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Superhydrophobicity from Two-tier Roughened Texture: Microscale Carbon Fabrics Decorated with Carbon Nanotubes

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Superhydrophobic carbon fabric with micro/nanoscaled two-tier roughness was fabricated by decorating carbon nanotubes (CNTs) onto microsized carbon fibers, using a catalytic chemical vapor deposition and subsequent fluorination surface treatment. The superhydrophobic surfaces are based on the regularly ordered carbon fibers (8–10 µm in diameter) that are decorated by CNTs with an average size of 20–40 nm. The contact angle of water significantly increases from 148.2 ± 2.1° to 169.7 ± 2.2° through the introduction of CNTs. This confirms that the wettability of carbon fabric changes from hydrophobicity to superhydrophobicity due to structural transformation. This finding sheds light on how the two-tier roughness surface induces superhydrophobicity of rough surfaces, and how the presence of CNTs reduces the area fraction of a water droplet in contact with the carbon surface with two-tier roughness.

1. Introduction

It is generally recognized that the self-cleaning of a lotus leaf is ascribed to two criteria: (i) the hierarchically combined micro- and nanoscaled structure of the surface (physical factor) and (ii) the low-surface-tension compound covered on the structure (chemical factor). Obeying the rule of "learning from nature", several researches have fabricated superhydrophobic surfaces, including fluorinated carbon nanofiber (CNF) or surface-modified carbon nanotube (CNT) arrays, stack of nanoparticles, and hierarchical structures by binary colloid assembly.

In the present work, we develop a catalytic chemical vapor deposition (CCVD) technique to branch or decorate carbon nanotubes (CNTs) on carbon fabric from polyacrylonitrile (PAN), thus forming a carbon/carbon junction structure. This unique carbon structure thus results in a micro/nanoscaled two-tier roughness that is believed to improve surface hydrophobicity. To reduce the surface tension of carbon fabric, a spin coating enables coating of perfluoroalkyl methacrylic copolymer over the carbon fabrics. This work sheds some light on the superhydrophobicity of the resultant carbon surface, showing a resemblance to lotus leaves in nature, and on how the decoration of CNTs affects the wetting property.

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2. Experimental

PAN-based carbon fabric supplied by Taiwan Carbon Technology Co., Taiwan, was used as matrix decorated with CNTs in this work. The fabric has a thickness of 0.4 0.6 mm, and the diameter of the carbon fibers in the fabric is approximately 8 10 μm. Chemical oxidation was applied to implant surface oxide groups, in which the fabric was well mixed with nitric acid at 90°C for a period of 8 hr. After that, the treated fabric was rinsed by distilled water several times until the pH value of the slurry was higher than 5. To uniformly disperse metal nanocatalysts onto the oxidized fabric, the procedure for the fabrication of metal-carbon fabric composites is described as follows: 0.5 g oxidized carbon fabric was mixed with 0.5 M Ni ionic nitrate, and then the carbon-based slurries were stirred under Ar atmosphere at an ambient temperature for 6 hr. This wet process enables Ni^{2+} ions to interact with each surface acidic group. After that, the ionic-adsorbed fabric was separated from the Ni-salt solution by using a filtration apparatus. Then a direct heating process was performed at 350°C under a H_2 atmosphere, thus, resulting in Ni-attached fabric composites.

A CCVD technique was employed to grow CNT branches on Ni-attached fabric, using a mixture of carbon precursor ($Ar:H_2:C_2H_2 = 94:1:5$ in v/v/v). The vapor-growth process was carried out in a vertical furnace at 900°C for a growth period of 1 hr. To reduce the surface tension of the carbon fabric, a spin coating was performed to coat perfluoroalkyl methacrylic copolymer (Zonyl 8740, Dupont Co.; the composition of copolymer/water: 7/3 in v/v) over the carbon fabrics. After the hydrophobic coating, the fluorinated carbon fabric was dried in an oven overnight, inducing a fluorocarbon coating on the surface of the carbon samples.

