

Structural deformation

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4 *In situ* observation of dewetting-induced deformation of vertically aligned
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7 single-walled carbon nanotubes
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60 ABSTRACT
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63 We investigated dynamical processes of capillary-mediated deformation of vertically aligned
64 single-walled carbon nanotubes (VA-SWCNTs) via *in situ* observation of their wetting and
65 dewetting behaviors using an environmental scanning electron microscope (ESEM). Three types
66 of wetting behaviors on a VA-SWCNT sample were confirmed, including conical shaped water
67 aggregates, spherical droplets on tips of conical shaped water aggregates, and extensively
68 distributed water layers. While the former two types both resulted in dimples on the VA-
69 SWCNT surface and failed to induce large-scale deformation of VA-SWCNTs, the latter caused
70 the formation of wall-like structures and crack propagation in the VA-SWCNT film during the
71 dewetting process due to directional retraction of vapor-liquid interfaces. This dewetting-induced
72 large-scale deformation that was confirmed by the *in situ* ESEM observation for the first time
73 represented initial stages of capillary processes, leading to the self-organization of VA-SWCNTs
74 reported in recent literatures. Compared to the previous studies based on *ex situ* observations of
75 dried samples, our *in situ* observation successfully captured temporal evolution of the dewetting-
76 induced deformation, facilitating the more precise construction of predictive models of final
77 morphologies of VA-SWCNT films after capillary-mediated densification.
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Keywords: Single-walled carbon nanotubes; Dewetting; *In situ* observation; Environmental scanning electron microscope

