Superhydrophobic Vertically Aligned Treelike Carbon Nanostructures

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The lotus leaf shows superhydrophobicity and extreme nonsticking properties due to the two-level roughness features of its surface in addition to the low surface energy. In the thin film of vertically aligned treelike carbon nanostructures, each nanostructure is a multiwalled carbon nanotube aligned vertically to the plane of the substrate with carbon films attached to the nanotubelike branches, giving the overall treelike appearance. These nanostructures also have two-degree roughness due to their unique geometry, which makes the wettability of the material an interesting property to study. The change in hydrophobicity of the material as a function of the deposition time is studied to understand the mutual dependence of the geometry of the nanostructures and the hydrophobicity of the film. The material exhibits superhydrophobicity, showing a static water contact angle as high as 165° for certain deposition conditions with extreme nonsticking properties.

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I. INTRODUCTION

Many natural surfaces, both in the plant and the animal realms, exhibit superhydrophobic nonsticking properties and the most well-known among such surfaces is the lotus leaf. The microstructure of the lotus leaf exhibits a multilevel roughness with micron-scale conical papillae (5–50 μm) and nanoscale branchlike wax tubules (100–500 nm) on the papillae. This unique two-level roughness along with the intrinsic hydrophobicity of wax is thought to be the contributing factor toward the superhydrophobicity of a lotus leaf. Many research groups have tried to achieve superhydrophobicity or duplicate the "lotus leaf effect" by creating microstructures like those in the lotus leaf. Such bio-mimicking surfaces are fabricated by different methods, such as photolithography, electrospinning, and plasma etching, and have been applied as self-cleaning, anti-icing, anti-fouling, corrosion-resistant surfaces, and so on [1–5].

Multiscale roughness, to achieve superhydrophobicity, has been explored in carbon nanostructures as well [6], especially with the thin films of vertically aligned carbon nanotubes (VACNT), which is a well-studied superhydrophobic surface [7–11]. Two strategies are usually undertaken to achieve the dual roughness: (a) micropatterning the substrates on which the film is growing and (b) introducing microscale patterns on the film after deposition of VACNT [12–15]. For both cases, the micropatterns work as the microscale of roughness, while the carbon nanotubes contribute to the nanoscale of the roughness, thus giving the desired multiscale roughness to the film. The micropatterns on the substrate can be in the form of a honeycomb or pillars and are generally grown by lithographic techniques [12–14]. Less conventionally, some groups have tried a one-step synthesis method by making two layers of the nanotubes of different roughnesses or by bundling the nanotubes into microscale pillars using a template method to get the dual roughness [16,17]. Sometimes, a conformal coating of low surface energy material such as fluorocarbon, silicone, and so on is also used on carbon nanotube films is to further improve the hydrophobicity of the carbon nanotube films and to dissuade the intrinsic hydrophilic nature of the films due to hydroxyl groups, which are sometimes present on the surface of nanostructured carbon films [18–21].

The thin film of vertically aligned treelike carbon nanostructures [22] has a multilevel roughness, that is, with a microlevel central multiwalled nanotube ("trunk" of the treelike nanostructure) and nanolevel "branches" on the nanostructure. The dual roughness, like that of a lotus leaf, is speculated to give a very high hydrophobicity along with the "branches," stopping the seeping of the water into the air pockets between the "trees" and leading to less sticking of the water. Thus, a study of the hydrophobicity of the as-deposited material is undertaken and is reported in this paper.

II. EXPERIMENTAL DETAILS

The vertically aligned treelike nanostructures are deposited on polished silicon substrates by electron cyclotron resonance (ECR) assisted by the plasma enhanced chemical vapor deposition (PECVD) method. All depositions are done at 500 W of microwave power

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at a negative substrate bias of 200 V with respect to ground potential and with acetylene and hydrogen as the feed gases at a ratio of 3:1 (hydrogen flow 5 sccm) at a temperature of 750 °C on a seed layer of nickel. The details of the synthesis process and characterizations of the film are described in our previous publication [22]. The morphology of the nanostructures is studied by field emission scanning electron microscopy (FESEM, Ultra 55, Carl Zeiss). To study the wettability of these nanostructured carbon thin films, the static contact angle of water with the surface and droplet roll off is studied by using the goniometer set up (OCA 20 from Dataphysics instruments Gmbh). The image is taken within 5 s of dispensing a droplet of water of 10 μl using the dispensing mechanism of a goniometer. The contact angle values reported here are the average of three readings taken consecutively for the same sample at three different spots. Drop impact study is done using a high-speed imaging camera (Photron FastCam SA4) capturing 10 000 frames/s. A 10-μl water droplet is impacted on the surface from a height of 5 cm.

