understand the effect of curvature on the wettability of the exterior CNT surface, we examined the correlation between wettability and curvature of individual CNTs with diameters ranging from 1.4 to 23 nm, which were conducted using an atomic force microscope (S-image, SII). Ionic liquid and water were used as the liquid specimens in these experiments. The tip of an isolated CNT was adhered to a cantilevered probe tip for scanning probe microscopy (CSG01/Pt, NT-MDT) in advance. Then the CNT was brought into contact with the liquid surface and the force curve was measured (Fig.1). The tube diameter (d) was measured by transmission electron microscopy (TEM). According to Wilhelmy's method, the force applied to the CNT due to wetting (F) can be expressed as $F = \pi d\gamma\cos\theta$, where γ and θ are the surface tension and contact angle, respectively. Since γ and θ are substance-specific at the macroscale, $F/\pi d$ (= $\gamma\cos\theta$) is constant. In contrast, the experimental data obtained in this study indicate the diameter-dependent deviation of this value when d is less than 10 nm as shown in Fig. 2. The measured value of $F/\pi d$ decreased with d values decreasing from 10 to 4.5 nm, which is consistent with the theoretical prediction [1]. However, CNTs with d < 4.5 nm exhibited the opposite tendency as $F/\pi d$ increased with decreasing d values. The possible reasons for this will be discussed in the presentation.

To evaluate the wettability of the inner CNT surfaces, we measured the contact angle of molten metal filled inside the CNT. The molten metal was loaded into an open-ended CNT aided by thermomigration. Firstly, separate thinner CNT supporting platinum nanoparticles was connected to the tip of open-ended CNT using a nanomanipulator system (fabricated by SANYU electron) in a TEM. Subsequently, the platinum migrated toward the open-ended CNT by Joule heating [3]. Figure 3 depicts TEM images of loaded platinum inside the CNTs with inner diameters of d_{in} = 1.9 and 4.4 nm, and measured contact angles of 134° and 158°.

However, due to observed fluctuations of the liquid-vapor interface inside the CNT, it was difficult to precisely determine the liquid-vapor interface and the contact angle.

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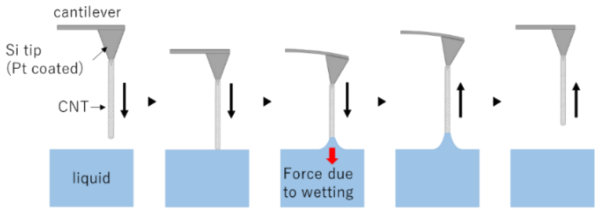

Figure 1. Schematic of force measurements when the CNT is brought into contact with the liquid.

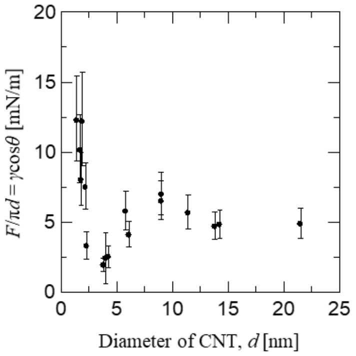

Figure 2. Diameter dependence of the measured *F*/π*d* value. The ionic liquid was used for this measurement.

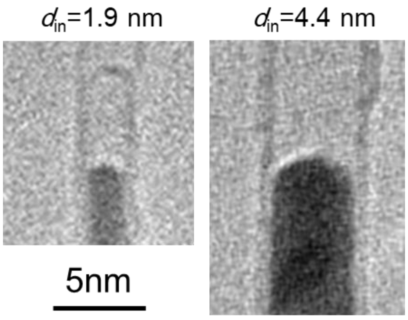

Figure 3. TEM image of the Pt loaded inside CNTs with inner diameters of 1.9 and 4.4 nm.