Self-Organization of Carbon Nanotubes in Evaporating Droplets

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Received: March 13, 2006; In Final Form: June 1, 2006

Here, we report a simple and efficient way for organizing carbon nanotubes, in particular, single-wall carbon nanotubes (SWNTs) into ordered structures from their dilute solutions. It was found that drying a droplet of carbon nanotube solution at room temperature on a wettable surface such as glass or silica wafer led to redistribution, accumulation, and organization of carbon nanotubes along the perimeter of the droplet. Unlike the aggregation behaviors of colloid nanoparticles, anistropic carbon nanotubes tended to show two orientations in a ring deposit: one parallel to the outer perimeter of the ring and the other normal to it in the interior. Drying droplets of SWNT solutions at high temperatures exhibited a long-range ordered structure. In addition, droplet drying may cause size separation of carbon nanotubes and pattern formation through interactions between droplets. This result helps us not only to further understand fluid dynamics during the drying process but also to provide a promising and simple strategy for either assembling carbon nanotubes on a surface or organizing them into well-aligned films and fibers.

Introduction

Liquid droplet evaporation on a solid surface has attracted increasing interest in scientific and engineering communities.[1] This is because it could serve as a simple and good model system for investigating micro-fluid dynamics. More importantly, it has a potential to serve as a means for surface patterning, self-assembly, and size-discriminative transportation and nanomaterials separation without a need to apply any external forces.[2−4] Droplet evaporation is a common phenomenon in everyday life, which looks simple but with a complex mechanism. The distribution evolution of a solute during the droplet-drying process is a consequence of the interplay among many factors, including wetting properties, surface tension (Marangoni effect), capillary forces, gravity effect, and convective flow. In general, when a solution droplet dries on a surface, although a variety of patterns might form, the most often formed pattern after drying is a dense, ringlike deposit formed along the perimeter of the initial droplet. Although by far the mechanism of ring formation is not fully understood, the generally accepted explanation is that the pinning of the contact line between droplets and substrates is a prerequisite for ring formation and that the pinning process is induced either by surface irregularities of the substrates or by self-pinning, triggered by the adhesion of suspended solute to the substrate.[3,5,6] Once the contact line is pinned, there is an outward and radial flow, also called capillary flow, which is formed to prevent the shrinkage of the droplet. This capillary flow is found to be capable of driving virtually all the dispersed solute in the droplet to the edge and redistributing the suspended particles when the droplet is dried. Therefore, the droplet-drying process may be developed as a potential simple approach to direct the movement of the solutes and eventually pack them into a desired structure.

Carbon nanotubes are a typical one-dimensional nanomaterial. In the as-synthesized state, they are often entangled with each other, making it difficult to disperse and assemble them into ordered structures needed for many applications.[7,8] In the present study, we found that drying a droplet of carbon nanotube aqueous suspension led to the formation of a ring-shaped deposit on a wettable surface, such as glass, silicon wafer, etc. More interestingly, in this process, self-organization of carbon nanotubes, especially single-wall carbon nanotubes can be easily achieved with a dilute suspension, independent of the droplet size and substrate material so long as they can be wetted by carbon nanotube suspensions. Such capillary-flow-induced orientation behaviors may open up new opportunities in the processing of carbon nanotubes.

Experimental Methods

The single-wall carbon nanotubes (SWNTs) used in this study were synthesized by catalytic vapor deposition (CVD) using methane over an Fe catalyst supported on MgO,[9] and multiwall carbon nanotubes (MWNTs) were synthesized by a toluene−ferrocene injection CVD method.[10] The average diameters of SWNTs and MWNTs were around 1−2 and 20−100 nm, respectively. The preparation of their stable dispersions in water or other solvents will be described latter. The "*droplet-drying*" process was carried out by dropping 1−100 μL of the carbon nanotube suspension onto a substrate and then drying it at a desired temperature.