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172 **1. Introduction**
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175 Carbon nanotubes (CNTs) [1,2] possess excellent electrical [3], optical [4], mechanical [5],
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177 and thermal properties [6]. CNTs, thus, have been widely studied for various applications. In
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179 addition to nanostructures of an individual CNT, there is a need to control macroscale
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181 morphologies of CNT ensembles, which depends on intended applications. For instance,
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183 horizontally aligned CNTs [7] are suitable for field-effect transistors [8], while vertically aligned
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185 (VA-) CNTs [9,10] are efficiently used for thermal interface materials [11]. The morphology of
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187 VA-CNTs can be further adjusted via post-growth processing. Capillary-mediated self-
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189 organization of VA-CNTs [12,13] is one of the attractive approaches in terms of its scalability
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191 and low-cost. Such a simple liquid-induced process has realized various CNT morphologies by
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193 tuning original VA-CNTs and treatment methods, such as honeycomb-like networks [12,13],
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195 tepee structures [14], densified arrays [15], and more complex architectures [15,16]. These
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197 shape-engineered CNTs have demonstrated their superior performance as cell seeding scaffolds
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199 [17], field-emitters [18], super-capacitors [15], sliding electrical contacts [19], and CNT-Si
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201 heterojunction solar cells [20].
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215 In general, when nanopillars such as VA-CNTs are immersed in water and pierce the vapor-
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217 liquid interface, capillary force causes nanopillars to bend and buckle [21–26], resulting in their
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228 collapse or clustering [27]. Some studies have proposed predictive models for the final
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231 morphology of VA-CNTs after capillary-mediated densification [27,28]. However, most studies
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234 to date have been based on *ex situ* observations of the dried structures [12,16,19,29], paying
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237 much less attention to dynamical processes of VA-CNT deformation during wetting and
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240 dewetting. The elucidation of these dynamical processes can contribute to constructing more
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243 precise models that enable the prediction of the final morphology according to experimental
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246 conditions; therefore, allowing the opportunity to tailor morphologies for certain purpose.
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249 However, it is still a challenge to observe microscale dynamical processes of the VA-CNT
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252 deformation using an optical microscope via conventional direct immersion of VA-CNTs in
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255 water [12,30] or exposure of VA-CNTs to vapor [16,19,29]. Therefore, the present study aims to
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258 capture the dynamical processes of the capillary-mediated deformation of vertically aligned
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261 single-walled carbon nanotubes (VA-SWCNTs) by *in situ* observation of their wetting and
