1a (55.0 mg, 0.26 mmol) in degassed $ClCH_2CH_2Cl$ (1.6 mL) was added to the mixture. The reaction mixture was stirred at 65 °C for 18 h. After removal of the solvent, the residue was purified by column chromatography on silica gel to afford **3a** (0.16 mmol, 62%) along with **2a** (0.034 mmol, 13%) and **2a′** (0.015 mmol, 6%). Selected spectral data of **3a**: IR (neat): $\tilde{\nu} = 3024, 2934, 1708, 1654, 1496, 1456\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.67-1.82$ (m, 2H), 2.03–2.18 (m, 2H), 2.31–2.76 (m, 6H), 3.63 (m, 1H) 5.23 (dddd, $J = 11.1, 3.2, 2.0, 2.0$ Hz, 1H), 5.76 (dddd, $J = 11.1, 6.7, 6.7, 1.9$ Hz, 1H), 7.16–7.31 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 21.8$, 29.4, 31.8, 33.2, 44.0, 48.4, 125.7, 125.8, 126.8, 128.2, 128.3, 128.4, 131.2, 141.8, 208.9; EI-LRMS: m/z: 214 $[M^+]$, 123, 110, 104, 91; EI-HRMS calcd for $C_{15}H_{18}O$ 214.1358, found 214.1346. **2a**: IR (neat): $\tilde{\nu} = 2960, 2854, 1740, 1453, 1149\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.68-1.88$ (m, 2H), 2.00–2.42 (m, 6H), 2.68–2.76 (m, 3H), 5.47 (dd, $J = 15.6, 6.1$ Hz, 1H), 5.60 (dt, $J = 15.6, 6.3$ Hz, 1H), 7.17–7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 20.7$, 29.8, 34.4, 35.7, 37.7, 52.2, 125.8, 126.6, 128.2, 128.2, 128.4, 128.4, 132.4, 141.8, 218.9; EI-LRMS: m/z: 214 $[M^+]$, 123, 110, 105, 91; EI-HRMS calcd for $C_{15}H_{18}O$ 214.1358, found 214.1362. **2a′**: IR (neat): $\tilde{\nu} = 2924, 2856, 1718, 1648, 1096\ cm^{-1}$; ^1H NMR (400 MHz $CDCl_3$): $\delta = 1.81$ (tt, $J = 7.6, 7.6$ Hz, 2H), 1.93 (dddd, $J = 7.6, 7.6, 7.6, 7.6$ Hz, 2H), 2.18 (dt, $J = 7.6, 7.6$, Hz, 2H), 2.34 (dd, $J = 7.6, 7.6$ Hz, 2H), 2.52–2.57 (m, 2H), 2.67 (t, $J = 7.6$ Hz, 2H), 6.57 (dddd, $J = 7.6, 7.6, 2.7, 2.7$ Hz, 1H), 7.15–7.32 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 20.0$, 26.9, 29.3, 30.1, 35.6, 38.7, 125.7, 128.1, 128.1, 128.2, 128.2, 135.4, 137.4, 141.5, 206.7; EI-LRMS: m/z: 214 $[M^+]$, 130, 123, 110, 91; EI-HRMS calcd for $C_{15}H_{18}O$ 214.1358, found 214.1365.

Received: December 3, 2001 [Z18311]

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Super-Hydrophobic Surface of Aligned Polyacrylonitrile Nanofibers[**]

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The wettability of solid surfaces is a very important property that is governed by both the chemical composition and the geometrical microstructure of the surface.[1–3] Super-hydrophobic surfaces, with a water contact angle (CA) greater than 150°, have attracted much interest because of potential practical applications.[4] Conventionally, super-hydrophobic surfaces have been produced mainly in two ways: One is to create a rough surface (e.g., with a fractal structure)[5] and the other is to modify the surface with materials of low surface free energy, such as fluorinated or silicon compounds.[6]

