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Drying induced upright sliding and reorganization of carbon nanotube arrays

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Abstract
Driven by capillary force, wet carbon nanotube (CNT) arrays have been found to reorganize into cellular structures upon drying. During the reorganization process, individual CNTs are firmly attached to the substrate and have to lie down on the substrate at cell bottoms, forming closed cells. Here we demonstrate that by modifying catalyst structures, the adhesion of CNTs to the substrate can be weakened. Upon drying such CNT arrays, CNTs may slide away from their original sites on the surface and self-assemble into cellular patterns with bottoms open. It is also found that the sliding distance of CNTs increases with array height, and drying millimetre tall arrays leads to the sliding of CNTs over a few hundred micrometres and the eventual self-assembly into discrete islands. By introducing regular vacancies in CNT arrays, CNTs may be manipulated into different patterns.

1. Introduction

Ordered assemblies of carbon nanotubes (CNTs) are attractive for a wide range of applications, including building blocks for battery electrodes [1], field emitters [2], microwave filters [3], and membrane filters [4]. Recently, it has been found that vertically aligned CNT arrays can self-assemble into two-dimensional (2D) cellular structures through a simple drying process [5, 6]. Such a self-assembly of CNT arrays is driven by capillary forces formed during the drying process. In these reported cases, all CNTs were found firmly anchored to the substrate surface, and CNTs in the cell bottom areas collapsed toward the cell walls. Only CNTs in the walls maintained their initial upright orientation [5, 6]. Consequently, the bottoms of individual cells are covered and closed by CNTs.

In the present study, we found that the adhesion between the bottom of a CNT array and the substrate played a significant role in the reorganization of CNTs during a drying process. By introducing a buffer layer between the Fe catalyst film and the Si wafer substrate, the as-grown CNT arrays showed weak bonding to the substrates. Upon drying, such CNTs may be uprooted by capillary force and can slide on the substrate while maintaining their upright orientation, enabling the self-assembly of short arrays into open-bottom cellular structures and long arrays into discrete islands. This phenomenon not only helps us to understand the capillarity associated with the CNT array drying process, but also provides for a promising strategy to manipulate CNTs into desired assemblies.

2. Experimental procedure

CNT arrays with lengths ranging from 20 μm to 1 mm were synthesized with two kinds of Fe catalyst film preparations: (i) 5 nm Fe film directly sputtered on a Si wafer (hereafter referred to as 5 nm Fe/Si); (ii) a 10 nm Al_2O_3 buffer layer deposited on a Si wafer with the ion-beam assisted deposition technique and then 1 nm Fe film sputtered onto Al_2O_3 layer (hereafter referred to as 1 nm Fe/Al_2O_3/Si). In both cases, the Si wafer had a 1 μm initial SiO_2 layer. The CNT arrays were synthesized in a horizontal quartz-tube furnace at 750 °C using ethylene as carbon source and Ar (or Ar + 6% H_2) as carrier gas. The growth mode of all CNT arrays synthesized in this study was base-growth, and the diameters of individual carbon nanotubes are 10–15 nm. For self-assembly experiments, the

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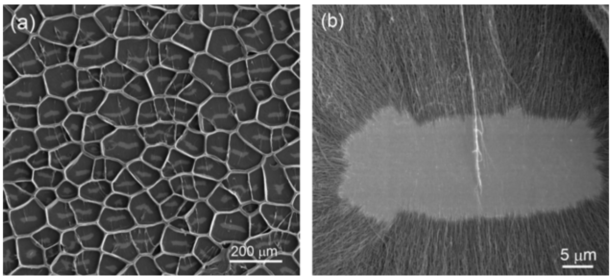

Figure 1. (a) An SEM image showing the cellular structures formed by self-assembly during the drying of a 50 μm tall CNT array grown on 5 nm Fe/SiO$_2$. (b) An enlarged image of a cell bottom in (a) showing the CNT arrangement and a CNT-free area. It reveals that the formation of cellular structure was accompanied by the collapse and slight root-sliding of CNTs toward cell walls.

CNT arrays were first immersed into an ethanol solution, and then dried at room temperature by evaporation.