Results and Discussion

MWNTs are more chemically active than SWNTs and therefore can be effectively functionalized by being refluxed in

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10.1021/jp061554c CCC: $33.50
Published on Web 06/22/2006

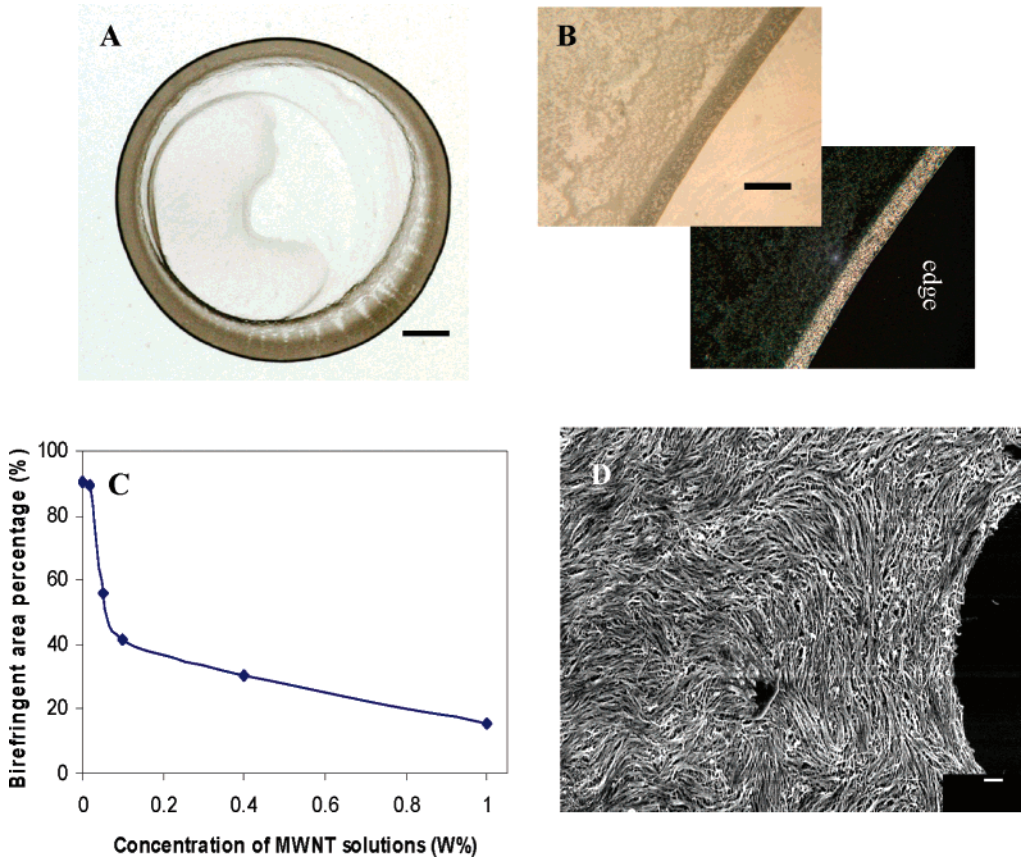

Figure 1. (A) Optical microscopy image of a ring formed by droplet evaporation of a MWNT suspension (0.04%) on a glass surface at room temperature. The scale bar corresponds to 1 mm. (B) A typical polarized optical microscopy image of a ring deposit without (upper) and under (lower) cross-polar conditions. The scale bar corresponds to 50 μm. (C) The effect of the concentration of the MWNT suspension on the fraction of ordered area formed in the ring. (D) SEM image of the MWNT deposit formed at the edge of a droplet. The scale bar indicates 1 μm.

a $HNO_3-H_2SO_4$ oxidative acid mixture and redissolved in water with a concentration of up to 5% (wt %).[11] Room-temperature evaporation of a droplet of such MWNT solution with a concentration of less than 1% on a wettable surface (such as glass slide, aluminum plate, and SiO_2 coated Si wafer) tended to form a ringlike deposit along the perimeter of the droplet, and a typical image is shown in Figure 1A. As seen in Figure 1B, different from what was observed under an optical microscope with no polarizer, a clear birefringent phenomenon appeared at the periphery of the ring deposit under cross-polar conditions, indicating that MWNTs aggregated into ordered structures during the ring formation. Evaporation of a MWNT solution droplet with initial concentrations higher than 0.1% led to wider rings with more spreading MWNTs deposit at the inner edge of the rings. In contrast, when the initial concentration was lower than 0.05%, the resulting ring deposit had higher MWNT uniformity and ordering. Figure 1C shows the effect of the concentration of MWNT solutions on the fraction of ordered areas formed in a ring. It was observed that a different initial concentration of MWNT suspension did not obviously change the evaporation rate of the droplet. However, the concentration exerted a large influence on the self-organization behaviors of MWNTs. A lower concentration favored the aggregation of MWNTs with a higher degree of ordering. For example, nearly 90% of the ring area showed birefringent phenomenon upon drying of the MWNT suspension droplet with concentrations lower than 0.02%. This tendency could be explained by the fact that, at lower concentrations, the nanotubes were less likely to entangle and therefore can easily reach the periphery of the droplet to arrange themselves into ring patterns with higher ordering.