III. RESULTS AND DISCUSSIONS

The FESEM image of the cross-section view of the vertically aligned treelike nanostructures (deposition time of 15 min) on a polished silicon substrate is shown in Fig. 1(a). The thickness of the film is 1.5 μm. There are as roughly 10^4 trees per cm^2 of film. The diameter of the thickest portion of the trees is 175 nm (average). The film shows a uniform growth of the material with dual roughness contributed by the “branches” of the treelike nanostructures and by the nanostructures themselves. The contact angle of the droplet (10 μl) of water on the film is 153° with a sliding angle of less than 2°,

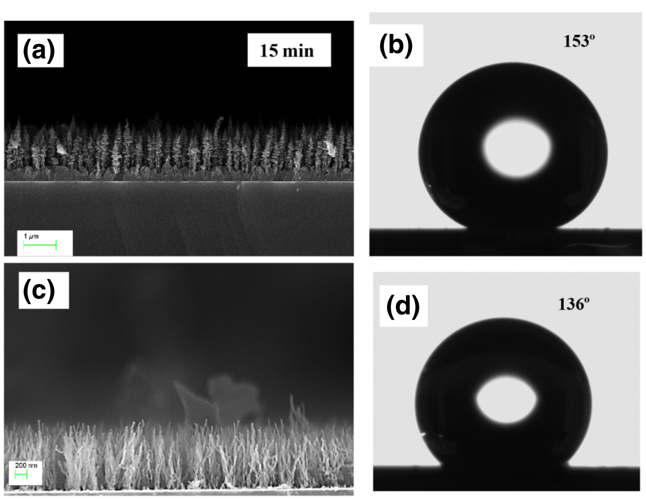

FIG. 1. (a) and (c) FESEM image of vertically aligned treelike carbon nanostructures and vertically aligned carbon nanotubes, respectively. (b) and (d) show the water droplet on the surface of the respective films.

VIDEO 1. Droplet roll off for the 15 min-sample.

showing the extremely low hysteresis and superhydrophobic nature of the material [Fig. 1(b) and Video 1]. The nanostructured treelike material retains its hydrophobicity even while remaining exposed to the atmosphere for six months and shows the same static contact angle without any degradation. To further examine the hydrophobicity under dynamic conditions, a droplet of the same volume is impacted on the surface of the film from a height of 5 cm (Video 2). It is seen that the water droplet completely bounces off the surface without leaving any residue on the surface with a contact time of 10.9 ms. On comparing the hydrophobicity of the material with that of a VACNT film of similar thickness (1.2 μm) as shown in Fig. 1(c), it is found that the contact angle of a water droplet of the same volume on the VACNT film deposited on a silicon substrate is 136° [Fig. 1(d)]. Thus, the incorporation of the “branches” on the aligned nanotubes have led to a definite improvement in the hydrophobicity of the films. Therefore, instead of using the two-step procedures to achieve hierarchical roughness, such as micropatterning the substrate by lithography and depositing the nanostructured film on

VIDEO 2. Droplet impact from height of a 5 cm for the 15-min sample.

the substrate [12,13] or doing a postdeposition pattering of the aligned carbon nanotube film by laser pruning or photolithography [14,15], a one-step method of synthesizing a superhydrophobic film with two levels of roughness is presented. The value of the contact angle is higher than most reported values of CNT films with comparable hysteresis values [12–15]. It is speculated that the incorporation of the "branches" to the micron-level nanotubes will inhibit the seepage of water between the nanostructures and thus an air pocket will form below the water surface. This leads to lower sticking of water with the material and will prevent a transition to the Wenzel mode of wetting. Branches will suspend the droplet in the nonwetting Cassie mode [23,24] with water droplets suspended on the nanofeatures and thus produce a more stable superhydrophobic nature like that of the lotus leaf [25]. It is to be also noted that there is a resemblance of the vertically aligned treelike nanostructures to the micropapillae of the lotus leaf, which scientists are striving to mimic to achieve the superhydrophobicity and self-cleaning properties on the level of a lotus leaf [1–3].

