Superhydrophobic Nanofibers

Creation of a Superhydrophobic Surface from an Amphiphilic Polymer**

Lin Feng, Yanlin Song, Jin Zhai, Biqian Liu, Jian Xu, Lei Jiang,* and Daoben Zhu*

Superhydrophobic surfaces, with a water contact angle (CA) greater than 150°, have attracted great interest for both fundamental research and practical applications.[1] Conventionally, superhydrophobic surfaces are fabricated by combining appropriate surface roughness with low-surface-energy materials (hydrophobic materials, CA greater than 90°).[2–18] It has been commonly acknowledged that it is impossible to obtain superhydrophobic surfaces from amphiphilic materials. Herminghaus reported that it was theoretically possible to construct a water-repellent surface from a material with a CA less than 90°,[19] however, this has never been proven by experimental results. Herein, we report the creation of a superhydrophobic surface (CA = 171.2°) consisting of nanofibers fabricated from amphiphilic poly(vinyl alcohol) (PVA). The PVA nanofibers were prepared using the template-based extrusion method,[2] namely, the extrusion of a PVA precursor solution through a template composed of a nanoporous anodic aluminum oxide membrane. This phenomenon is attributable to the rearrangement of PVA molecules during the initial stage of the extrusion process, which is accompanied by the reorientation of hydrophobic groups ($-CH_2-$) at the air/solid interface. This method can be extended to prepare superhydrophobic surfaces using many types of materials.

The templates of anodic aluminum oxide membranes were prepared by a published route,[20] with pore diameters in the range of 20–500 nm. Control of the diameters and densities of the prepared PVA nanofibers can be easily achieved by using templates with different pore diameters. In the present study, a template with an average pore diameter of 68.7 nm, and a density of approximately 1.23×10^{10} pores per square centimeter was used. Figure 1 a shows a typical scanning electron microscopy (SEM) image of the substrate, as viewed from above, coated with well-spaced PVA nanofibers. The average diameter of the nanofiber tips is 72.1 nm, which is in good agreement with the pore diameter of the template. The average interfiber distance is 361.8 nm, while the nanofiber density is approximately 7.07×10^8 fibers per square centimeter. Figure 1 b shows a cross-sectional SEM image of the as-synthesized PVA nanofibers, which shows that the length of the fibers is approximately 14.3 μm. The ends of the aligned nanofibers are very sharp, although there are often some aggregations along their length.

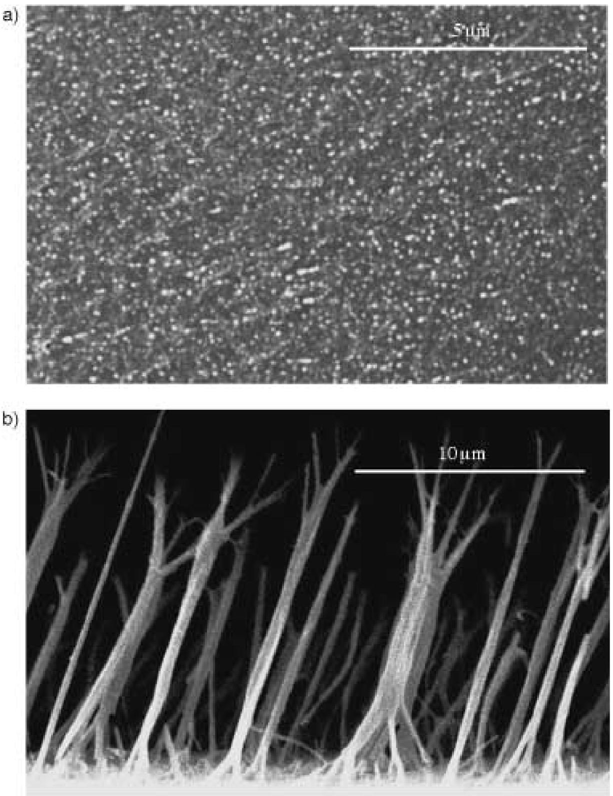

Figure 1. a) SEM image of a substrate coated with PVA nanofibers, as viewed from above; b) cross-sectional SEM image of the as-synthesized PVA nanofibers.