Carbon nanotubes can be observed to exhibit liquid crystalline behaviors when the concentration of their solution is 5% or higher.[10] However, considering the concentration dependence in the droplet-drying process, the driving force for such self-assembly behavior cannot be simply attributed to concentrating solutes at the droplet edge. We believe that it was the capillary flow that induced self-organization of MWNTs. To confirm this hypothesis, we did the following experiments: (1) Drying a MWNT droplet on a platform placed in a water bath covered with a lid.[5] In this case, the evaporation rate of the solution along the drop interface was approximately spatially uniform, and hence, the role of capillary flow was greatly depressed. Experimental results showed that although a ring was produced, no birefringence could be observed. (2) Drying the droplets in an ethanol environment, in which the role of the Marangoni effect (surface tension effect) was enhanced. MWNTs were observed to concentrate toward the top of the drop, and no ring or birefringence could be seen under such conditions. (3) Drying a droplet under the exposure of microscopic light at the perimeter, in which random thermal movement of the solute (Brownian motion) was enhanced. The resulting ring deposit over this area showed a weakened birefringence compared with that formed without light exposure. This implied that enhancement of Brownian motion of the solute might interfere with the self-organization of MWNTs. All of the above evidence supported the hypothesis that capillary flow played a major role in the self-assembly of carbon nanotubes.

Scanning electron microscopic (SEM) characterization of the ring deposit provided detailed evidence on the structure of MWNT assembly. As shown in Figure 1D, at the outmost edge, MWNTs tended to align themselves along the periphery of the

