Single-Walled Carbon Nanotube Pillars: A Superhydrophobic Surface

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A series of SWNT arrays have been constructed by disproportionation of carbon monoxide on Co—Mo catalyst films deposited on flat Si wafer substrates. The arrays include a two-dimensional SWNT thin film prepared by spraying a SWNT suspension, as well as random SWNT networks, and vertically aligned SWNT. In addition, a novel SWNT array has been developed and termed SWNT “pillars”. These pillars are prepared by controlled synthesis of SWNT over a templated substrate. When water droplets are deposited on these surfaces, it is observed that the static contact angle changes dramatically with the type of SWNT array. The higher is the degree of surface roughness (at the nano and microscales) of these structures, the higher is the contact angle. The novel SWNT pillars exhibit superhydrophobicity (i.e., contact angle ~ 160°). To quantify the effect of surface roughness, two simple models have been employed. The Wenzel model can be used to quantify the behavior of the SWNT thin films while the Cassie—Baxter model is used for the SWNT arrays with three-dimensional structure (grass, forest, and pillars).

1. Introduction

The extraordinary intrinsic properties of a single-walled carbon nanotube (SWNT) have been the subject of extensive investigations. However, in many applications, the arrangement of SWNT at the microscale is the critical factor that determines the performance of the nanotube-based devices, such as nanosensors,1 nanomanipulation,2 and microfluidic devices.3 Extensive efforts have been dedicated to develop synthesis methods for growing SWNT directly on substrates for electronic devices.3 Extensive efforts have been dedicated to develop synthesis methods for growing SWNT directly on substrates with specific arrangements, for example, vertically oriented forests.4–9 This is particularly challenging for SWNT compared to MWNT, since the former are much more sensitive to catalyst structure and carbon feedstock than the latter. In this contribution, we show an example of dramatic changes in physical properties observed when the microarrangement of nanotubes is varied, while using the same nanomaterial, which in this case is SWNT prepared by CO disproportionation on Co—Mo catalysts supported on silica.

Previous studies on vertically aligned multiwalled carbon nanotube (MWNT) arrays have demonstrated water nonwetting behavior in MWNT forests.3,10–15 In some cases, chemical modification of nanotube surface has been found necessary to achieve stable superhydrophobicity.14–17 A recent report18 indicates that MWNT display an interesting range of hydrophobicity when varying parameters like ionic strength, nature of the electrolyte, or pH of the water droplet. Moreover, it was found that the droplet behavior can be switched from superhydrophobic to hydrophilic by application of an electric field. In this contribution we demonstrate dramatic changes in hydrophobicity of SWNT microstructures of varying arrangement. These microstructures include 2-dimensional SWNT films, random networks of SWNT (grass), vertically aligned SWNT (forest), and a novel array of bundled SWNT (pillars).

Essentially total water repellency has been observed on the surface of SWNT pillars grown from morphology-controlled catalyst surfaces synthesized by the nanosphere templating method. In concurrence with previous studies on superhydrophobic systems, in which a combination of microscale roughness and nanoscale roughness appears to be essential,19,20 we propose here that the highest hydrophobicity achieved with the SWNT pillar structure can be ascribed to a double structural roughness of the surface. The first level of roughness is at the nanoscale and is a consequence of the presence of entangled SWNT on the top of each pillar. The second level of
roughness is at the microscale and is associated with the orderly spaced pillars. These conditions of superhydrophobicity are similar to those found in some natural phenomena. It is well-known that the wings of some insects exhibit superhydrophobicity, which is commonly ascribed to surface roughness. For example, periodic arrays of non-close-packed pillars are present on the cicada wings to provide self-cleaning superhydrophobic surfaces, and these structures have served as inspiration for development of biomimetic coatings.\(^{(21,22)}\) Similarly, the leaves of certain plants, most notably lotus (Nelumbo), are superhydrophobic, and this property is ascribed to the presence of microscale papillae covered by hydrophobic wax crystals. The combination of the hydrophobicity of the wax and the unique hierarchical structure of microscale papillae and nanoscale crystals is responsible for the famous lotus effect. The structure-induced roughness makes these two surfaces become hydrophobic with contact angles close to 170°.\(^{(23)}\) The superhydrophobicity of lotus leaves has been theoretically analyzed\(^{(24)}\) in terms of a surface geometry that involves double-roughness structures, which include the presence of slender pillars, analogous to those described in this contribution.