3. Results and discussion

Evaporating wet CNT arrays grown on pre-deposited catalysts was found to lead to the reorganization of CNTs into cellular patterns. Figure 1 shows a typical cellular CNT structure formed by self-assembly of a 50 μm tall CNT array synthesized on the 5 nm Fe/Si catalyst structure. The CNT array was grown at 750 °C for 10 min with flowing ethylene and Ar at 200 and 300 sccm, respectively. As shown in figure 1(a), driven by capillary force, the CNTs collapsed, compacted and reorganized to form polygonal patterns, similar to those reported previously [5, 6]. In the polygonal structure, the height of the walls of polygonal cells approximately equals the original length of the array. Scanning electron microscopy (SEM) reveals that each cell bottom shows a light-coloured elongated area surrounded by a darker area. An enlarged SEM image of a cell bottom reveals that the light-coloured area is the bare substrate surface denuded of CNTs (see figure 1(b)), while the darker area is formed by CNTs laid down on the substrate and aligned toward the cell walls. These observations differ from previous reports on the drying of CNT arrays grown with floating catalysts [5, 6], in which CNT roots on cell bottoms did not move during drying. In the case shown in figure 1, the bonding between the CNT roots and the substrate is relatively strong. As a result the capillary force can only pull a small fraction of the CNTs from their roots and most CNTs remained anchored on the substrate.

In principle, there are two major factors that affect the self-assembly of CNTs during the drying of a wet array. The first one is the magnitude of the capillary force formed in the array, and the second one is bonding strength of the CNT roots with the substrate. When dense nanotube arrays are wetted by a liquid, the small inter-tube separation (normally ranging from 10 to 100 nm in our samples) results in a large capillary pressure ($\Delta p = \gamma / r$, where γ is the surface tension of the liquid and r is the distance between adjacent tubes) and consequently a strong capillary attraction force between CNTs [6, 7]. Under the action of this force, the CNTs can bend and agglomerate. However, the adhesion between the nanotubes and the substrate is relatively strong in our samples shown in figure 1. As a result, only CNTs in the centre area of each cell were uprooted, leading to a structure with CNTs bent and aligned toward the cell walls (figure 1(b)). If the adhesion between a CNT array and its substrate is weaker, CNTs might be able to be fully uprooted by capillary force and form denser assemblies.

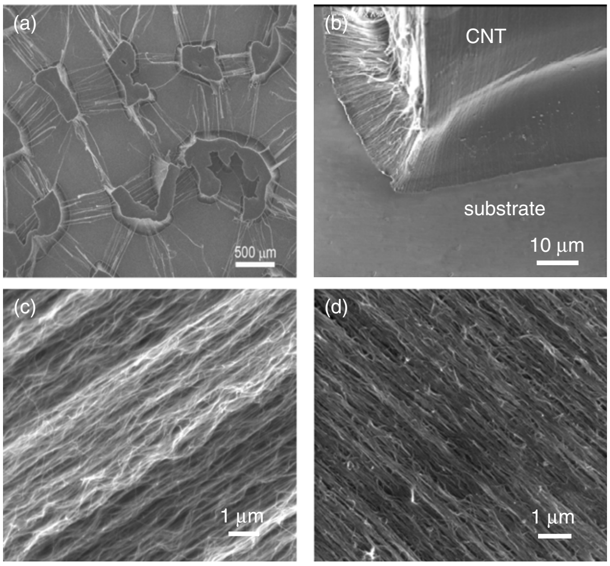

Figure 2. SEM images showing the structures formed by upright self-assembly of CNTs during the drying of a 1 mm CNT array synthesized on 1 nm Fe/Al$_2$O$_3$/Si catalyst. (a) Discrete islands; (b) an enlarged SEM image showing the bottom edge of a discrete island with no CNT lying down on the substrate surface; (c) and (d) showing the obvious change in the density of CNTs before and after the drying, respectively.

Thinner Fe catalyst film might help to weaken the bonding between the CNT array and its substrate, as our work in progress revealed that thinner Fe film led to the formation of smaller catalyst particles and thinner CNTs. However, on Si substrates, the decrease of the thickness of Fe film resulted in the severe deterioration in the length, density and alignment of as-grown arrays. It has been reported that an Al$_2$O$_3$ buffer layer between very thin Fe film and its Si substrate can improve the growth of CNT arrays [8, 9]. In this study, we used the 1 nm Fe/Al$_2$O$_3$/Si catalyst structure to synthesize CNT arrays with a weak bonding to the substrate. This catalyst structure resulted in the fast growth of high-quality CNT arrays [10]. The buffer layer likely helped Fe film to break up into fine particles and prevent the diffusion of Fe into the Si substrate [11]. In comparison with the arrays grown on 5 nm Fe–Si catalyst, CNT arrays grown with the 1 nm Fe/Al$_2$O$_3$/Si catalyst are found to be very easy to flip off when touched, leaving the substrate surface smooth and clean, suggesting that a very weak bonding was indeed formed between the CNT array and the substrate.