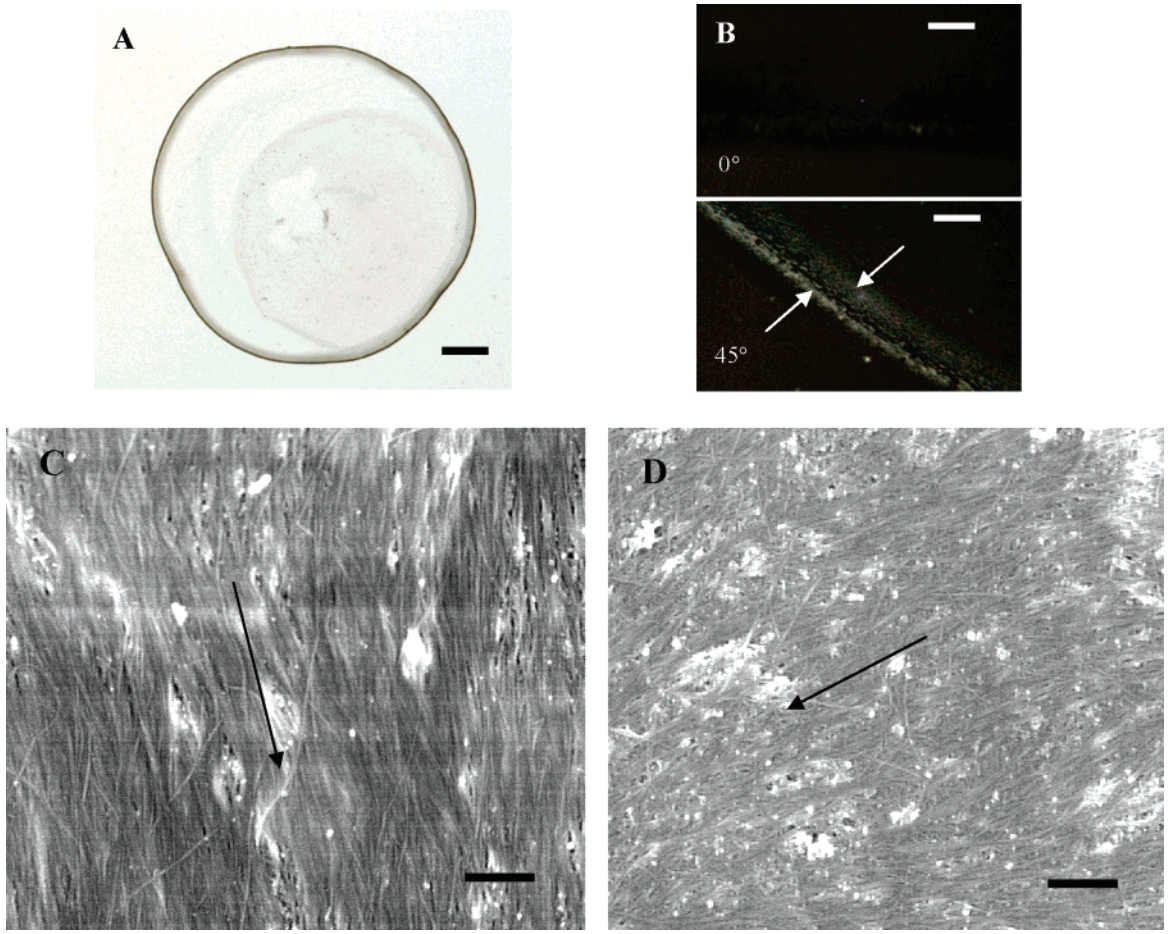

Figure 2. (A) Optical microscopy image of a ring formed by drying a drop of SWNT suspension (0.2 mg/mL) on a glass surface at room temperature. The scale bar indicates 1 mm. (B) Polarized optical microscopy images of a typical ring deposit under cross-polar conditions: the ring position was 0° (upper) and 45° (lower) with respect to the polarizer. The scale bar corresponds to 50 μm. (C and D) SEM images of the SWNT deposit formed at the edge and inner part of the ring shown in part B, respectively. The arrow indicates the orientation direction of SWNT assembly. The scale bar corresponds to 100 nm.

ring. In the interior, MWNTs were assembled with the dominant orientation perpendicular to the edge. A transition existed between these two domains, where MWNTs were found bent and less ordered.

An improved self-organization behavior was found with SWNTs, which have a longer aspect ratio and are more flexible than MWNTs. We prepared a SWNT suspension with the assistance of a surfactant, in which their pristine structures and length can be well maintained.[8] As shown in Figure 2A, when a drop of SWNT suspension (0.2 mg/mL) was dried on a glass surface at room temperature (20 °C), it also left a dark, ringlike deposit along the perimeter of the drop. However, this ring deposit showed much a higher degree of ordering than the deposit formed from MWNTs. A clear birefringence was observed under cross-polar optical microscopy over the ring area (see Figure 2B), with extinction at 0 or 90° where the nanotube orientation direction is parallel to the polarizer or analyzer, respectively, and with a maximum transparency at 45°. In addition, a dark region was observed between two bright regions, indicating the presence of a transient region with a different orientation or less ordering. The SEM images shown in parts C and D of Figure 2 confirmed the presence of two main domains as well, with SWNTs aligned parallel and normal to the droplet edge, respectively. However, compared with the case of MWNTs, the degree of ordering and the fraction of ordered areas in both domains were found to be greatly improved, especially at the outermost edge of the ring where SWMTs are parallel to the droplet edge.