Recently, we have succeeded in preparing densely packed aligned carbon nanotubes (ACNTs).[7] The water contact angle on this nanostructured ACNT film was $(158.5 \pm 1.5)^\circ$, that is, the ACNT film has super-hydrophobic properties. The water contact angle increased to $(171 \pm 0.5)^\circ$ after modification with a fluoroalkysilane. This high value is believed to be due to the nanostructure and the presence of fluoroalkysilane groups. Here we describe a novel method to synthesize aligned polyacrylonitrile (PAN) nanofibers, which have a nanostructure similar to that of the ACNTs but a much lower density. The surface of the as-synthesized PAN nanofibers shows super-hydrophobicity ($CA = (173.8 \pm 1.3)^\circ$). This is the first report of a water contact angle greater than 170° without any modification of the surface. We also note that the density of the aligned nanostructures is very important for the super-hydrophobicity.

Compared with other template syntheses,[8–10] the method used here to synthesize PAN nanofibers is very simple. Only extrusion of the PAN precursor solution into the solidifying solution under pressure is necessary.[11] The template was an anodic aluminum oxide membrane, prepared according to ref. [12], with a diameter of 13 mm, a thickness of 60 μm, and a porosity consisting of an array of parallel, straight channels. Aligned nanofibers with different diameters and densities can be easily obtained by using templates with different pore diameters, and the alignment process can be applied to different polymer precursors such as poly(vinyl alcohol), polystyrene, polyesters, and polyamides.

Figure 1a shows a scanning electron microscopic (SEM) image of the surface of the as-prepared anodic aluminum oxide membrane used as template. The pores are arranged in a regular hexagonal pattern with an average pore diameter of

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[**] The authors thank the State Key Project Fundamental Research (G1999064504), the Special Research Foundation of the National Nature Science Foundation of China (29992530, 20/25/02) for continuing financial support.

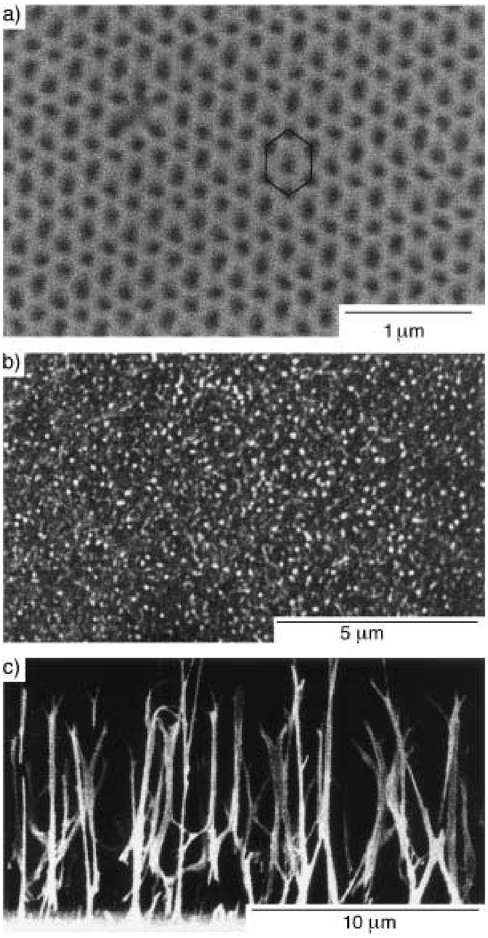

Figure 1. SEM images of a) surface of the as-prepared anodic aluminum oxide membrane; b) surface of the PAN nanofibers; c) cross-sectional view of the as-synthesized PAN nanofibers.

about 102.4 nm and a pore density of about 6.43 × 10^9 pores per square centimeter. Figure 1 b, a typical SEM image of the surface of PAN nanofibers, shows that aligned PAN nanofibers with end tips were obtained. The average diameter of the nanofiber tips is about 104.6 nm, which is in good agreement with the pore diameter of the template. The average interfiber distance was about 513.8 nm, and the density of the PAN nanofibers was about 2.78 × 10^8 fibers per square centimeter. Figure 1 c shows the cross-sectional SEM image of the as-synthesized PAN nanofibers; the length of the aligned fibers is about 10.7 μm.