To correlate the hydrophobicity and the morphology of the material, the geometry of the nanostructure is varied by deposition during the PECVD process. Time is varied from 5 to 35 min in steps of 10 min. The FESEM images of the as-deposited vertically aligned treelike nanostructures are shown in Figs. 2 and 3. From the FESEM images of the samples, it can be observed that with the time of deposition, the height of the trees as well as the length of the "branches" increases while retaining the general structure. The sample deposited for 5 min has the lowest length of the "branches" and a thickness of 0.75 μm with an average diameter of the portion with the largest "branches" (as can be seen from the top view of the sample) of 75 nm. As mentioned earlier, for the sample deposited for 15 min,

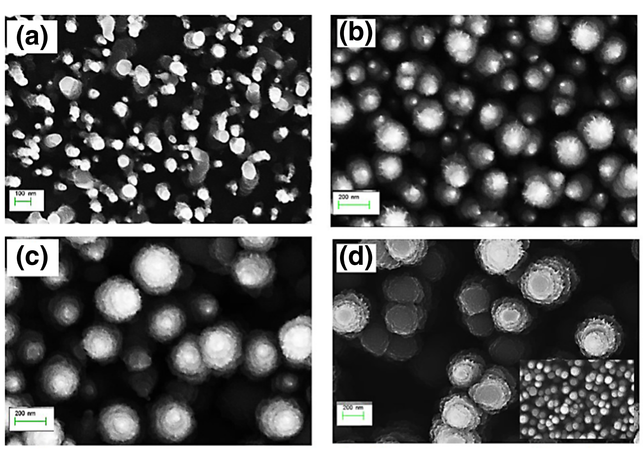

FIG. 2. Top view FESEM image of vertically aligned treelike nanostructures deposited for time duration (a) 5 min, (b)15 min, (c) 25 min, and (d) 35 min, respectively (inset showing uniform growth of the nanostructures at a lower magnification).

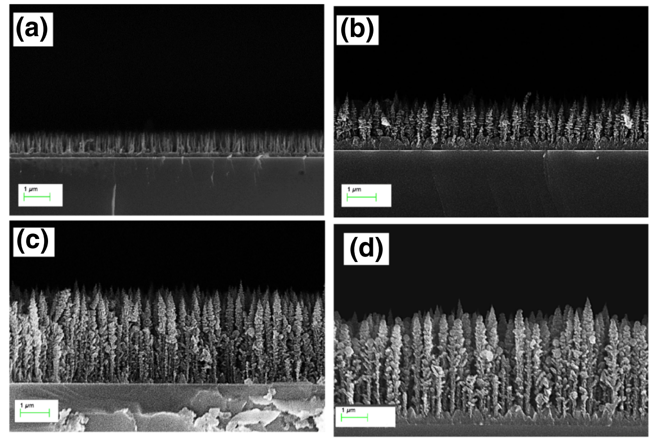

FIG. 3. Cross-section view of the vertically aligned treelike nanostructures from FESEM of the sample deposited for a duration of (a) 5 min, (b) 15 min, (c) 25 min, and (d) 35 min.

the diameter of the thickest portion and the thickness of the film are 175 nm and 1.5 μm, respectively. The same values for the 25-min sample are 320 nm and 3.5 μm. At 35 min, the length of the nanostructures has increased to about 4 μm and the average diameter of the portion with the longest "branches" is about 400 nm. After a deposition time of 25 min, the nanostructures are observed to be losing sharpness at the tip and the portion with longer "branches" is shifting more toward the tips of the treelike nanostructures. In other words, the tip of the treelike nanostructures is thickening at higher deposition times. The increase in time results in nanostructure growing in both the lateral and the vertical directions, but after a certain point, the growth in the vertical direction saturates at the cost of more growth in the lateral direction, leading to the formation of top-heavy treelike nanostructures [Fig. 3(d)]. The early saturation of the growth in the vertical direction is most probably due to more etching at the tip due to impingement of the etchant species in the vertical direction energized by the substrate bias. At a longer ,time of deposition, there can be redeposition of the etched-out species on the top of the "trees," causing the observed thickening of the tip of the "trees." The approximate number of trees per unit area, that is, the areal density of the trees, is approximately 4×10^4 cm^{-2}, 10^4 cm^{-2}, 7000 cm^{-2}, and 3750 cm^{-2} for samples deposited for 5, 15, 25, and 35 min, respectively.

