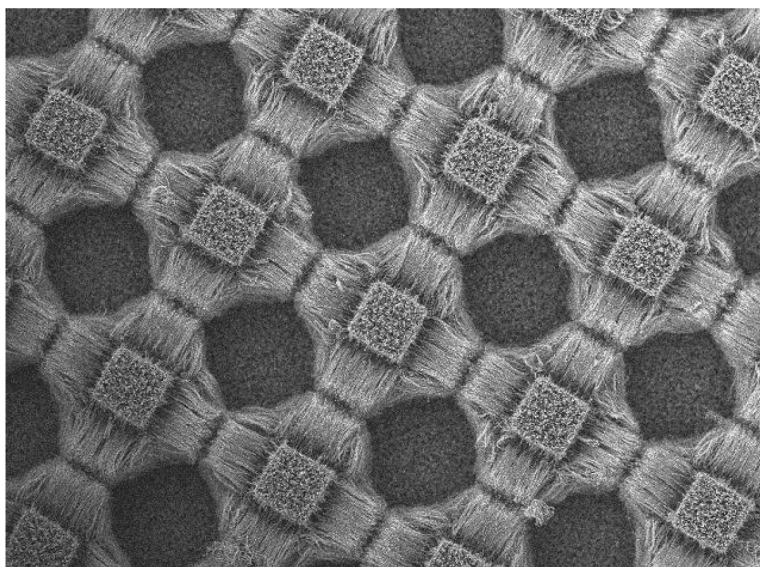Communication

Control over the Wettability of an Aligned Carbon Nanotube Film

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Control over the Wettability of an Aligned Carbon Nanotube Film

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Surface structures have been paid great attention for their influence on wettability;[1−5] for example, the cooperation of micro- and nanostructures of lotus and rice leaves[3] and some artificial surfaces[3] can induce superhydrophobicity. However, the wettabilities of surfaces with anisotropic,[4a] especially three-dimensional anisotropic structures, have rarely been reported. The wettability of carbon nanotubes has been extensively studied for their potential applications on the nanometer scale.[5] In a previous paper, we demonstrated that an aligned carbon nanotube (ACNT) film with a fluoroalkylsilane coating showed superamphiphobic properties.[6a] This study opens up a novel strategy for controlling the surface wettability by adjusting the anisotropic structure of surface. In this contribution, we fabricated three-dimensional anisotropic ACNT films by the chemical vapor deposition (CVD) method on silicon templates with well-defined structures and studied its influence on wettability. We show that superhydrophobicity with a water contact angle (CA) larger than 150° and hydrophilicity with a water CA smaller than 30° can both be achieved on the anisotropic ACNT films by simply varying the structural parameter without alteration of chemical composition, which can be explained by the coexistence of the horizontal and vertical ACNT arrays. It reveals that anisotropic microstructures can bring about better controllability over the surface wettability.