Figure 1 b also shows that the surface of the PAN nanofibers is rough enough that air can be present in the troughs between individual nanofibers. Therefore, the surface of the nanofibers can be regarded as a composite surface consisting of nanofibers and air. Since surface roughness is very important to hydrophobicity,[5, 13–15] the hydrophobicity of these PAN nanofibers was investigated. Figure 2 a shows the shape of a water droplet on the surface of our PAN nanofibers; the water contact angle is $(173.8 \pm 1.3)^\circ$. In contrast, a native PAN film with a smooth surface, prepared by coating the PAN precursor solution onto plane glass, had a water contact angle of only $(100.8 \pm 0.6)^\circ$ (Figure 2 b). That is, the PAN nanofibers with a rough surface are super-hydrophobic, while the native PAN film with a smooth surface is merely hydrophobic. These results reveal that the nanostructure is responsible for the super-hydrophobicity. Formation of a nanostructured super-hydrophobic surface without any modification by materials of low surface free energy has not previously been reported. A possible explanation for this result is that, when nanostructured surface roughness develops, the molecules rearrange so that the number of hydrophobic groups on the surface increases. Therefore, the surface of the PAN nanofibers is super-hydrophobic but oleophilic (the contact angle for rapeseed oil is $(26.7 \pm 0.6)^\circ$). In addition, the advancing and receding angles for the PAN nanofibers are (191.2 ± 1.3) and $(136.7 \pm 0.8)^\circ$, respectively.

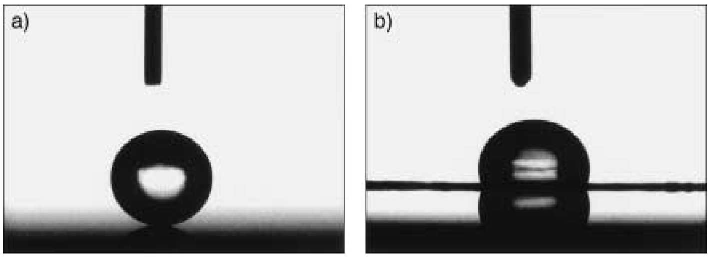

Figure 2. Shapes of water droplets on a) the PAN nanofibers with a rough surface; b) the native PAN film with smooth surface.

To thoroughly understand the hydrophobicity of the PAN nanofiber surface, theoretical considerations are necessary. The contact angle on a composite surface (θ_r) can be expressed by Equation (1).[16] Here θ_r and θ are the contact

$$\cos\theta_r = f_1 \cos\theta - f_2 \tag{1}$$

angles on the PAN nanofibers with a rough surface and on the native PAN film with a smooth surface, respectively; f_1 and f_2 are the fractional interfacial areas of the PAN nanofibers and of the air in the troughs between individual nanofibers, respectively (i.e., $f_1 + f_2 = 1$). It is easy to deduce from this equation that increasing f_2 increases θ_r, that is, the fraction of air in the surface is important to the super-hydrophobicity.

According to Equation (1), the f_2 value of the PAN nanofiber surface is estimated to be 0.967 from the contact angles obtained from Figure 2, which indicates that the fraction of air in the surface is very high. Interestingly, the f_2 value in this case is even larger than that of the modified ACNT film (0.94).[7] In comparison, the obvious difference is that the density of the PAN nanofibers (2.78 × 10^8 fibers per cm^2) is much lower than that of the ACNTs (2.43 × 10^{10} tubes per cm^2). Therefore, the density is also important for super-hydrophobicity. Decreasing the density (i.e., increasing the interfiber distance) should improve the water repellency. To confirm this assumption, further experiments are required.