2. Experimental Section

2.1. Catalyst Film Preparation. The various nanotube arrangements investigated in this study were synthesized by CO disproportionation on Co—Mo catalyst, a synthesis method that we have successfully used for several years.\(^{(8,9)}\) The synthesis process comprises three steps: deposition of the catalyst on the substrate, thermal pretreatment, and nanotube growth. As described elsewhere,\(^{(3)}\) an isopropanol solution of Co and Mo salts (Co:Mo molar ratio of 1:3) was added dropwise to the surface of a p-type Si wafer to form an uniform thin film. Different concentrations of metals (0.001–3.8 wt %) total loading, keeping constant molar Co/Mo ratio of 1/3) in aqueous solution were used to obtain different SWNT arrays, as discussed below. After deposition, the wafer was placed in a covered Petri dish to allow for a slow drying. Following the drying step, the wafer containing the catalyst was calcined in a convection oven at 500 °C.

We have developed a novel synthesis method to grow SWNT that bundle up in periodically spaced pillars. This method utilizes the so-called nanosphere lithography technique to deposit the catalyst in a predetermined arrangement, over which the SWNT grow forming the pillars. Before depositing the catalyst, a uniform coating of polystyrene nanospheres (from Alfa Aesar, 2 μm diameter) was deposited on the Si wafer surface. To obtain a uniform distribution, the nanospheres suspended in water/methanol (1:1 weight ratio) were spincoated over the surface at the rotating speed of 2000 rpm. A thin layer of SiO\(_2\) was then deposited by the sol–gel process over the nanosphere template. Uniform “craters” remained on the surface after the nanospheres were washed away by acetone. After calcining the templated surface, the Co—Mo catalyst solution was deposited over the surface that had a controlled roughness.

2.2. Nanotube Growth and Characterization. After the calcination pretreatment, the wafers were placed in a horizontal quartz reactor, with the wafer oriented parallel to the direction of the flowing gas. Prior to the production of SWNT by the CO disproportionation reaction, the catalyst was heated in He up to the reaction temperature (750 °C) at a flow rate of 500 cm\(^3\)/min. When the temperature was stable, the inlet gas was switched to pure CO at a flow rate of 250 cm\(^3\)/min, at atmospheric pressure. The SWNT growth was allowed to happen during 30 min.

In order to confirm that the nanotubes produced in each case where SWNT, the carbon product obtained for the various arrays was characterized on the original Si wafer substrate by Raman spectroscopy, using a JY Horiba LabRam 800 spectrometer, equipped with three lasers (633, 514, and 488 nm) and by transmission electron microscopy (TEM) conducted in a STEM JEOL 2000-FX. To characterize the microscopic arrangements of the various constructions, a scanning electron microscope (JSM-880 SEM) was employed.

2.3. Construction of Different Nanotube Arrays. We have developed methods to vary in a controlled manner the arrangement of SWNT grown on a flat substrate such as a silicon wafer. In this contribution, we have constructed five different SWNT arrays to compare their hydrophobicity. First, as previously shown,\(^{(5)}\) by simply adjusting the concentration of Co and Mo in the precursor solution, the distribution of catalyst particles on the substrate can be varied, and consequently different nanotube arrays can be obtained. That is, when a low (Co—Mo) metal concentration (i.e., 0.02 wt %) is used in the precursor solution, a disordered SWNT network (so-called grass) is obtained during growth (this is schematically illustrated as array 1 in Figure 1).

By contrast, by increasing the Co—Mo concentration in the solution to the optimum value (0.19 wt %), vertically aligned SWNT (forest) are obtained (illustrated as array 2 in Figure 1). As previously shown, this forest is capped by a crust of entangled SWNT that forms at the beginning of the growth process and holds the forest together, creating the characteristic smooth top of these structures.\(^{(5)}\) By ultrasonication in dimethylformamide (DMF) solvent we can open up the crust and suspend the SWNT material. Subsequently, by spraying the SWNT/DMF suspension with a nozzle over a clean Si wafer substrate, a very uniform thin film of SWNT was obtained (illustrated as array 3 in Figure 1). The concentration of the suspending solution was 0.01 wt % SWNT in DMF. After 1 h of horn sonication, the suspension was centrifuged for 30 min at 15 000g force. The supernatant fluid was collected and used for spraying using a nozzle connected to a He gas source over the Si wafer surface. To make smooth uniform films, 10 spray passes were done over the Si wafer.