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264 dewetting behaviors using an environmental scanning electron microscope (ESEM). The
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267 formation of wall-like structures and crack propagation in a VA-SWCNT film during the
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270 dewetting process of water were confirmed, which supports the initial stage of capillary-
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273 mediated modifications of VA-SWCNT morphologies.
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284 **2. Materials and methods**
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287 **2.1. Vertically aligned single-walled carbon nanotubes (VA-SWCNTs)**
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290 VA-SWCNTs were synthesized on a Co/Mo dip-coated Si/SiO₂ substrate using the alcohol
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292 catalytic chemical vapor deposition process [10,31], as shown in Fig. 1. The high *G/D* ratio
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294 obtained by the Raman spectroscopy (see Supplementary material S1) ensured the high quality
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296 of the VA-SWCNTs. The average diameter of the VA-SWCNTs and the film thickness were
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298 about 2 nm and 5 μm, respectively. The number density of the VA-SWCNTs was ~ 10¹² cm⁻²,
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300 leading to the porosity of ~ 97% [32]. The VA-SWCNT film had a disordered and dense crust
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302 layer on the top region [33].
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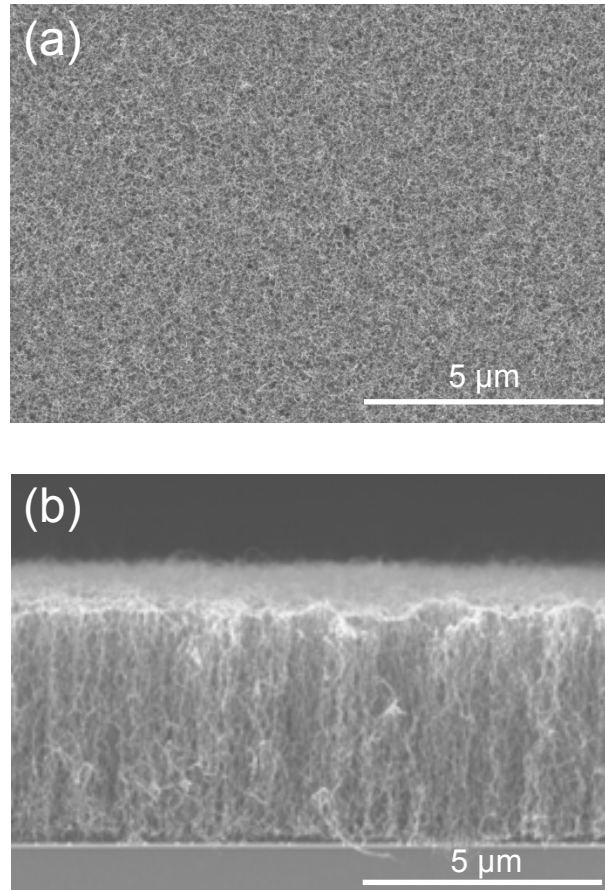


Fig. 1. Scanning electron microscope (SEM) images of the VA-SWCNT film from a top view (a) and a side view (b).

2.2. Experimental identification of water-induced deformation of VA-SWCNTs

It was reported that the exposure of VA-CNTs to vapor results in self-assembled microhoneycomb networks [20], although its microscale dynamical processes are yet to be understood (see Supplementary material S2). In the present study, we employed an

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396 environmental scanning electron microscope (ESEM, FEI Quanta 250) for the *in situ* observation
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399 of water-induced deformation of VA-SWCNTs, as illustrated in Fig. 2. The sample was mounted
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402 on a copper holder in contact with a Peltier cooling stage at 1.0 °C. The sample was tilted by 65°
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405 with respect to the horizontal direction to observe the water distribution and shapes of water
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408 aggregates on the sample. The ambient temperature inside the vacuum chamber, except in the
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411 vicinity of the sample, was about 23 °C (i.e., room temperature). The working distance was 3
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414 mm. The acceleration voltage and the probe current were 20 kV and 0.28 nA, respectively. The
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417 pressure of water vapor was initially kept at $P \approx 680$ Pa and elevated to $P \approx 760$ Pa to initiate the
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420 vapor condensation. Subsequently, the vapor pressure was reduced to $P \approx 680$ Pa to induce the
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423 water evaporation. This pressure range roughly originated from the saturation vapor pressure
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426 (657 Pa) at 1 °C [34], although a larger pressure was actually required to trigger vapor
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429 condensation on the VA-SWCNT film because the film temperature was higher than that of the
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432 Peltier cooling stage.