PVA is an amphiphilic material, with a water contact angle on native PVA films with smooth surfaces of only 72.1 ± 1.1° (Figure 2 a). However, the PVA nanofibers reported herein have rough surfaces, and can be shown to be superhydrophobic. Figure 2 b shows the shape of a water droplet on the surface of a PVA nanofiber, where the water contact angle is 171.2 ± 1.6°. These results confirm that nanostructure has a profound effect on superhydrophobic properties.

There have been numerous reports over the past 60 years describing the preparation of superhydrophobic surfaces using hydrophobic materials ($\theta > 90°$).[2–18] For example, Onda et al.[7] have demonstrated a superhydrophobic fractal surface formed from an alkylketene dimer (AKD, $\theta = 109°$), while Öner and McCarthy reported the preparation of a rough surface that exhibited superhydrophobic properties, through the silanization of silicon wafers ($\theta_A = 107°$, $\theta_R = 109°$; θ_A and θ_R are the advancing and receding contact angles, respectively).[8] We have also prepared a superhydrophobic surface of aligned nanofibers using polyacrylonitrile (PAN, $\theta = 100.8°$) as the precursor.[2] In addition, there have been many other reports concerning the preparation of

---

[*] Prof. J. Xu, Prof. L. Jiang, Dr. L. Feng, Prof. Y. Song, Dr. J. Zhai, B. Liu, Prof. D. Zhu
Center of Molecular Sciences
Institute of Chemistry, Chinese Academy of Sciences
Beijing 100080 (P. R. China)
Fax: (+86) 10-8262-7566
E-mail: jxu@infoc3.icas.ac.cn
jianglei@infoc3.icas.ac.cn

[**] The authors thank the State Key Project for Fundamental Research (G1999064504) and the Special Research Foundation of the National Nature Science Foundation of China (29992530 and 20125102) for continuing financial support.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

© 2003 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 0044-8249/03/11507-0824 $ 20.00+.50/0

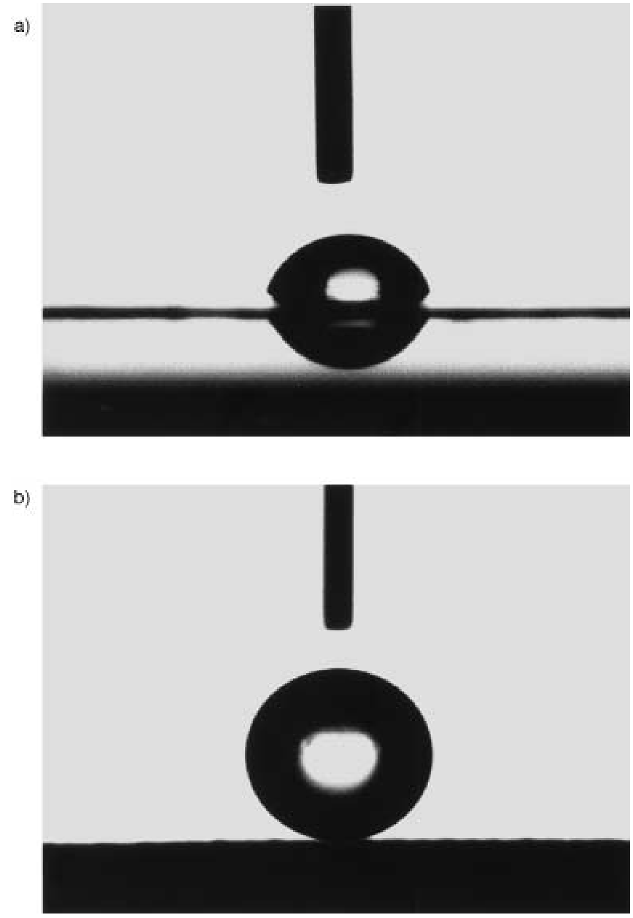

Figure 2. Pictures showing the water contact angles of a native PVA film with a smooth surface (a) and the synthesized PVA nanofibers with a rough surface (b).

superhydrophobic surfaces that have been modified by hydrophobic materials, such as polytetrafluoroethylene (PTFE, $\theta = 108°$)[9,10] and various fluoroalkylsilanes (FASs, $\theta = 107°$).[11–18] Wenzel[3] first derived Equation (1) to show

$$\cos\theta_r = r\cos\theta \qquad (1)$$

the relationship between the contact angle of a liquid on a smooth surface (θ) and on a rough surface (θ_r) made of the same material, where r is the roughness factor.