Contact angles of de-ionized water (72.3 mN/m for surface tension) were evaluated as the ability of water-repellency of the carbon fabrics coated with fluorinated polymer. An optical contact angle meter was adopted to measure the contact angle of water droplet on the prepared surfaces. Each droplet was dropped to the sample surface from a distance of 5 cm by vibrating the syringe. The volume of the droplet was controlled at around 5 μL. The sample plate was vibrated slightly by tapping the sample stand before each measurement to obtain the equilibrium contact angle. The carbon fabric decorated with CNTs was characterized by field-emission scanning electron spectroscope (FE-SEM, JEOL JSM-5600).

3. Results and Discussion

Fig. 1a-1f illustrate the FE-SEM images for carbon fabrics with and without CNT branches. In comparison, these images clearly indicate that the original carbon fiber has a smooth surface, whereas a large amount of CNTs are branched and decorated on the surface of carbon fibers after CCVD treatment. It is generally believed that nickel is one of effective catalysts in catalytic decomposition of carbon precursor, inducing the growth of CNTs. Thus, these Ni particulates can be used as catalytic sites for growing CNTs on the sidewalls of the carbon fibers, resulting in random growth of CNTs at different axes. As shown in the inset of Fig. 1f, a single nanotube is found to have an average diameter of 20–40 nm and a length of several micrometers. This length of nanotube is possibly dominated by a faster poisoning of the catalyst particles by amorphous carbon on the catalytically active surfaces. Fig. 1a and 2b show the FE-SEM images for fluorinated carbon fabric decorated with CNTs. We observe that after the fluoropolymer coating, cilium-like CNTs can protrude out of the microscale carbon fibers, offering the secondary roughness on the two-tier texture.

To identify the superhydrophobicity of the fluorinated carbon surfaces, five drops of water were placed at different locations on a horizontal carbon surface. Five readings of the contact angle were then taken. The derivation of the contact angles measured in this study was within 2.2°. Cross-sectional views of water droplets on the fluorinated carbon fabric and micro/nanoscaled carbon fabric are shown in Figs. 2a and 2b, respectively. After accurate measurements, the contact angle of water significantly increases from 148.2 ± 2.1° to 169.3 ± 2.2° through the introduction of two-tier micro/nanoscaled structure. This confirms that the wettability of carbon fabric has changed from hydrophobicity to superhydrophobicity due to structural transformation. Generally, the micro/nanostructural carbon surface is created to mimic the surface of a lotus leaf, which is textured with 3–10 μm hills and valleys that are decorated with nanosized particles of a hydrophobic wax-like material. The hills and valleys ensure that the surface contact area available to water is very low, while the hydrophobic nanoparticles prevent penetration of water into the valleys. The net result is that water cannot wet the surface and therefore forms nearly spherical water droplets, thus leading to a superhydrophobic surface.

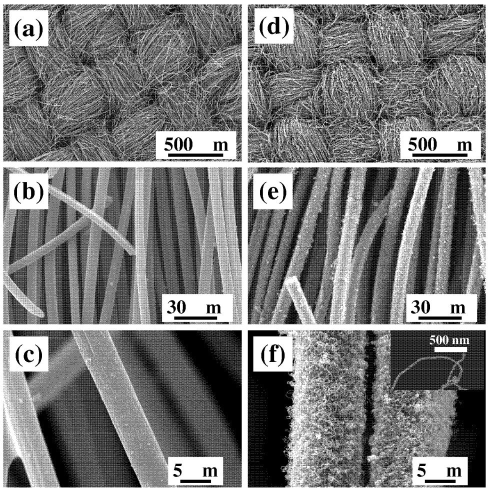

Fig. 1. FE-SEM images for (a), (b), (c) the original carbon fiber and (d), (e), (f) the carbon fiber decorated with CNTs with different magnifications. The inset of (f) represents single CNT grown on carbon fiber.

It is worth noting that the water drop was sitting on carbon fabric decorated with CNTs, leaving a layer of air underneath the water droplet, which is marked in the cross-sectional view of water drop in Fig. 2b. Since the spherical water drop can be suspended on the two-tier roughened texture, this can be inferred that an air pocket exists in the carbon fabric against water droplet. After a long period of 0.5 hr, the droplet still sits on the existing air film, obeying the Cassie model.