The weak bonding led to unique self-assembly behaviours during the drying of the CNT array synthesized with the 1 nm Fe/Al$_2$O$_3$/Si catalyst. Figure 2(a) shows a self-assembled structure that is dramatically different from any of those reported previously: discrete CNT islands. They are formed by self-assembly of a 1 mm tall CNT array synthesized with the 1 nm Fe/Al$_2$O$_3$/Si catalyst, in which the nanotube diameter is around 10 nm. The average distance between two adjacent

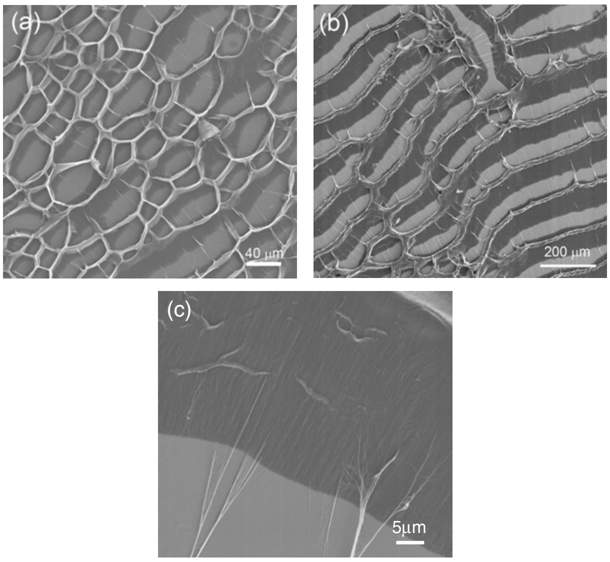

Figure 3. SEM images showing cellular CNT structures formed by upright self-assembly during the drying of CNT arrays grown on 1 nm Fe/Al_2O_3/Si: (a) formed from a 20 μm tall CNT array, (b) formed from a 100 μm tall CNT array, (c) an enlarged SEM image of a polygonal wall formed in (b).

islands is around 700 μm, and no carbon nanotubes are observed lying on the surface between discrete islands (as seen in figure 2(b)). In addition, the islands were connected by CNT strands produced during their sliding and separation. Careful examination of the CNT islands revealed that the CNTs mostly maintained their upright orientation, indicating that the CNTs were fully uprooted and moved in a coordinated manner over a long distance while maintaining their upright orientation (figure 2(b)). Due to the upright self-assembly, nearly half of the array film has been shrunk away and the density of CNT aggregates is found to be greatly improved, as seen in figures 2(c) and (d).

When drying shorter arrays that were synthesized using the same 1 nm Fe/Al_2O_3/Si catalyst but for shorter growth times, open-bottom cellular structures were formed by upright self-assembly (see figure 3). As shown, the geometry and size of the cells are affected by the height of the CNT arrays. Figure 3(a) is a CNT cellular structure formed by upright self-assembly of a 20 μm tall CNT array. It can be seen that small cells are usually equiaxed while larger cells are more elongated. The average width of cells is 40 μm. Figure 3(b) is a CNT cellular structure formed by upright self-assembly of a 100 μm tall CNT array, in which all cells are elongated with an average cell width of 120 μm. A closer examination of the structures in figure 3(b) reveals that CNTs tend to pack themselves toward the cellular walls (see figure 3(c)) while maintaining their upright orientation via longer CNT migration on the substrate surface. Comparing figure 3(b) with 3(a) reveals that taller CNT arrays formed larger and more elongated cells by longer-distance CNT sliding. In addition, the cell walls are much thicker in figure 3(b) than in 3(a), which was caused by the fact that taller CNT arrays form larger cells with larger areas of CNTs uprooted and moved to form a unit length of cell walls. Careful examination of the cell walls in both figures 3(a) and (b) reveals that the CNTs mostly maintained their upright orientation except some of those near the wall edges. This observation is in sharp contrast with previous reports of cellular CNT structures where individual CNTs did not move at their roots and those CNTs rooted in the cell bottom had to lie down on the substrate. In addition, it also reveals that the high aspect ratio of CNTs may enhance the capillarity formed in the arrays. The longer the arrays, the stronger the capillary force that will be generated, and therefore the farther the CNTs may slide on substrate surface.