ACNTs can be aligned on large-scaled surfaces[7] by the CVD method, and the alignments are almost normal to the substrate and densely packed with fairly uniform length. Therefore, ACNT arrays of different orientations can be integrated together through predetermination of the substrate topography in a single CVD process.[8] Patterned silicon templates with a well-defined quadrate pillar array were fabricated by photolithography[9] and the inductive coupling plasma deep etching technique. The pillars are 30 μm high, their side length is 10 μm, and the spacing between silicon pillars can be adjusted. In the present study, five spacings of 6, 10, 13, 15, and 20 μm were selected. Three-dimensional anisotropic ACNT films were deposited on these templates by the CVD method. Figure 1A, B, and C shows SEM images of periodic patterns of ACNT microstructures on silicon templates with spacings between quadrate pillars of 20, 15, and 10 μm, respectively. Mutually orthogonal ACNT microstructures can be clearly seen in the higher magnification image (Figure 1D) of Figure 1A. The areas of (a) and (b) respectively represent the vertical ACNTs on the top of quadrate silicon pillars and horizontal ACNTs from the side faces, while area (c) represents ACNTs grown from the bottom of the templates. The ACNTs were densely packed with a fairly uniform length (about 10 μm) and diameters ranging from ∼25 to ∼50 nm. It is shown from the SEM images that when the pillar spacing is 20 μm, the horizontal ACNTs are rather straight, while for the reduced spacing of 15, 10, and 6 μm, they bend upward, some extents of disorder of ACNT growth appear due to space hindrance, and the extents of bending and disorder increase with the decrease of pillar spacing.
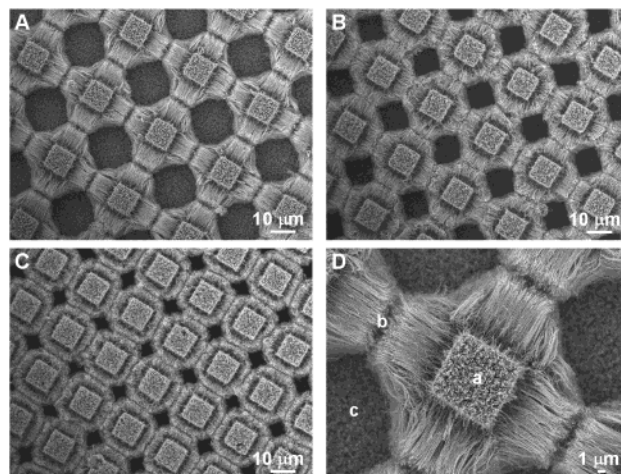
Figure 1. SEM images of three-dimensional anisotropic ACNT microstructures constructed by the CVD method on silicon templates with a well-defined quadrate micropillar array. (A, B, and C) Periodic ACNT arrays with pillar spacings of 20, 15, and 10 μm, respectively. (D) Magnified image of mutually orthogonal ACNT arrays on a single silicon pillar of image (A). (a) Vertical ACNT array on the top face of a pillar; (b) horizontal ACNT array grown from the side faces of the pillar; and (c) ACNTs grown from the bottom of the templates.

The wettability of the untreated, vinyltrimethoxysilane (VTMS) and (2-(perfluorooctyl)ethyl)trimethoxysilane (FETMS) modified anisotropic ACNT films was investigated. As we have reported before,[6] the ACNT films (both untreated and fluorinated) without anisotropic structures exhibited superhydrophobic properties, which were determined by the vertically aligned structure and the very large proportion of air trapping. The water CAs for the untreated and VTMS modified ACNT films on flat substrates are 158 ± 1.5° and 149.3 ± 0.8°, respectively. However, the wettability of the untreated and VTMS modified anisotropic ACNT films shows great dependences on the pillar spacing of templates. For untreated films with a pillar spacing of 20, 15, 10, and 6 μm, the equilibrium CAs are 22.2 ± 4.1°, 142.9 ± 1.8°, 25.5 ± 2.7°, and 10 ± 1.5°, respectively, while those for the VTMS modified films with pillar spacings of 20, 15, 13, 10, and 6 μm are 21.2 ± 1.5°, 153.3 ± 3.3°, 154.9 ± 1.5°, 27.2 ± 1.8°, and 20.8 ± 2.3°, respectively. These results indicate that the films can change from very hydrophilic to very hydrophobic by simply varying the structural parameter. Furthermore, we have also observed that the spreading behaviors of water drops on the three hydrophilic films with different pillar spacings were also different. The water drops spread rapidly on films of 10 and 6 μm, while for that of 20 μm, the water drop could stand on the film for several seconds before its rapid spreading. The water spreading behaviors on the VTMS modified anisotropic ACNT films are shown in Figure 2, with a comparison of ACNT film on a flat substrate. However, when modified with FETMS, films with pillar spacings of 20, 15, 10, and 6 μm all
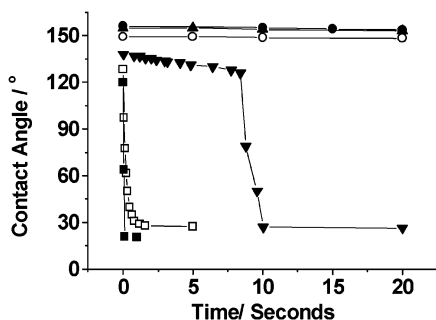
Figure 2. Water spreading behaviors on anisotropic ACNT films with pillar spacings of ■, 6 μm; □, 10 μm; ●, 13 μm; ▲, 15 μm; ▼, 20 μm, and on O, flat silicon substrate.

show superhydrophobic properties with water CAs of 162.7 ± 1.5°, 159.6 ± 0.9°, 154.2 ± 1.8°, and 153.8 ± 2.6°, respectively.