Previous studies have pointed out that the wettability of F-coated flat surfaces is hydrophobic with an average contact angle of 100–120°. The carbon fabric consists of a number of intersections of fibers with the mean diameter of 8–10 μm. The microscaled fiber used here as the primary roughness improves the water repellency. Therefore, the contact angle of fluorinated carbon fabric is much greater than that of a flat surface. After the growth of CNTs on carbon fibers, the CNTs serve as the secondary roughness that is similar to the secondary roughness on lotus leaves. This appearance of CNTs is believed to play an important role in preventing the penetration of a water drop. Thus, air can be trapped in grooves or valleys on the two-tier rough surfaces, as shown in Fig. 2a and 2b. The hydrophobic performance of micro/nanoscaled carbon fabric is thus enhanced. In this case, it is suggested that the coiled-type CNTs with high density could provide enough height for trapping air film, thus preventing water penetration.

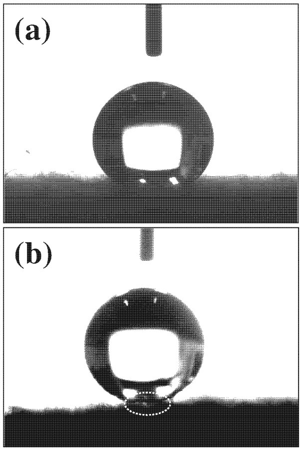

Fig. 2. Cross-sectional view photographs for water droplets sat on (a) the fluorinated carbon fabric and (b) the fluorinated carbon fabric with two-tier roughness.

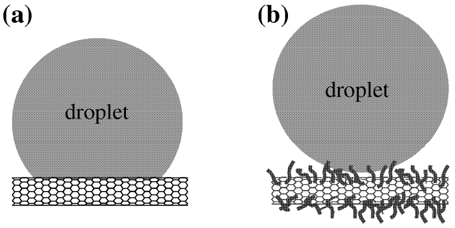

Fig. 3. Illustration for water droplet sat on (a) the fluorinated carbon fabric and (b) the fluorinated carbon fabric with two-tier roughness.

Based on the above deduction, the growth of CNTs on the regular carbon fabrics results in the unique architecture with combines a micro and a nanoscaled surface topology, which prevents the transition from Cassie to Wenzel state. Under ambient conditions, air can be trapped between the liquid and the carbon fabric. Thus, the superhydrophobicity of the two-tier carbon structure prefers to obey the Cassie state, demonstrated by Fig. 2b. The Cassie-Baxter wetting mechanism on superhydrophobic surfaces indicates that only the hills of the rough surfaces are wetted, while the water drop does not penetrate into the valleys. Accordingly, we propose the Cassie-Baxter model to describe the wettability of fluorinated carbon fabric with micro/nanoscaled two-tier roughness. This relationship between the apparent contact angle Θ^* observed on a rough surface and the equilibrium contact angle Θ obtained on a smooth surface is based on the same chemical composition:

$$cos\,\Theta^* = -1 + \Phi_S(cos\,\Theta + 1) \qquad (1)$$

where the surface fraction Φ_S corresponds to the ratio of the surface of each pillar in contact with the liquid to the apparent surface of the substrate. Basically, the equation is considered to represent the effect of roughness on wettability: air may be trapped on the rough surface, which enhances the hydrophobicity because the water drop is then partially sitting on air. In this case, the contact angles of water on the flat surface, the carbon fabric, and the micro/nanoscaled carbon fabric are 110°, 148.2°, and 169.3°, respectively. Thus, the surface fractions Φ_S can be estimated to be 22.8 % and 2.5 % for the carbon fabric and the micro/nanoscaled carbon fabric, respectively. The much lower surface fraction reveals that the CNT forest produces a large amount of air trapping between the microstructure of carbon fabric and the nanostructure of CNTs. This indicates that the presence of CNTs would reduce the area fraction of a water droplet in contact with the carbon surface with two-tier roughness. Such superhydrophobicity of the unique surface is mainly contributed from the unique micro/nanocsaled structure and the subsequent fluorination surface treatment.