This equation indicates that a rough surface can be superhydrophobic when the surface is composed of hydrophobic materials. From this point of view, it is very surprising that superhydrophobic surfaces can be synthesized from an amphiphilic polymer. We know that PVA is an amphiphilic molecule composed of both hydrophilic (−OH) and hydrophobic ($-CH_2-$) groups. It has been proposed that when the precursor of the PVA solution is compressed into the nanometer-scale pores of the template, strong orientation of the PVA molecules can be induced, and intermolecular hydrogen bonds are created.[21–25] Furthermore, most of the hydrophobic groups may be exposed at the surface, which would minimize the free energy of the system. Figure 3 represents the possible conformation of PVA molecules at the air/solid interface, where $-CH_2-$ groups are present at the

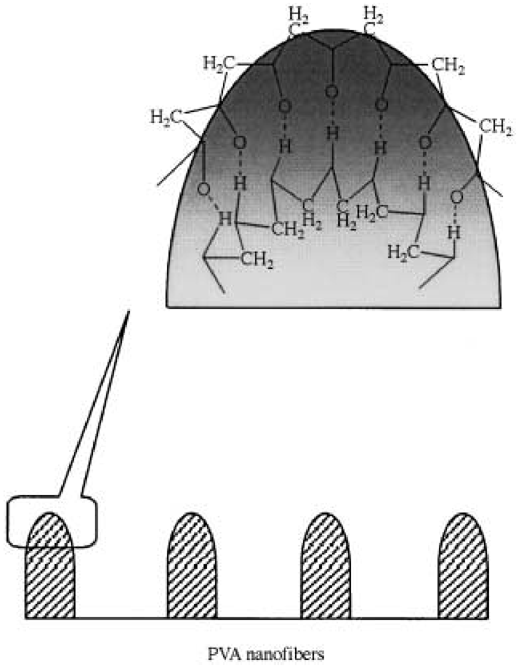

Figure 3. Possible conformation modes of the PVA molecules at the air/solid interface.

surface, and hydrogen bonds are formed in the interior. It has been shown that angle-resolved X-ray photoelectron spectroscopy (XPS) can provide useful information about the conformation of the polymer at the surface.[26] Figure 4a shows the results of an angle-resolved XPS study of the PVA nanofiber/air interface, where the detection angles are 5, 30, 60, and 90°, respectively. Figure 4b shows the effect of varying the detection angle on the ratio of carbon (both $-CH_2-$ and $>CH-$) to oxygen atoms that were detected. The ratio of $-CH_2-$:O decreases while that of $>CH-$:O increases as the detection angle is increased. Since the detected thickness will be greater upon increasing detection angle, it can be deduced that the PVA backbone at the surface is mainly composed of $-CH_2-$ groups. As a result, the surface free energy of the PVA nanofibers decreases. In contrast, angle-resolved XPS results of native PVA films (See Supporting Information) indicate that the content of hydrophobic and hydrophilic groups is almost the same in the surface as in the interior, which is a result of the free arrangement of PVA molecules at the initiation of the spin-coating process. These results demonstrate that the conformation of molecules at the surface plays the most important role in surface activity.

In conclusion, a superhydrophobic surface of aligned PVA nanofibers has been prepared, even though the PVA molecule is inherently amphiphilic. We believe that a reorientation of the PVA molecules occurs when they are confined to a nanosized space. Since the hydrophobic groups in this case are located at a rough surface, the surface free energy decreases. This is the first example of an amphiphilic material being used to prepare a superhydrophobic surface. The method might successfully be used to prepare superhydrophobic surfaces from a wide variety of materials.