Experimental and theoretical studies on the drying of colloidal suspension droplets with particle sizes ranging from 0.1 to 1 μm revealed that when the polarity contrast between solvent and substrate is small, as in the case of an aqueous droplet evaporating on a hydrophilic substrate, pinning of the contact line would play a critical role for the ring formation.[3−6] When this polarity contrast is very high, as in the case of an aqueous droplet evaporating on a hydrophobic *n*-octadecyltrichlorosilane (OTS) surface, ring formation would become independent of pinning of the contact line.[6] Our study here fits the former case, in which the pinning of the contact line is essential for the formation of ring patterns. The pinning of the contact line may induce the fastest evaporation rate of the solvent molecules at the edge of the drop and eventually results in an outward capillary flow that can carry virtually all of the colloid particles to the edge. In the case of isotropic nanoparticles, with continuous pinning of the contact line and gradual decrease of the contact angle, the droplet-drying process can only end up with a simple result, that is, packing and ordering of nanoparticles. However, in the case of the one-dimensional carbon nanotube system, in addition to the presence of anistropic interaction between tubes, rodlike materials tend to have a reduced angular mobility, and therefore are more liable to align up in the flow direction.[12] As a result, the aggregation behaviors of carbon nanotubes may reflect some detailed information on the dynamic fluid flow during the drying process.

The results from drying both MWNT and SWNT droplets indicated that the carbon nanotubes at the outer edge aligned

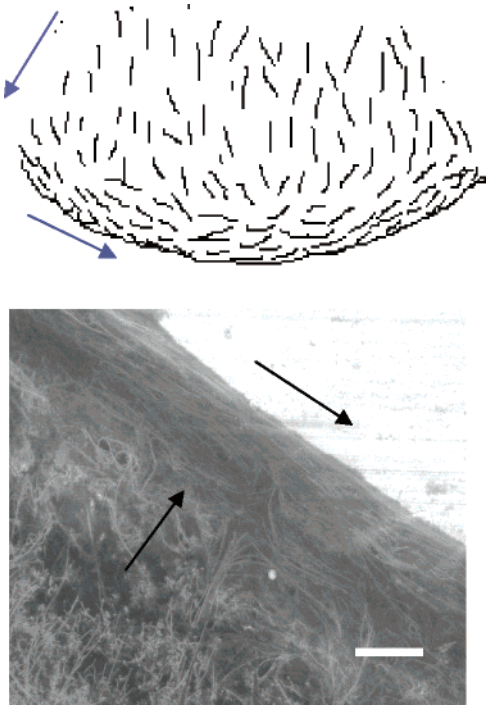

Figure 3. Schematic illustration of the self-organization of carbon nanotubes during the droplet-drying process (top) and SEM evidence on the alignment of SWNTs at the outmost edge of the drop and transition between two domains (bottom). The scale bar indicates 1 μm, and the arrows indicate the orientation direction of carbon nanotubes.

parallel to the edge due to the effect of geometrical constraint, in which shear force and surface tension were likely to pull carbon nanotubes along the triple-phase junction line and make the line pinned. In other words, due to the edge effect, carbon nanotubes moving close to the edge have to change their directions so that their axial directions become parallel to the periphery of the drop, as displayed in Figure 3. As SWNTs are more flexible than MWNTs, they are easier to bend and adjust their orientations at the outer edge to form a larger fraction of ordering area and higher ordering degree. With the continuous pinning of the contact line and an increase in the evaporation rate of the solvent, capillary flow was significantly enhanced and therefore nanotubes have to align with the flow direction.

When drying a droplet of SWNT solution at a high temperature, the evaporation rate of the solvent at the air−liquid interface is accelerated, the upward diffusion of solute competes with its outward diffusion, and the contact line can not be pinned anymore. Under this condition, the deposit tends to aggregate concentrically. Amazingly, a temperature enhanced self-assembly behavior of SWNTs was also observed. Large area and long-range ordered structures of SWNTs could be formed by evaporating the solvent at temperatures higher than 80 °C. The degree of alignment in the resulting deposits was found to be dependent on the concentration. Figure 4 shows the effect of SWNT concentration (ranging from 0.5 to 1.5 mg/mL) on their self-assembly behaviors at 80 °C. At a high concentration (1.5 mg/mL), small SWNT bundles assembled into larger bundles and were laterally packed. The tubes at the edge of the assemblies were more flexible and less ordered than those in the middle. It was worth mentioning that when the concentration of the suspension was further increased to 2 mg/mL, SWNTs aggregated with no orientation ordering. However, when lowering the concentration of the SWNT suspension to 1 mg/mL, the degree of self-organization of SWNT assemblies was obviously increased. A lower concentration resulted in better