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434 Note that before measurements, almost all gases in the chamber were purged by water vapor
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437 through purge-flood cycles, ensuring that the fraction of non-condensable gases was lower than
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440 1%. Then, the water vapor pressure inside the chamber was controlled via the microscope's
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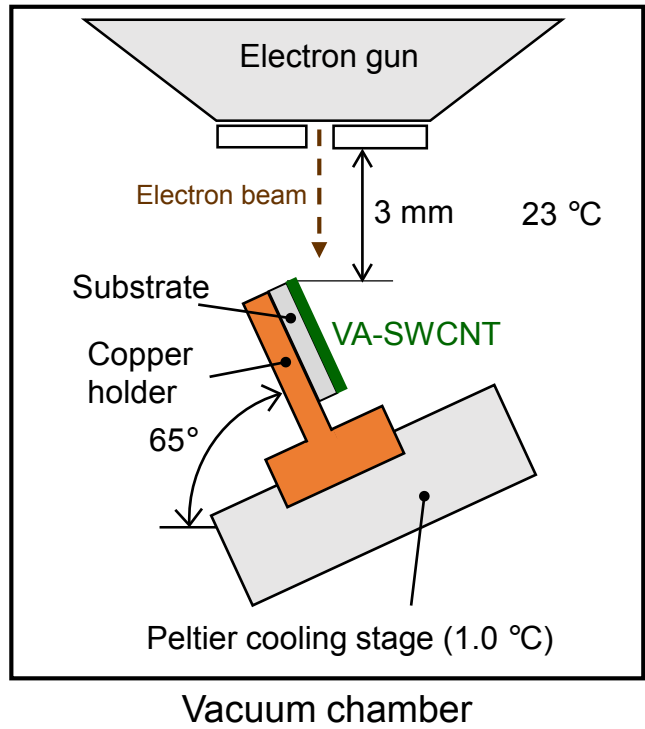


Fig. 2. A schematic presentation of the ESEM measurement system. The sample was mounted on a copper holder in contact with a cooling stage at 1.0 °C via a Peltier cooling system. The sample was tilted by 65° with respect to the horizontal direction. The ambient temperature inside the chamber was about 23 °C. Dimensions are not to scale.

After the *in situ* observation of the VA-SWCNT deformation induced by water vapor condensation and evaporation, a scanning electron microscope (SEM) (Hitachi High-Tech, S-4800) was also employed to complement the observation.