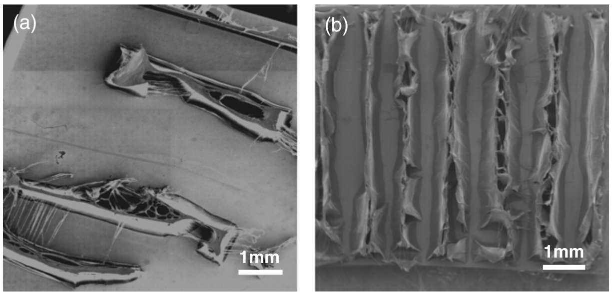

Figure 4. Patterns formed during drying a CNT array grown on 1 nm Fe/Al_2O_3/Si by introducing low-density lines via (a) cutting the CNT array with a thin blade, and (b) scratching lines on the Fe catalyst film before CNT growth.

The sliding of CNTs on a substrate surface may serve as an indication of the bonding strength of a CNT array to its substrate. In previous studies [5, 6], CNT arrays were synthesized using a floating catalyst method under high temperatures (>800 °C). This method tended to generate larger Fe particles, which consequently produced thicker nanotubes with diameters in the range 30–50 nm. Such CNT arrays have strong bonding to their substrates [12], which is why CNTs remained attached to the substrate during the self-assembly due to drying. By pre-depositing a thin Fe film on Si wafer, dense and well aligned CNT arrays could be obtained at a lower temperature of 750 °C, which produced CNTs with a smaller average diameter of 15 nm. As shown in figure 1, during the drying/self-assembly, some CNTs in elongated areas near cell centres were uprooted, but a large fraction of cell bottoms are still covered by CNTs lying on the substrate. After further weakening the bonding by growing CNT arrays on 1 nm Fe/Al_2O_3/Si, CNTs were easily uprooted during the drying and formed cellular or discrete island structures by upright self-assembly (see figures 2 and 3). Therefore, a weak bonding is critical to upright self-assembly.

Inhomogeneous CNT density in the CNT array is the cause for the formation of cellular patterns [6]. In general, the low-density areas generated during the growth or introduced after growth may serve as nucleation sites for the reorganization of CNTs into different patterns. When the low-density areas were introduced into a CNT array which has a weak binding to its substrate, CNTs were found to slide away from the low-density area and meet with CNTs in the high-density area to form compact assemblies. Low-density areas can be directly introduced in a CNT array film after its synthesis. As shown in figure 4(a), when we cut a CNT array into four domains with a sharp and thin blade, the domains shrunk into four dense stripes. Low-density areas can also be introduced before the CNT growth. We tried to grow a CNT array with low-density CNT lines by scratching the catalyst film before CNT growth. During the drying of the arrays in both cases, CNTs remarkably slid away from the cuts or scratch lines, and CNT walls were formed when CNTs sliding from opposite directions came together. As the inter-space between two low-density lines was too large in our cases, the domains formed still had CNTs with inhomogeneous densities. Therefore, some small cavities were formed in the walls. In practice, if low-CNT-density areas can be introduced into CNT arrays periodically with desired interspacing by lithography or other techniques, uniform CNT assemblies can be formed with controllable size and shape. This makes it attractive to design and fabricate CNT structures by a simple drying process.

In summary, we have successfully formed open-bottom cellular structures and discrete CNT islands by upright self-assembly of CNT arrays. During the self-assembly, CNTs were pulled up from their roots and were moved in a coordinated manner while maintaining their upright orientation. The driving force for the self-assembly is the capillary force formed during the drying of a wet CNT array, and the force is larger for taller CNT arrays. The upright self-assembly was made possible by engineering a weak bonding between the CNT roots and the substrate. By introducing low-density sites in the array film periodically, regular pattern structures with upright CNTs could be formed with the low-density sites as nucleation sites.

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