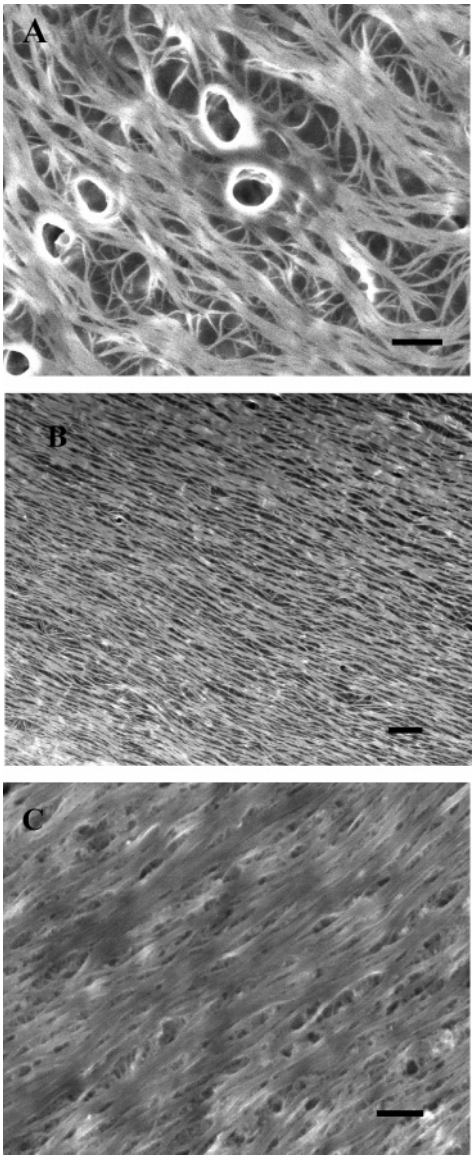

Figure 4. Effect of the concentration of the suspensions on the self-assembly behaviors of SWNTs upon droplet drying on Al substrates: (A) 1.5 mg/mL; (B) 1 mg/mL; (C) 0.5 mg/mL. The scale bars in images A, B, and C correspond to 1 μm, 1 μm, and 100 nm, respectively.

aligned and more closely packed films. Very dilute suspensions (<0.05 mg/mL) led to the assembly of SWNTs into superbundles with no definite orientation.

The self-assembly induced by high-temperature droplet evaporation was found to be unique to SWNT solutions. Repeating this process with MWNT suspensions in which surfactant was maintained at the same concentration as that in the SWNT suspensions did not lead to a similar alignment result. Therefore, the role of the surfactant in this process can be excluded. Droplet evaporation at high temperatures was different from that at room temperature in which the contact line could not be pinned. Sommer's model[6,13] provides an explanation for the shrinkage of the droplet evaporating at a high temperature: the outward capillary flow is severely impeded by an opposite force arising from the action of the vertical temperature gradient, which may drive suspended particles to the drop apex. SWNTs could move faster than MWNTs because they are much thinner. Consequently, they are able to self-organize into ordered structures during such a fast evaporation process.

Droplets may also have interactions between themselves. When a few droplets of carbon nanotube suspensions were put

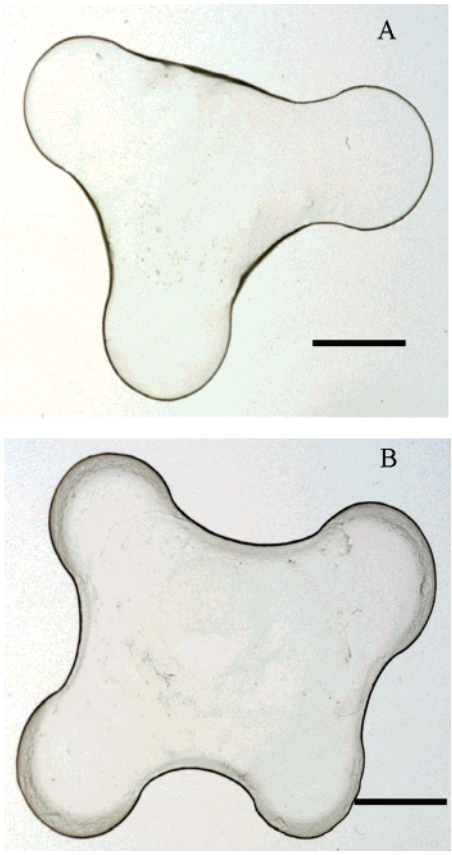

Figure 5. Different patterns formed by the interactions between drops: (A) interactions between three drops of SWNT solutions; (B) interactions between four drops of MWNT solutions. The scale bar corresponds to 2 mm.