The diameter and the space between the nanostructures as well as the height are the controlling factors of the contact angle of water depending on the wetting mode of the droplet on the surface [25]. The variation of the contact angle of the vertically aligned treelike nanostructures with the change in morphology via changing of the time of deposition is shown in Fig. 4. As soon as the droplet is released from the dispensing pin of the goniometer setup, the water droplet moves away from the surface because

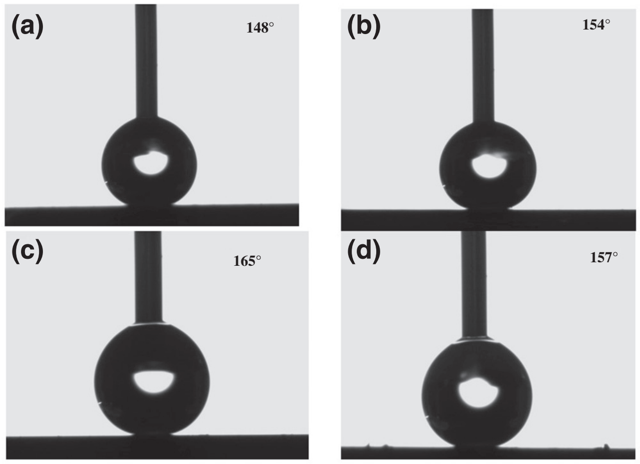

FIG. 4. Water droplets on the surface of the vertically aligned treelike nanostructures deposited for (a) 5 min, (b)15 min, (c) 25 min, and (d) 35 min (the values in the top righthand corner are the average contact angle values for the samples of three measurements).

of the high hydrophobicity for some of the samples, especially the samples exhibiting higher contact angles [as shown in Figs. 5(d)–5(g) and Video 3]. The rolling away of the water droplet placed on the surface of the film even on a flat stage (there may be a slight tilt, which is not measurable) shows that the roll-off angle and hysteresis are very low (less than 2°). Thus, to keep uniformity in the representation of the water droplets and the contact angle measurements, all the droplet pictures are taken at the instant when the droplet from the liquid-dispensing pin touches the surface. Figure 4 shows that the contact angle of the water droplet on the surface of the material gradually increases with the increase in the time of deposition up to 25 min. The sample with 25 min of deposition gives a contact angle as high as 165° showing superhydrophobicity, while the sample deposited with a time of deposition of 5 min shows the lowest water contact angle of 148°. Note that the sample with 5 min of deposition time has the shortest length of the "branches" and the nanostructures have the lowest height. Figures 5(a)–5(c) shows the stills from the video depicting the behavior of a droplet on impingement on the surface of the film deposited for the 5-min duration. The droplet sits on the surface after impingement, but as can be seen from Figs. 5(d) to 5(g), the droplet on impingement on the surface of the film deposited for the sample deposited for 25 min does not stick but rolls away from the surface of the film (Video 3). To further characterize the superhydrophobicity under dynamic conditions for the 25-min sample, a droplet impact experiment is performed with a droplet of 10-μl volume from a height of 5 cm. It is observed that the droplet bounces off the surface without leaving any residual drop on the surface, showing the extreme hydrophobicity of the material (Video 4).

To explain the variation of the contact angle with the surface morphology, the Cassie equation [23–28] has to be considered. The general Cassie equation, which relates the apparent contact angle of a surface with features (θ_r) with a contact angle of a smooth surface of the same chemical composition (θ_e) is

$$\cos\theta^r = f_1 \cos\theta_e - f_2, \tag{1}$$

where f_1 is the ratio of the wetted area of the solid to the area of the material without features or patterning and f_2 is the ratio of the not wetted area (due to air gaps) to the area of material without any features [25].