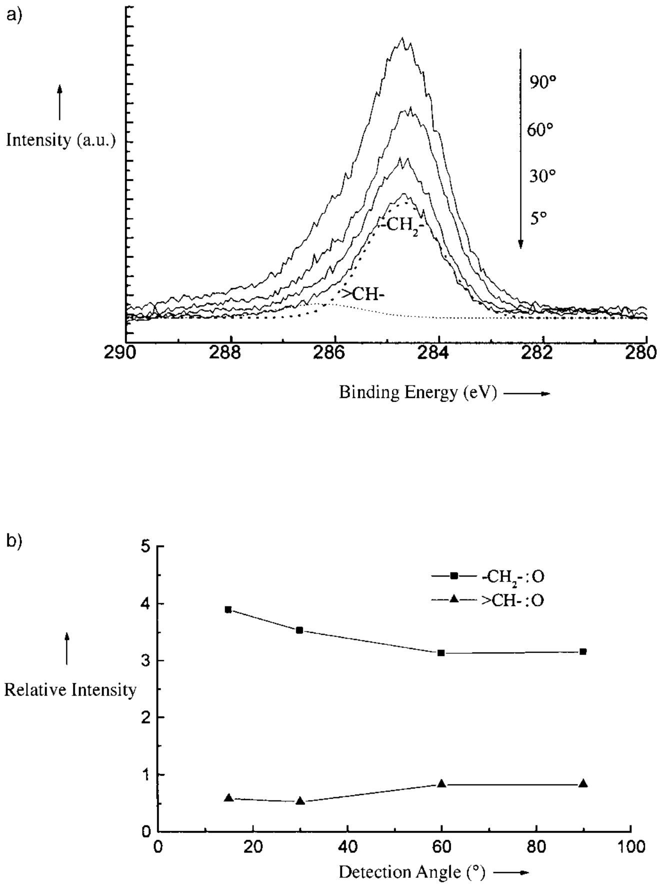

Figure 4. a) X-ray photoelectron spectra illustrating the dependence of the detection angle for the C$_{1s}$-core spectra of PVA nanofibers (—— real XPS spectra; ----- fit to a Gauss–Lorenz function); b) chart showing the relation between the $-CH_2-$:O and $>CH-$:O ratio to the detection angle.

Experimental Section

The precursor was prepared by dissolving polyvinylalcohol (8.823 g, atactic, $M_W = 1750 \pm 15$) in stirred deionised and deaerated water (50 mL) at 90 °C, which formed a 15 wt % aqueous polyvinylalcohol solution. Aqueous solutions of sodium sulfate (400 g L^{-1}) were prepared for use as the solidifying solution. A commercial anodic aluminum oxide membrane with a pore diameter of 68.7 nm was used as the template. The synthesis and characterization process were the same as that reported in Ref. [2]. The native PVA film was prepared by spin-coating the PVA solution on a clean glass slide. XPS results were recorded using a VG ESCALAB MKII spectrometer with an Al$_{K\alpha}$ monochromatic X-ray source.

Received: July 23, 2002
Revised: November 4, 2002 [Z19807]

---

[1] a) L. Jiang, R. Wang, B. Yang, T. J. Li, D. A. Tryk, A. Fujishima, K. Hashimoto, D. B. Zhu, *Pure Appl. Chem.* **2000**, *72*, 73; b) P. Aussillous, D. Quéré, *Nature* **2001**, *411*, 924; c) A. Nakajima, K. Hashimoto, T. Watanabe, *Monatsh. Chem.* **2001**, *132*, 31; d) L. Feng, S. H. Li, Y. S. Li, H. J. Li, L. J. Zhang, J. Zhai, Y. L. Song, B. Q. Liu, L. Jiang, D. B. Zhu, *Adv. Mater.* **2003**, in press.

[2] L. Feng, S. H. Li, H. J. Li, J. Zhai, Y. L. Song, L. Jiang, D. B. Zhu, *Angew. Chem.* **2002**, *114*, 1269; *Angew. Chem. Int. Ed.* **2002**, *41*, 1221.

[3] R. N. Wenzel, *Ind. Eng. Chem.* **1936**, *28*, 988.

[4] A. B. D. Cassie, *Discuss. Faraday Soc.* **1948**, *3*, 11.

[5] G. Wolansky, A. Marmur, *Langmuir* **1998**, *14*, 5292.