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508 **3. Results and discussion**
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511 Figure 3 shows water aggregates condensing on the sample at the vapor pressure of $P \approx 760$
512 Pa in the ESEM chamber. Water aggregates under the crust layer were visible because the VA-
513 SWCNT film was transparent, owing to its high porosity ($\sim 97\%$) which allowed the electron
514 beam (secondary electrons) to enter inside (escape from) the film. The bottom left region
515 bounded by the green dashed-dotted line was initially exposed to electron beams for observation,
516 followed by the change of view. Clearly, there was negligible condensed water in the initial
517 observation area due to electron beam heating effects [35,36]. Meanwhile, an evident amount of
518 water aggregates were found at the boundary of the initial observation area swept by the electron
519 beam. In addition, a number of small water aggregates were observed out of the initial
520 observation area. Three types of wetting behaviors on the VA-SWCNT sample were confirmed,
521 including (I) conical shaped water aggregates, (II) spherical droplets on the tips of conical
522 shaped water aggregates, and (III) extensively distributed water layers. While the water
523 aggregates of types (I) and (II) were mainly observed out of the initial observation area, the
524 water layers were only observed along the edge of that area. We infer that this intriguing
525 phenomenon originates from the balance between suppression and enhancement effects of vapor
526 condensation by electron beams. While heating effects due to electron beams [35,36] suppressed
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564 vapor condensation, positively charged water molecules (H_2O^+) in the ESEM chamber interacted
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567 with negatively charged surfaces [37] and became H_2O , enhancing the nucleation of liquid water.
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570 Specifically, the boundary of the initial observation area was exposed to more electron beams
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573 because of the turnarounds of the electron beam sweep. Vapor condensation, thus, was enhanced
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576 and overwhelmed the evaporation due to heating effects. This allowed for the formation of
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579 extensively distributed water layers (III) in the ESEM environment. For the water aggregates of
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582 type (I), the nucleation was considered to occur at the interface between the substrate and VA-
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585 SWCNTs (Fig. 2), where the temperature was lower than that at the tips of VA-SWCNTs. The
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588 condensation growth subsequently proceeded upwards until the crust region was reached, which
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591 suppressed further growth in the height direction. The type (II) may originate from type (I), i.e.,
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594 water aggregates of type (I) turned to be type (II) after penetrating through the crust region. As
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597 we discuss below, the extensively distributed water layers (III) mainly contributed to the
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600 formation of wall-like structures and crack propagation.
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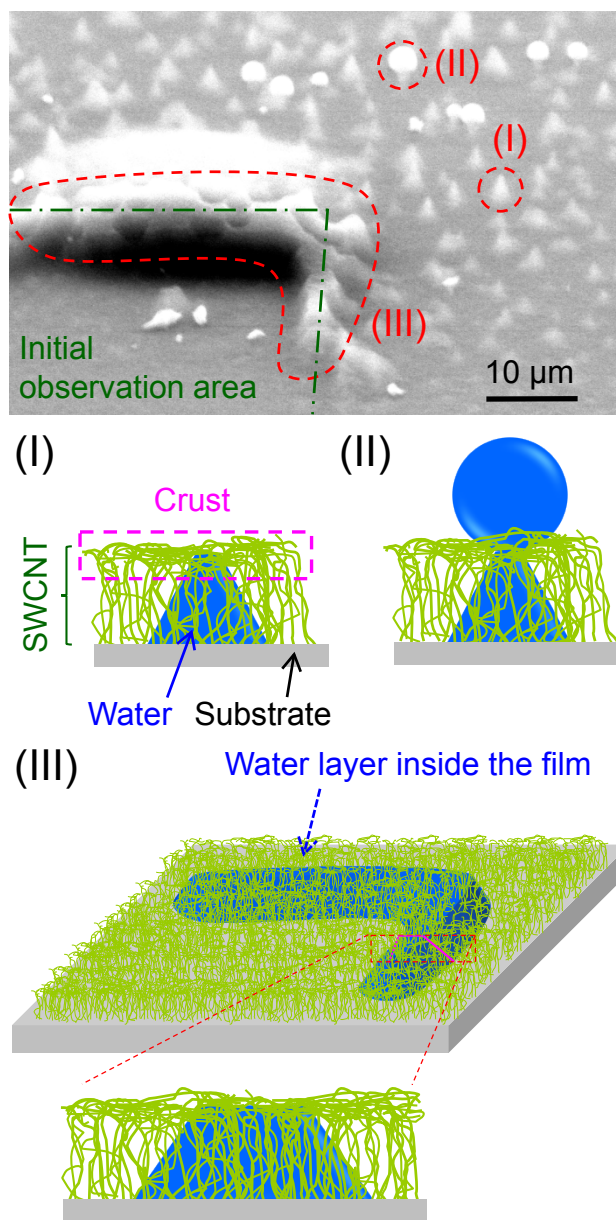