With the increase in the time of deposition, the number of "trees" per unit area decreases due to the increase in the gap between the "trees" and the increase in the length of the "branches." If the droplet is in an ideal Cassie mode (droplet sitting on the top of the surface without any liquid penetrating the gap between nanostructures), the f_1 of the material, which will be then defined by the area of the tip of the "trees" to the total surface area, should also decrease with the decrease in the number of "trees" per unit area (if the area of the tip of the nanostructure remains constant). The f_2 (ratio of the air gap to the total area) should increase in an ideal Cassie mode with a decrease in the number of "trees." Thus, with an increase in time, as long as the tips of the nanostructures are not thickening, the apparent contact angle (θ_r) should increase with an increase in the time of deposition if the droplet is in an ideal Cassie mode of

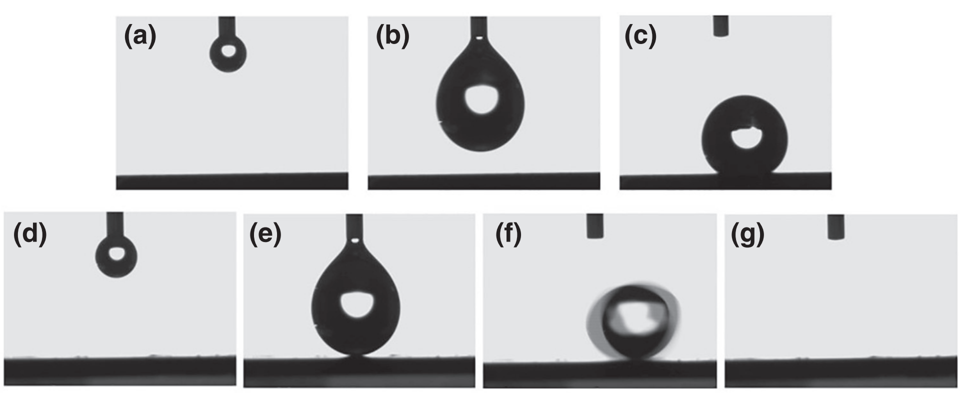

FIG. 5. The different stages of the impingement of a droplet on the surface (a)–(c) for a sample deposited with a time duration of 5 min and (d)–(g) for a sample deposited with a time duration of 25 min.

VIDEO 3. Droplet roll off for the 25-min sample.

wetting according to Eq. (1). At 35 min, when the tip of the “nanotrees” thickens, f_1 should be higher and f_2 should be lower than that of the sample deposited at 25 min, and should result in a decrease in contact angle for the 35-min sample with respect to the sample deposited for 25 min.

If the droplet is in a partially wetting mode (the water partially penetrates into the gap between the nanostructures), with an increase in time, the f_1 should increase due to the increase in height because of an increase in the wetted area due to an increase in height, so f_2 should also increase due to the increase in the gaps between the “trees,” thus increasing the contact angle with time. The same should happen when the time of deposition changes from 25 to 35 min and thus the sample with 35 min of deposition time should have a higher contact angle, which is not the case observed here. If the droplet is in a complete wetting mode (i.e., the liquid penetrates into the gap between nanostructures completely and wets all available exposed surfaces), an increase in height of the nanostructures as well as an increase in the length of the “branches,” which is happening with an increase in time, should be increasing the contact angle without any exception, which is also not matching the experimental observations.

VIDEO 4. Droplet impact from a height of 5 cm for the 25-min sample.

On observing the extreme nonsticking of the water droplet on the material for high contact angles as well as an ideal Cassie mode providing most the fitting explanation of the interrelation morphology and contact angle, it can be concluded safely that the material is in ideal Cassie mode of wetting. Thus, the material, which can be grown on any type of substrate as shown in our previous studies [22] in one step with superhydrophobic as well as nonsticking properties with an ideal Cassie mode of wetting, is an alternative direction in the field of superhydrophobic nanostructures with two-level roughness.

IV. CONCLUSIONS

In this study, motivated by the dual-scale roughness of the vertically aligned treelike carbon nanostructures like that of the lotus leaf, the hydrophobicity of the material is studied using the static water contact angle method. The material is found to be superhydrophobic with very low sticking and a contact angle of 153°, which is higher than that for the thin film of vertically aligned carbon nanotubes of similar thickness. In the quest to find the optimum structure of these treelike carbon nanostructures for the highest hydrophobicity, the morphology of the material is varied by changing the duration of deposition of the material. It is found that with the time of deposition, the height of the “tree” and the length of the “branches” as well as the gap between the individual nanostructures changes to change the hydrophobicity of the material. The maximum contact angle of 165° is achieved for the sample deposited for 25 min. These results pave the way for the design of a possible alternative type of superhydrophobic material. Even better and more robust surfaces can be aimed at by coating the material conformally by low surface energy material such as polydimethylsiloxane, fluorocarbon, and so on.

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