Alternatively, the SWNT forest can be flipped over, exposing the original roots of the forest instead of the compact crust. This transfer can be readily accomplished by sticking an adhesive tape to the top of the forest and peeling off the entire forest (illustrated as array 4 in Figure 1).

Figure 1. Schematic illustration of the five different SWNT arrangements over Si wafers, formed by controlled growth and/or handling. The five arrays are (1) random network of SWNT (grass), (2) vertically aligned SWNT (forest), (3) two-dimensional SWNT film prepared by spraying a SWNT suspension, (4) flip-over SWNT forest, and (5) periodic array of bundled SWNT (pillars).

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Finally, when the SWNT were grown over the patterned Co–Mo surface obtained by the nanosphere lithography method described above, an arrangement of pillars of SWNT periodically spaced was obtained. This construction is depicted as array 5 in Figure 1.

3. Results and Discussion

3.1. Characterization of the Individual Nanotubes Composing the Arrays. Figure 2 illustrates a typical Raman spectrum obtained with the 633 nm laser on the SWNT product. The strong characteristic RBM bands observed in the range 150–400 cm⁻¹ together with a very low D/G band intensity ratio (about 1/27) are indicative of high-quality SWNT.25–30 Similar D/G ratios were obtained with the other two lasers and over all the array constructions investigated, showing that in all cases the nanotubes are SWNT. As illustrated in Figure 3, the TEM images are in agreement with the Raman results and show that the product obtained on these flat-substrate catalysts are primarily SWNT, with no indication of the presence of MWNT or carbon fibers. Similar observations were made for all constructions.

3.2. Structural Characterization of the Arrays. In previous studies we have reported the presence of a crust of entangled SWNT that forms during the initial stages of growth. The role of this crust is crucial because it determines the final structure of the SWNT forest.9 We have also indicated that when the Co–Mo catalyst film is deposited in a patterned, discontinued form, separate crusts are formed for each domain, and separate forests are formed, making distinctive circular arrangements.9 Therefore, in this study, in which we attempt to create different arrays of SWNT, we have made use of this phenomenon to direct the nanotube forest growth into different structures. As illustrated in Figure 4a, when the Co–Mo catalyst was deposited on the rough side of the silicon wafer, the nanotube growth occurred on separate domains that correspond to the shallow depressions present on the rough surface, with each domain generating a separate crust. As a result, each crust led to growth of a SWNT tower, as clearly seen in the SEM image. The curvature of the crust top on these small domains contrasts with the much flatter surface observed on the broader area forests, for which the limiting effect of the edges is less pronounced.

To create a more reproducible and orderly surface array, we prepared the SWNT pillars, as described above. As predicted by the proposed mechanism, SWNT grew preferentially from catalyst located in the craters and formed crust cap in each crater. Subsequent growth of SWNT pushed the crust cap up to form pillars. As demonstrated in Figure 4b,d, each pillar stems from a separate crater and the curvature of each pillar top is similar to that of the corresponding crater.

Figure 5 illustrates a series of SWNT structures fabricated by the methods mentioned above: (a) random network of SWNT grass (array 1); (b) top of vertically aligned SWNT forest (array 2); (c) two-dimensional SWNT films (array 3); (d) flip-over forest (array 4); (e) SWNT pillars (array 5); (f) bare Si wafer. The hydrophobicity of these six surfaces is compared below.

3.3. Comparing the Hydrophobicity of the Various Arrays. The static wetting angle of water droplets over the different arrays of Figure 5 were evaluated by imaging water droplets of similar size (~2 mm) sitting on the various surfaces. Prior to this sessile drop evaluation test, the samples were baked in a vacuum oven at 150 °C in order to remove the adsorbed organics which may affect surface affinity to water molecules. Figure 6a–e illustrates the significant variation in contact angle for some of the microstructures shown in Figure 5. Clearly, the 2-dimensional SWNT film displays a rather low contact angle.
This array is composed of laterally intercrossing nano-tubes (Figure 5c) mostly oriented parallel to the surface. Therefore, the roughness of this SWNT film is in the scale of a few nanometers. Measurements on several films were repeated to test the reproducibility, and in every case the contact angle was the same within the experimental error.
Remarkably, this thin film is slightly hydrophilic as determined by the measured contact angle (about 80°) close to that of graphite (86°). Next, the crust at the top of the forest, regardless whether it is an incipient forest (grass of Figure 5a) or a few-micron-tall forest (Figure 5b), contains SWNTs entangled isotropically with large void spaces. This void space generates roughness at the nanoscale given by the dimensions of the SWNT bundles, and this roughness causes the formation of a hydrophobic surface with contact angles ca. 150°. Even higher contact angles are obtained on the transferred upside-down forest in which the bottom “roots” appear better aligned in the vertical direction (Figure 5d).