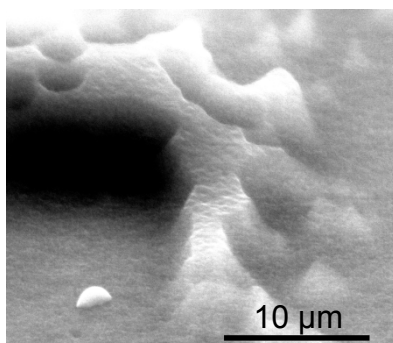
Fig. 3. Wetting behaviors of VA-SWCNTs observed in the ESEM chamber having the vapor pressure of $P \approx 760$ Pa. Water aggregates under the crust layer were visible because of high porosity of the VA-SWCNT film. Three types of wetting behaviors were exhibited, i.e., (I)

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676 conical shaped water aggregates, (II) spherical droplets on the tips of conical shaped water
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679 aggregates, and (III) extensively distributed water layers inside the VA-SWCNT forest. The
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682 bottom left area bounded by the green dashed-dotted line was initially exposed to electron beams
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685 for observation.

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691 Figure 4 shows the type (III) wetting behavior of VA-SWCNTs during vapor condensation
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694 observed in the ESEM chamber. VA-SWCNTs became evidently wet for the pressure of $P \approx 760$
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696 Pa, exhibiting extensively distributed water layers as discussed above. We note that there was no
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699 evident structural deformation of the VA-SWCNTs during the wetting process for more than 5
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702 min. In contrast, structural deformation of the VA-SWCNTs was clearly confirmed during the
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705 dewetting process, as shown in Fig. 5. By decreasing the pressure to $P \approx 680$ Pa, a dimple
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708 appeared in wet SWCNTs as shown in Fig. 5(a). Subsequently, vapor-liquid interfaces retracted
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711 from the dimple along the edges of the initial observation area (Fig. 3) as indicated by the dashed
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714 arrows in Figs. 5(b)–(f), generating structural deformations of SWCNTs along these directions.
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717 This directional retraction of the vapor-liquid interfaces played a key role in the large-scale
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720 structural deformation of VA-SWCNTs.

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(a) $t = 0$



(b) $t = 324$ s

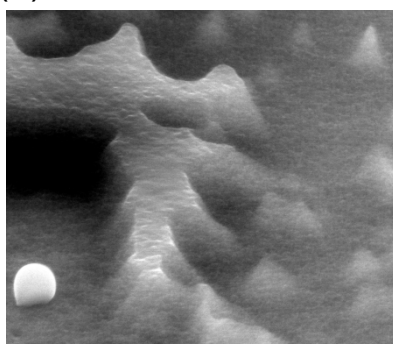


Fig. 4. The type (III) wetting behavior of the VA-SWCNTs during vapor condensation observed in the ESEM chamber having the vapor pressure of $P \approx 760$ Pa; (a) $t = 0$ s, (b) $t = 324$ s.