As people[1a,10b] generally consider that surface structures make the hydrophilic surfaces more hydrophilic, and the hydrophobic surfaces more hydrophobic, therefore, the above phenomena cannot be explained by the traditional Wenzel equation[11] describing the influence of surface roughness or by the modified Cassie equation[12] describing the influence of air trapping by the rough surface. We consider that it is due to the three-dimensional anisotropy, the coexistence of horizontal and vertical ACNT microstructures.

To determine the role of horizontal ACNT arrays, we etched the flat silicon surface by a YAG laser with wavelength of 532 nm to create an array of straight parallel grooves, which provided an anisotropic nature as horizontal ACNT arrays. We also modified the grooved surface with VTMS and studied its influence on wettability. The water drop spread immediately along the direction of grooves when it was dropped onto the surface. As indicated by J. Bico et al., for a rough surface, when the CA of the flat surface is smaller than a critical value that is governed by the surface structure, imbibition of the liquid by the rough surface will occur, which is a result of the capillary effect.[10] Therefore, for the microgroove array on silicon substrate, when the intrinsic CA of VTMS coated surface is smaller than the critical CA for water imbibition, the capillary effect will happen and water will spread along the groove direction.

The geometry of the horizontal ACNT array is just like a well-grooved surface. Therefore, for the untreated and VTMS modified ACNT films, the horizontal ACNT arrays can provide a hydrophilic contribution to the film (the intrinsic CAs of flat surfaces are relatively small; for flat graphite and VTMS modified silicon surfaces, CAs are 86°[13] and 78.1 ± 1.8°, respectively). However, the vertically aligned structure and large proportion of air trapping determine the superhydrophobic property of the vertical ACNT arrays. So the abnormal wetting behaviors of VTMS coated anisotropic ACNT films can be explained as follows: For ACNT films with pillar spacings of 10 and 6 μm, because of the large extent of upward bending of horizontal ACNTs due to the space hindrance during the process of CVD, the water drop can easily come into contact with them and quickly spread horizontally. However, for films of 13, 15, and 20 μm, it is not easy for the water drop to contact with the horizontal ACNTs which are relatively very straight and the vertical ACNT arrays on the top of silicon pillars can provide a hydrophobic force supporting the water drop, which is proportional to the quantity per unit area. The hydrophobic force for films of 13 and 15 μm periodicity is larger

than that for a film of 20 μm, for the former has more vertical ACNT arrays per unit area. Therefore, the hydrophobic force for the ACNT film of 20 μm may be insufficient to support the water drop, and thus the drop would slowly descend before its rapid spreading when it comes into contact with the horizontal ACNTs. For the FETMS modified ACNT films, because the intrinsic CA of the carbon nanotube surfaces is large (water CA for FETMS modified flat silicon surface: 111.9 ± 2.1°), the imbibition effect will not occur and water cannot spread along the direction of the ACNT array. Therefore, all ACNT films exhibited superhydrophobic properties.

In conclusion, we fabricated three-dimensional anisotropic ACNT films on patterned silicon templates and studied their influence on wettability. The results show that ACNT arrays of different orientations can play different roles in controlling the surface wettability. Anisotropic microstructures can bring about better control over the surface wettability. The ACNT films can be both very hydrophilic (CA < 30°) and superhydrophobic (CA > 150°) when the spacing between micropillars of silicon templates is varied, which cannot be explained by traditional Wenzel or Cassie's equations. It may have great significance on the study of wettability and relevant applications.