Finally, extraordinary hydrophobicity was achieved on the surface of the SWNT pillars which exhibit the hierarchical combination of roughness scales. That is, in addition to the primary roughness at the nanoscale, the separation between pillars generates a secondary roughness at the microscale (Figure 5e). Remarkably, the measured contact angles (see Figure 7) on these SWNT arrays are greater than that on a Teflon surface.

It was further observed that the sliding angle for a water droplet on the SWNT pillar surface is less than 2°, and the apparent drag effect was reduced to an extent much greater than that on other SWNT microstructure. A simple water repellence test was performed as shown in Figure 8. Water droplets were sent over a slightly tilted SWNT pillar surface at a velocity of 0.5 m/s from a stainless steel needle fixed at a constant height above the surface. The dropping process was recorded continuously using a Sony hard drive camcorder at 30 fps with fastest shutter speed. Selected frame images for sequential drops have been chosen to illustrate in Figure 7 the behavior of a single droplet dropping. It is clearly shown that the repulsive force at the interface keeps the water droplet from sticking to or spreading on the surface and helps recover kinetic energy of the droplet through shape transformation so that it bounces off the surface like a ball. Since all the samples have been pretreated in vacuum to remove adsorbed organics, any significant effect of adsorbed species on hydrophobicity should be ruled out. Moreover, since the surface chemistry is the same for SWNT constituents of every array, the structure-induced roughness should be taken as the primary cause responsible for the large variance in hydrophobicity of these surfaces. Increases in hydrophobicity by rough or microstructured surface are often interpreted in terms of two possible models, originally described by Wenzel and by Cassie and Baxter. In the Wenzel model, the liquid is in contact with the entire solid surface. The effect of the surface roughness in this model is simply to increase the surface area. Therefore, the enhancement in hydrophobicity is a purely geometric effect. By contrast, in the Cassie-Baxter model, it is assumed that there is no penetration of water in the gaps and the liquid

Figure 6. Static contact angle of water droplets over the different SWNT arrays: (a) two-dimensional SWNT films, (b) random network of SWNT (grass), (c) vertically aligned SWNT (forest top), (d) flip-over forest, (e) SWNT pillars, and (f) Teflon surface.

rests on the rough features of the protruding solid material. The air bridging these features then acts as further support for the water droplet. Therefore, the water droplet can be considered to sit part on the solid and part on the air.

Let us first analyze the case of the SWNT thin films. They are produced by spraying the nanotube suspension on the flat surface. The SWNTs in this configuration end up so closely packed that the gap width and depth are small enough to safely assume that no air gets trapped between the water and the solid. In fact, recent simulations indicate that in small gaps water can penetrate into the gaps when the depth is smaller than 2 nm, which is around the range of roughness observed in our SWNT thin films. Therefore, the Wenzel model can be used to describe the wettability of this surface, and the Wenzel equation can be applied

$$\cos \theta_{\text{eff}} = r \cos \theta_Y$$

where $\theta_{\text{eff}}$ is the effective contact angle, $\theta_Y$ the Young angle (equilibrium contact angle), and $r$ the ratio of true wetted area to apparent (geometric) area. This simple relationship indicates that as roughness increases, a hydrophobic surface becomes more hydrophobic while a hydrophilic surface becomes more hydrophilic. That is, since $r > 1$, then $\theta_{\text{eff}} < \theta_Y < 90^\circ$ and $\theta_{\text{eff}} > \theta_Y > 90^\circ$. In our particular

case, it is easy to show that the ratio \( r \) for a surface covered by perfectly oriented SWNT is simply \( \pi/2 \). Therefore, in a first approximation, we can assume \( r = \pi/2 \). Therefore, if the observed contact angles for the thin films is \( \theta_{\text{eff}} = 80^\circ \) (Figure 7a), from eq 1 we can calculate the (intrinsic) equilibrium contact angle for the nanotube surface as \( \theta_Y = 83.5^\circ \), close to the contact angle of graphite, as expected.