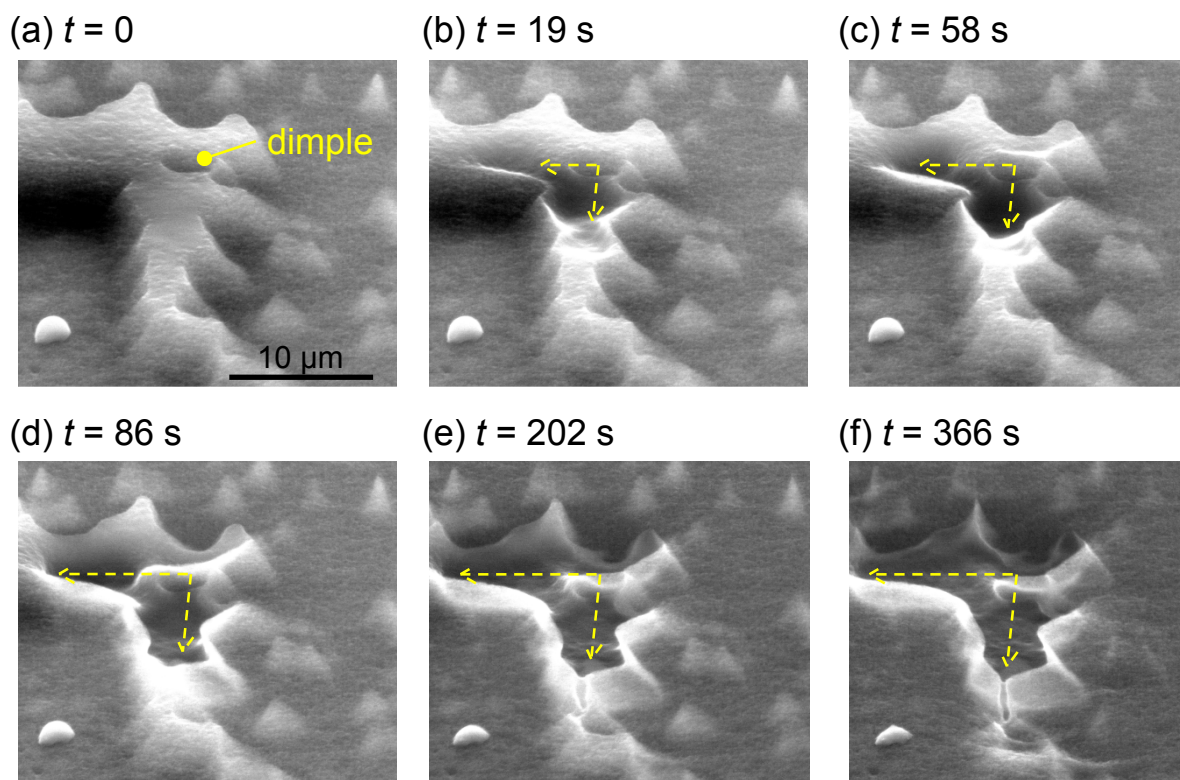


Fig. 5. Time evolution of dewetting-induced deformation of the VA-SWCNTs during evaporation of an extensively distributed water layer (the type (III) in Fig. 3) observed in the ESEM chamber having the vapor pressure of $P \approx 680$ Pa; (a) $t = 0$ s, (b) $t = 19$ s, (c) $t = 58$ s, (d) $t = 86$ s, (e) $t = 202$ s, (f) $t = 366$ s. The dashed arrows in (b)–(f) represent the directions of structural deformations.

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 844 To investigate the dewetting-induced deformation of the VA-SWCNTs in detail, Fig. 6
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 847 compares the *in situ* ESEM image with the subsequent SEM images after the exposure to vapor.
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 850 As shown in Fig. 6(b), collapsed SWCNTs were clearly observed. In addition, crack and wall-
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 853 like structures were also confirmed in Figs. 6(c) and (d). Again, extensively distributed water
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 856 layers (III) played an important role to induce large-scale deformation of the SWCNTs, resulting
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 859 in the collapse, crack propagation, and formation of wall-like structures.
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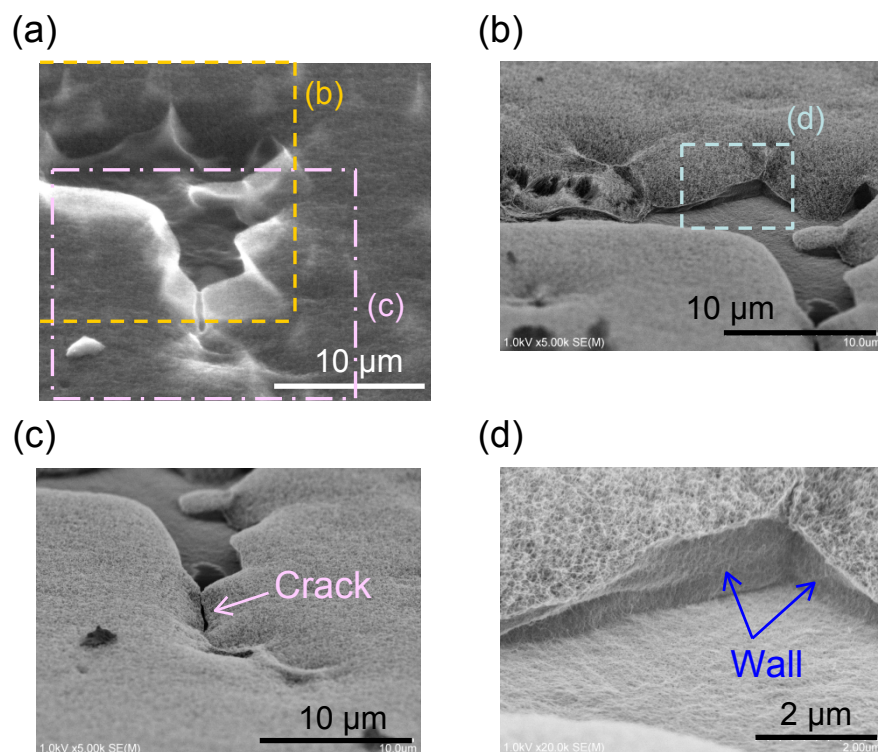