Figure 3 shows a simple idealized model of the surface structure of the PAN nanofibers. As-

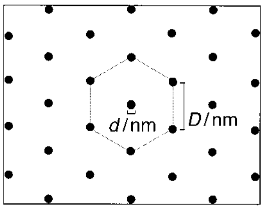

Figure 3. Model structure proposed for the surface of PAN nanofibers; d is the average tip diameter and D the average interfiber distance of the nanofibers.

suming that the nanofibers are arranged in a regular hexagonal array like the template, with an average tip diameter of d and an interfiber distance of D, the relationship of f_2, d, and D can be described simply by Equation (2).[17]

$$f_2 = 1 - k\left(\frac{d}{D}\right)^2 \qquad (2)$$

According to this equation, f_2 is calculated to be about 0.962 from the values of d and D extracted from Figure 1 b. This f_2 value is in good accordance with that of 0.967 estimated from Equation (1), and this indicates that Equation (2) is valid. In fact, the tip diameter of the nanofibers can be regarded as a constant, because it corresponds to the pore diameter of the template. Therefore, the interfiber distance D is the essential factor that affects the f_2 value. It is easy to conclude from Equation (2) that the f_2 value will be much larger and closer to unity when D increases, that is, increasing the interfiber distance will increase the water contact angle on the nanofiber surface. This conclusion is consistent with the experimental results.

In conclusion, aligned polyacrylonitrile nanofibers were synthesized by a simple extrusion process with an anodic aluminum oxide membrane as the template. The surface of the synthesized nanofibers, without any modification by materials of low surface energy, proved to be super-hydrophobic. It is believed that not only the nanostructure of the nanofibers but also their lower density contributes to the very large fraction of air in the surface, which is essential to the super-hydrophobicity. This may provide a new method of controlling the wettability of nanostructured surfaces by changing the density of the aligned fibers.

Experimental Section

Synthesis of the PAN nanofibers: polyacrylonitrile (10.976 g, $M = 120000$) was dissolved in dimethylformamide (DMF, 50 mL) with stirring at 70 °C to form an 18 wt% precursor solution. A mixture of 40 wt% DMF and 60 wt% deaerated Milli-Q water was used as the solidifying solution. An as-prepared anodic aluminum oxide membrane with a pore diameter of about 102.4 nm was used as template. The PAN nanofibers were synthesized by the following process: 1) Placing a clean and dry template onto a compact polytetrafluoroethylene film and pouring the precursor onto the template. 2) Extruding the precursor into the solidifying solution under water-pump pressure (0.1 MPa). Thus, PAN nanofibers were formed in the solidifying solution. 3) Removing the solidified PAN nanofibers and washing the completely solidified surface with deioned water several times and then drying in air. 4) Collecting the used template and washing it with deioned water and acetone in turn several times, after which the template can be recycled.

SEM images were obtained with a Hitachi S-530 scanning electron microscope at 25 kV. Contact angles were measured on a dataphysics OCA20 contact-angle system at ambient temperature. Water droplets (about 3.8 μL) were dropped carefully onto the PAN nanofiber surface and on the native PAN film. The average contact angle value was obtained by measuring at five different positions of the same sample.

Received: September 18, 2001
Revised: December 28, 2001 [Z17929]

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[17] If each hexagon composed of seven nanofibers is a unit, then f_2 can be regarded as being equal to the open area and expressed as follows:

$$f_2 = \frac{3(D\,D\sin 60^{\circ}) - 3\pi\left(\frac{d}{2}\right)^2}{3(D\,D\sin 60^{\circ}) = 1 - \frac{\pi}{2\sqrt{3}}}\left(\frac{d}{D}\right)^2 = 1 - k\left(\frac{d}{D}\right)^2.$$

$$k = \text{const.} = \frac{\pi}{2\sqrt{3}}.$$