Table 1. Advancing contact angle (Θ_A), receding contact angle (Θ_R), and contact angle hysteresis ($\Theta_H = \Theta_A - \Theta_R$) for the fluorinated carbon fabric and the fluorinated carbon fabric with two-tier roughness.

Sample	Θ_A (°)	Θ_R (°)	Θ_H (°)
Fluorinated carbon fabric	142.6 ± 2.2	151.3 ± 2.2	8.2 ± 2.2
Fluorinated carbon fabric with two-tier roughness	164.8 ± 2.1	169.5 ± 2.1	4.7 ± 2.1

It has been supported that the water contact angle hysteresis plays an important role in the sliding behavior of water droplets. Generally, a low contact angle hysteresis reflects that water droplets can slide easily on the surface, i.e., self-cleaning effect. The advancing and receding angles were obtained by increasing or decreasing the drop volume until the three-phase boundary moved over the surfaces. The measured water contact angle hysteresis (difference between the advancing contact angle and the receding contact angle) appears to decrease from 8.2 ± 2.2° to 4.7 ± 2.1° after the introduction of the two-tier micro/nanoscaled structure. The lower magnitude of the water sliding angle can be attributed to the presence of CNTs. It has been suggested that the three-phase contact line for microscaled fabric is more stable than the fabric decorated with randomly CNTs, which are tortuous in three-dimension. Pioneer studies have reported that the morphology of the three-phase contact line is the critical factor in determining the contact angle hysteresis: discontinuous, unstable, and contorted contact line is essential to form a superhydrophobic surface with low hysteresis. As shown in Fig. 3b, the coiled nanotubes would create a discontinuous three-phase contact line. Compared to microscaled carbon fabric, the micro/nanoscaled surface, comprising nanotubes and interspacing, can provide more space for air trapping. Therefore, suspended water drops lie on top of the “nanopillars” (i.e., CNTs) with air pockets beneath them, corresponding to the Cassie state. Then the water droplet can rotate smoothly and continuously on the surface when the surface is slightly tiled. Such micro/nanoscaled surface with a sliding angle of only 4.7 ± 2.1° gives wider applicability in self-cleaning fields.

4. Conclusions

We have investigated an approach to fabricate fluorinated carbon fabric with micro/nanoscaled two-tier roughness. A large amount of CNTs was catalytically grown on the microscaled PAN-based carbon fiber through a CCVD technique, using Ni nanoparticles and acetylene as catalyst and carbon source, respectively. The nanotube was successfully branched and decorated onto the carbon fiber at different axes, forming a micro/nano carbon structure. This unique carbon surface with two-tier roughness exhibited an excellent superhydrophobicity with a great contact angle of 169.7 ± 2.2° with water. This result can be supported by the argument that the CNT forest allows a large amount of air to be trapped between the microstructure of carbon fabric and the nanostructure of CNTs. Such superhydrophobic surfaces tend to open some promising applications including bioseparation devices, microfluidic devices, liquid transportation without loss, and so on. Additionally, since it has good electric conductivity and high surface area, the fabricated carbon fabric with two-tier roughness can be used as electrode material for high-performance electric double-layer capacitor and gas sensor with high selectivity and high sensitivity.

References

Hsieh CT, Chen JM, Huang YH, Kou RR, Lee CT and Shih HC., 2006, Influence of fluorine/carbon atomic ratio on superhydrophobic behavior of carbon nanofiber arrays, J Vac Sci Technol. 24,113-7.

Hsieh CT and Fan WS., 2006, Superhydrophobic behavior of fluorinated carbon nanofiber arrays, Appl Phys Lett. 88, 243120-2.

Hsieh CT, Chen JM, Kuo RR,. Lin TS and Wu CF., 2005, Influence of surface roughness on water- and oil-repellent surfaces coated with nanoparticles, Appl Surf Sci. 240,318-26.

Hsieh CT, Lin JY and Chou YW., 2007, Fabrication and electric capacitive behavior of hetero-junction carbon nanoclusters by using secondary chemical vapor deposition. Chem Phys Lett. 444, 149-54.

Onda T, Shibuichi S, Satoh N and Tsujii K., 1996, Super-water-repellent fractal surfaces. Langmuir. 12, 2125-7.