On the other hand, simulations predict \(^{35,36}\) that with small gaps and deeper surface features as those seen on the other SWNT arrays (grass, forest, and pillars), it is harder for water to penetrate into the gaps (10–100 nm) between SWNTs. Therefore, little or no penetration of water molecules can be expected on those surfaces. In this regime, the effect of spacing on the microscopic contact angle can be described by the Cassie–Baxter model that relates the effective contact angle (\( \theta_{\text{eff}} \)) on a composite surface to the equilibrium contact angle (\( \theta_Y \)) on a smooth surface of the same chemical composition for a given fraction of surface in contact with the liquid (\( \phi_d \)). The Cassie–Baxter equation is

\[
\cos \theta_{\text{eff}} = \phi_d \cos \theta_Y + (1 - \phi_d) \cos 180 = \\
\phi_d \cos \theta_Y + \phi_d - 1
\]

We can employ this equation in two steps to separately determine the effects of nanoscale roughness and microscale roughness in these arrays.

First, to determine the effect of nanoscale roughness, we can refer to the contact angles measured on the grass surface (i.e., array 1 in Figure 1 and image a in Figure 5) and on the “forest crust” surface (i.e., array 2 in Figure 1 and image b in Figure 5). The observed contact angles for both surfaces are very similar, that is, \( \theta_{\text{eff}} = \text{ca.} 145^\circ \) (Figure 7b). If we use eq 2 with the value of \( \theta_Y = 83.5^\circ \) determined for the thin films, then we can calculate that the fraction of the solid in contact with the liquid is \( \phi_d = 0.16 \). That is, on these surfaces, almost 85% of the water droplet is sitting on air.

Next, to explain the even higher contact angles obtained on the SWNT pillars, one needs to take into account that these pillars add another level of roughness, which further decreases the fraction of carbon over which the droplet rests. We can apply again the Cassie–Baxter equation but this time using as “equilibrium” angle the contact angle that one can expect on the crust of each individual pillar, that is, \( \theta_Y = 145^\circ \). Subsequently, by using the observed experimentally \( \theta_{\text{eff}} = 160^\circ \) (Figure 7c) to plug in eq 2, we can calculate what fraction of the droplet is now sitting on the pillar surfaces. In this case, it is \( \phi_d = 0.33 \). That is, only a small fraction of the droplet sits on the SWNT pillars, and as described above, only a small fraction of the top surface of the pillars is composed of solid SWNT. Therefore, on this surface, 95% of the water droplet is supported by air (i.e., the overall fraction of solid in contact with the liquid is \( \phi_{\text{tot}} = \phi_d \beta \phi_d = 0.16 \times 0.33 = 0.05 \)). As recently pointed out by Nosonovsky and Bhushan,\(^ {37} \) the transition between the two wetting regimes is a multiscale phenomenon. These authors emphasize that while the contact angle is a macroscale parameter, the contact angle hysteresis and the Cassie–Wenzel transition are governed by micro- and nanoscale effects.

### 4. Conclusion

We have developed a series of SWNT microstructures, including 2-dimensional SWNT film, random SWNT network (grass), vertically aligned SWNT (forest), and SWNT pillars, by controlled synthesis of SWNT directly on flat substrates and/or treatment after synthesis. Our study has demonstrated that the static contact angle on these surfaces changes dramatically with surface roughness of SWNT structures and depends on whether this roughness is in the nano- or microscale. The contact angle of a drop sitting on the flat SWNT thin films is described by the Wenzel model. By contrast, the behavior of the different three-dimensional arrays can be described in terms of the Cassie–Baxter model. In the former, the water penetrates the shallow gaps of the surface defects (in this case SWNT), and the surface exhibits a contact angle similar to that of flat graphite, with the roughness only increasing the surface area. In the latter, the water droplet is visualized as sitting on a patchwork of solid domains and air. Therefore, the hydrophobicity of SWNT grass, forest, and pillars is greatly enhanced by both a primary roughness at the nanoscale and a secondary roughness at the microscale, which is particularly effective in the case of the SWNT pillars.

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