[6] P. S. Swain, R. Lipowsky, *Langmuir* **1998**, *14*, 6772.

[7] a) T. Onda, S. Shibuichi, N. Satoh, K. Tsujii, *Langmuir* **1996**, *12*, 2125; b) S. Shibuichi, T. Onda, N. Satoh, K. Tsujii, *J. Phys. Chem.* **1996**, *100*, 19512; c) S. Shibuichi, T. Yamamoto, T. Onda, K. Tsujii, *J. Colloid Interface Sci.* **1998**, *208*, 287.

[8] D. Öner, T. J. McCarthy, *Langmuir* **2000**, *16*, 7777.

[9] a) W. Chen, A. Y. Fadeev, M. C. Heieh, D. Öner, J. Youngblood, T. J. McCarthy, *Langmuir* **1999**, *15*, 3395; b) J. P. Youngblood, T. J. McCarthy, *Macromolecules* **1999**, *32*, 6800.

[10] S. Veeramasuneni, J. Drelich, J. D. Miller, G. Yanauchi, *Prog. Org. Coat.* **1997**, *31*, 265.

[11] a) A. Nakajima, K. Abe, K. Hashimoto, T. Watanabe, *Thin Solid Films* **2000**, *376*, 140; b) A. Nakajima, C. Saiki, K. Hashimoto, T. Watanabe, *J. Mater. Sci. Lett.* **2001**, *20*, 1975; c) A. Nakajima, A. Fujishima, K. Hashimoto, T. Watanabe, *Adv. Mater.* **1999**, *11*, 1365.

[12] A. Hozumi, O. Takai, *Thin Solid Films* **1997**, *303*, 222.

[13] a) K. Tadanaga, N. Katata, T. Minami, *J. Am. Ceram. Soc.* **1997**, *80*, 1040; b) K. Tadanaga, N. Katata, T. Minami, *J. Am. Ceram. Soc.* **1997**, *80*, 3213; c) K. Tadanaga, K. Kitamuro, J. Morinaga, Y. Kotani, A. Matsuda, T. Minani, *Chem. Lett.* **2000**, 864.

[14] J. Bico, C. Marzolin, D. Quéré, *Europhys. Lett.* **1999**, *47*, 220.

[15] Y. Wu, H. Sugimura, Y. Inoue, O. Takai, *Chem. Vap. Deposition* **2002**, *8*, 47.

[16] H. Tada, H. Nagayama, *Langmuir* **1995**, *11*, 136.

[17] T. Nishino, M. Meguro, K. Nakamae, M. Matsushita, Y. Ueda, *Langmuir* **1999**, *15*, 4321.

[18] H. J. Li, X. B. Wang, Y. L. Song, Y. Q. Liu, Q. S. Li, L. Jiang, D. B. Zhu, *Angew. Chem.* **2001**, *113*, 1793; *Angew. Chem. Int. Ed.* **2001**, *40*, 1743.

[19] S. Herminghaus, *Europhys. Lett.* **2000**, *52*, 165.

[20] H. Masuda, K. Fukuda, *Science* **1995**, *268*, 1466.

[21] G. Hummer, J. G. Rasaiah, J. P. Noworyta, *Nature* **2001**, *414*, 188.

[22] K. Koga, G. T. Gao, H. Tanaka, X. C. Zeng, *Nature* **2001**, *412*, 802.

[23] B. Zhao, J. S. Moore, D. J. Beebe, *Science* **2001**, *291,* 1023.

[24] J. H. K. Ky Hirschberg, L. Brunsveld, A. Ramzi, J. A. J. M. Vekemans, R. P. Sijbesma, E. W. Meijer, *Nature* **2000**, *407*, 167.

[25] N. Nandi, B. Bagchi, *J. Am. Chem. Soc.* **1996**, *118*, 11208.

[26] a) J. Xu, L. H Shi, M. L. Ye, *J. Polym. Sci. Part B* **1997**, *35*, 827; b) J. Xu, L. H Shi, M. L. Ye, *J. Polym. Sci. Part B* **1999**, *37*, 2297; c) L. Li, C. M. Chan, L. T. Weng, *Polymer* **1998**, *39*, 2355.