Fig. 6. Specification of dewetting-induced deformation of SWCNTs by comparing the *in situ*

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900 ESEM image (a) with the subsequent SEM images after the exposure to vapor (b–d). The SEM
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903 observation angle was 65° in accordance with the ESEM observation. (a) ESEM image identical
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906 to Fig. 5(f). (b) SEM image corresponding to the region denoted by the dashed line in (a); (c)
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909 SEM image of the crack corresponding to the region denoted by the dashed-dotted line in (a); (d)
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912 SEM image of the wall-like structure corresponding to the region denoted by the dashed line in
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915 (b).
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921 Figure 7 shows the SEM images of the SWCNTs where the water aggregates of types (I) and
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923 (II) were present. While a number of dimples were present on the SWCNT surface, large-scale
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926 structural deformation of the SWCNTs was not confirmed, which is different from the area
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929 where the water layers (III) were extensively distributed. Basically, VA-SWCNTs that pierce a
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932 vapor-liquid interface are subject to a compressive force along the thickness and hence likely to
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935 buckle [27,38]. More specifically, for a circular rod clamped on a substrate, the critical buckling
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938 length is given by
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$$L_c = \frac{\pi}{2} \sqrt{\frac{EI}{F_{\text{cap}}}} \quad (1)$$

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941 where $E \sim 1$ TPa is Young's modulus of a single SWCNT [39], $I = \pi r^4/4$ is inertia moment with
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947 SWCNT radius of $r \sim 2$ nm, $F_{\text{cap}} = 2\pi r \cos\theta$ is capillary force with surface tension of $\gamma \approx 72$
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956 mN/m and contact angle of $\theta \approx 86^\circ$ corresponding to a water droplet on a graphite surface [40].
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959 Equation 1 yielded $L_c \approx 0.7 \mu\text{m} < H \approx 5 \mu\text{m}$ with H being the SWCNT length. The possibility of
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961 the SWCNT buckling, thus, was indicated. However, entanglements and crust regions together
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963 with the small amount of water prevented complete collapse of SWCNTs in the present
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965 conditions. In addition, no clear difference in the deformed structures was observed between the
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967 spots where the water aggregates of types (I) and (II) were present. Namely, both of type (I) and
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969 (II) water aggregates just yielded dimples and failed to induce large-scale deformation of the
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971 VA-SWCNTs in contrast to type (III). Directional retraction of vapor-liquid interfaces of
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973 spatially distributed water layers (Fig. 5) played a crucial role for the large-scale deformation of
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975 VA-SWCNTs, leading to crack propagation and formation of wall-like structures. Although the
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977 extensively distributed water layers observed in the present study stemmed from the vapor
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979 condensation enhancement due to electron beams, we expect that the directional retraction of
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981 their vapor-liquid interfaces could be a main factor of spatially distributed deformation of VA-
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983 SWCNTs in actual capillary process.
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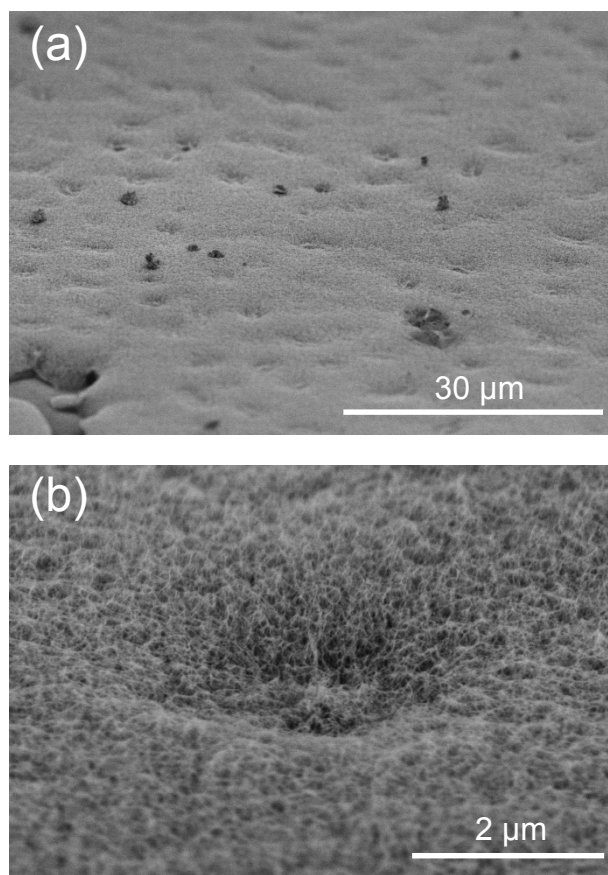


Fig. 7. SEM images of the SWCNTs where the water aggregates of types (I) and (II) were present in Fig. 3. The SEM observation angle was 65° in accordance with the ESEM observation (Fig. 2). (a) Dimples distributed on the SWCNT surface. (b) Enlarged view of a representative dimple.

Finally, self-assembled microhoneycomb networks reported by Cui et al. [20] were not observed in the present study. We note that the water vapor treatment [20] consisted of repetitive

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1068 two steps, i.e., (1) exposing a VA-SWCNT array to vapor from a hot water reservoir and (2)
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1071 turning the sample over and drying the array in an ambient environment (see Supplementary
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1074 material S2), which is considerably different from our experimental condition.
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1079 4. Conclusions

1082 We investigated dynamical processes of capillary-mediated deformation of vertically aligned
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1084 single-walled carbon nanotubes (VA-SWCNTs) by *in situ* observation of their wetting and
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1086 dewetting behaviors using an environmental scanning electron microscope (ESEM). We
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1088 confirmed the formation of wall-like structures and crack propagation in the VA-SWCNT film
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1090 during the dewetting process of water, which were caused by extensively distributed water layers
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1092 that resulted in directional retraction of vapor-liquid interfaces. Such dewetting-induced large-
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1094 scale deformation that was for the first time captured by the *in situ* ESEM observation
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1096 represented initial stages of capillary processes, leading to capillary-mediated self-organization
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1098 of VA-SWCNTs. Our findings can help to more precisely construct the predictive models of
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1100 final morphologies of VA-SWCNT films after capillary-mediated densification. Finally, it will
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1102 be interesting to use SWCNT films with microscale patterns fabricated via a lithography process
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1114 [38]. The pre-patterned surfaces would allow us to control the directions of SWCNT
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1124 deformation, enabling more systematic *in situ* observation of the dewetting-induced deformation
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1127 using an ESEM.
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1131 1132 1133 Acknowledgments

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1141 1142 1143 1144 Appendix A. Supplementary data

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1147 Supplementary data to this article can be found online at ***.
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