Supporting Information Available: Experimental details, optical micrograph of silicon templates, SEM images of treated and untreated ACNT films, XPS results, and photographs for contact angle measurements (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Shibuichi, T. S.; Onda, T.; Satoh, N.; Tsujii, K. *J. Phys. Chem.* **1996**, *100*, 19512−19517. (b) Tsujii, K.; Yamamoto, T.; Onda, T.; Shibuichi, S. *Angew. Chem., Int. Ed.* **1997**, *36*, 1011. (c) Erbil, H. Y.; Demirel, A. L.; Avci, Y.; Mert, O. *Science* **2003**, *299*, 1377−1380. (d) Öner, D.; McCarthy, T. J. *Langmuir* **2000**, *16*, 7777−7782. (e) Yoshimitsu, Z.; Nakajima, A.; Watanabe, T.; Hashimoto, K. *Langmuir* **2002**, *18*, 5818−5822.

(2) Herminghaus, S. *Europhys. Lett.* **2000**, *52*, 165−170.

(3) (a) Barthlott, W.; Neinhuis, C. *Planta* **1997**, *202*, 1−8. (b) Neinhuis, C.; Barthlott, W. *Ann. Bot.* **1997**, *79*, 667−677.

(4) (a) Feng, L.; Li, S.; Li, Y.; Li, H.; Zhang, L.; Zhai, J.; Song, Y.; Liu, B.; Jiang, L.; Zhu, D. *Adv. Mater.* **2002**, *14*, 1857−1860. (b) Feng, L.; Li, S.; Li, H.; Zhai, J.; Song, Y.; Jiang, L.; Zhu, D. *Angew. Chem., Int. Ed.* **2002**, *41*, 1221−1223. (c) Feng, L.; Song, Y.; Zhai, J.; Liu, B.; Xu, J.; Jiang, L.; Zhu, D. *Angew. Chem., Int. Ed.* **2003**, *42*, 800−802.

(5) Dujardin, D.; Ebbesen T. W.; Hiura, H.; Tanigaki, K. *Science* **1994**, *265*, 1850−1852.

(6) (a) Li, H.; Wang, X.; Song, Y.; Liu, Y.; Li, Q.; Jiang, L.; Zhu, D. *Angew. Chem., Int. Ed.* **2001**, *40*, 1743−1746. (b) Li, S.; Li, H.; Wang, X.; Song, Y.; Liu, Y.; Lei, J.; Zhu, D. *J. Phys. Chem. B* **2002**, *106*, 9274−9276.

(7) (a) Ren, Z. F.; Huang, Z. P.; Xu, J. W.; Wang, J. H.; Bush, P.; Siegal, M. P.; Prevencio, P. N. *Science* **1998**, *282*, 1105−1107. (b) Wang, X. B.; Liu, Y. Q.; Zhu, D. B. *Appl. Phys. A* **2000**, *71*, 347−348.

(8) Wei, B. Q.; Vajtai, R.; Jung, Y.; Ward, J.; Zhang, R.; Ramanath, G.; Ajayan, P. M. *Nature* **2002**, *416*, 495−496.

(9) (a) Wu, H.; Odom, T. W.; Whitesides, G. M. *J. Am. Chem. Soc.* **2002**, *124*, 7288−7289. (b) Wu, M.-H.; Park, C.; Whitesides, G. M. *Langmuir* **2002**, *18*, 9312−9318. (c) Love, J. C.; Wolfe, D. B.; Jacobs, H. O.; Whitesides, G. M. *Langmuir* **2001**, *17*, 6005−6012.

(10) (a) Bico, J.; Tord eux, C.; Quéré, D. *Europhys. Lett.* **2001**, *55*, 214−220. (b) Bico, J.; Thiele, U.; Quéré, D. *Colloids Surf., A* **2002**, *206*, 41−46.

(11) Wenzel, R. N. *Ind. Eng. Chem.* **1936**, *28*, 988−994.

(12) Cassie, A. B. D.; Baxter, S. *Trans. Faraday Soc.* **1944**, *40*, 546−561.

(13) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*, 6th ed.; Wiley: New York, 1997; p 365.

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