close enough to each other on a glass surface, they could merge with each other, and the solute was redistributed among them and eventually formed a new ringlike ordered deposit. This phenomenon was also effective when a droplet of water met with a droplet of carbon nanotube solution. As shown in Figure 5, different patterns can be formed by merging different numbers of droplets or droplets with different sizes. It is worth mentioning that the aggregation of MWNTs or SWNTs at the position with a negative meniscus showed a higher degree of ordering than that at the position with a positive meniscus. This may be due to the fact that a ring with a negative meniscus has additional capillary force that helps drive carbon nanotubes to move outward to the edge, and instead, the ring with a positive meniscus will produce an additional opposite flow.

Conclusions

In summary, evaporation of a droplet suspension on a wettable surface often leaves a ringlike deposit, and the formation of the outward capillary flow caused by pinning of the contact line of the drying droplet caused the redistribution and accumulation of the solute. Here, we found carbon nanotubes, in particular SWNTs, can be self-organized well along the perimeter of the droplet. During the initial pinning period, carbon nanotubes tend to orient themselves along the periphery of the droplet, normal to the radial outward flow direction, suggesting that there was a strong edge effect that twisted and organized them into highly ordered structures. With the formation of the ring and the evolution of the pinning where the edge effect was less important, carbon nanotubes started to align themselves along the direction of capillary flow. In addition, rapid evaporation by heating the droplet may also lead to the aggregation of carbon nanotubes into a long-range ordered structure. This self-organization behavior of carbon nanotubes was found to be largely independent of the nanotube concentration, the size of the droplet, and the type of substrate surface as long as it was wettable. As a result, this process can be potentially developed as a strategy for assembling carbon nanotubes on a surface or organizing them into well-aligned films and fibers. In addition, due to controllable sizes of formed patterns and orientation of targets in the patterns derived from this process, it will be of potential interest in the design on biomimicry patterns for guiding cell development in tissue engineering.

Acknowledgment. This work was financially supported by Cambridge-MIT Institute and Thomas Swan & Co. Ltd. The authors would like to acknowledge Dr. S. Zhang and Dr. W. Song for their help on the use of the polarized optical microscope.

References and Notes

(1) Laden, P. *Chemistry and Technology of Water Based Ink*; Blackie Academic & Professional: London, 1997.

(2) Gonuguntla, M.; Sharma, A. *Langmuir* **2004**, *20*, 3456.

(3) Deegan, R. D.; Bakajin, O. *Nature* **1997**, *389*, 827.

(4) Sommer, A.; Ben-Moshe, M.; Magdassi, S. *J. Phys. Chem. B* **2004**, *108*, 8.

(5) Deegan, R. D.; Bakajin, O. *Phys. Rev. E* **2000**, *62* (1), 756.

(6) Sommer, A. P.; Rozlosnik, N. *Cryst. Growth Des.* **2005**, *5* (2), 551.

(7) Wang, Y. H.; Maspoch, D.; Zou, S. L.; Schatz, G. C.; Smalley, R. E.; Mirkin, C. A. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 2026.

(8) Wang, H.; Zhou, W.; Ho, D. L.; Winey, K. I.; Fischer, J. E.; Glinka, C. J.; Hobbie, E. K. *Nano Lett.* **2004**, *4* (9), 1789.

(9) Li, Q. W.; Yan, H.; Cheng, Y.; Zhang, J.; Liu, Z. F. *J. Mater. Chem.* **2002**, *12* (4), 1179.

(10) Singh, C.; Shaffer, M. S.; Windle, A. H. *Carbon* **2003**, *41* (2), 359.

(11) Song, W. H.; Kinloch, I. A.; Windle, A. H. *Science* **2003**, *302*, 1363.

(12) Xin, H.; Woolley, A. T. *Nano Lett.* **2004**, *4* (8), 1481.

(13) Sommer, A. P. *J. Phys. Chem. B* **2004**, *108*, 8096.