Directional Transport of Polymer Sheet and a Microsphere by a Rationally Aligned Nanowire Array

Weiwei Wu, Li Cheng, Suo Bai, Zhong Lin Wang, and Yong Qin**

Anisotropic micro/nanostructure is widely used by nature in biology to achieve important functions through ingenious designs. A dragonfly's head and neck interlock with each other by microtrichia (small hairs) on the rear surface of the head and post-cervical sclerites of the neck.[1] Beetles have the ability to attach their wings to their body through arrays of microtrichia.[2] Benefiting from the gradient nanostrips obliquely aligned on their wings, butterflies protect themselves from wetting by forcing water droplets to move away from their body along the wings.[3] Because of a one-dimensional aligned parallel chain of papillae, a water droplet easily rolls off along the edge of a rice leaf, but is pinned in the perpendicular direction.[4] Shorebirds feed on small crustaceans and other invertebrates by surface tension–induced transport of prey in millimetric droplets through a capillary ratchet in their long thin beaks.[5] Rectangular polydimethylsiloxane (PDMS) flaps are used to mimic high-to-low frictional-adhesion toe pads.[6] Among all kinds of anisotropic micro/nanostructures, aligned oblique nanowire arrays (AONWAs) have special importance for animals and plants. Artificial AONWAs, inspired by these natural anisotropic structures, have great potential to achieve similar functions and even new applications that may not exist in the natural world may be designed. Compact slanted parylene nanorod films show unidirectional wetting properties for water drops, which is potentially useful for digital microfluidic devices.[7] Oblique silicon nanopillar arrays coated with polymer show the phenomenon of unidirectional liquid spreading.[8] Although there are many irreplaceable applications of AONWAs in the natural world, research into artificial AONWAs and their applications is so far very limited owing to the difficulties of controllable fabrication of AONWAs.

At present, a tension-induced nanowire (NW) deflecting method,[8–10] anisotropic chemical etching,[11] oblique angle vapor deposition and polymerization,[12] and high energy Br^{7+} ion (30 MeV) track etching at an accelerator and subsequent chemical etching process[13] have been explored to fabricate oblique nanostructures, but controllable fabrication of oblique nanostructures is still a great challenge. In this Communication we present a mask-assisted low energy (several kiloelectronvolts) ion milling method to rationally fabricate polymer AONWAs on a large scale and at low cost. This method can precisely control the NWs' obliquity, length, diameter, and density and fabricates NWs with good mechanical properties. When stimulated by sound wave vibrations caused by music, a poly(ethylene terephthalate) (PET) sheet with an AONWA grown in situ from the same material can be unidirectionally moved horizontally, and it can even climb up a 3.6° slope. Also, using this kind of PET AONWA, a polystyrene (PS) microsphere can be directionally transported for a distance of 0.28 cm up a 1.6° slope. Moreover, PET AONWAs show the unidirectional wetting property of water droplets, just like anisotropic parylene nanorod films[7] and polymer-coated Si nanopillar arrays.[8]

To fabricate PET AONWAs, a PET sheet covered with Au film is bombarded by Ar^+ ions with an accelerating voltage of 4 kV at a fixed incident angle. The obliquity of the AONWAs is modified by adjusting the incident direction of the Ar^+ ions. **Figure 1** shows scanning electron microscopy (SEM) images of PET AONWAs with obliquity 10°, 20°, 30°, and 40°. For each obliquity, the NWs are relatively uniform in length and diameter. The bottom of a NW has a larger diameter than its top. This implies that the NWs' tops are positively charged and repel the following Ar^+ ions during the fabrication process. Under the effect of Coulomb force, Ar^+ ions will deviate from their incident direction when they move through NWs, which causes the large diameter at the NWs' bottom. To clarify whether the NWs' surface is electropositive, the electrical properties of the surface were measured using a Keithley 6517A electrometer (Keithley Instruments Inc., Cleveland, OH) after the PET sheet had been bombarded with Ar^+ ions for 1 h. Measurement results indicated that the surface is positively charged and the density of electric charge is about 70 pC mm^{-2}, which proved that bombarding with Ar^+ ions leads to an electropositive surface. The reason for the appearance of positive charges may be outlined as follows. The energetic ions hit the PET surface and they transfer energy to the electrons of the solid as well as the atoms. The excited electrons are emitted as secondary electrons, leaving the surface positively charged.[14] In addition, from cross-sectional views of PET AONWAs (Figure 1e–h) it is seen that their obliquity is the same as the incident angle of the Ar^+ ions, indicating that the AONWAs' obliquity can be well controlled from 10° to 40° by adjusting the Ar^+ ions' direction of incidence.

The length of the oblique NWs is closely related to the bombarding time of Ar^+ ions. As shown in Figure S1 (Supporting Information), with increasing bombarding time, NWs become longer during the first stage (shorter than 1.5 hours), but with a further increase in bombarding time, there is almost no change

Dr. W. W. Wu,[+] Dr. L. Cheng,[+] Dr. S. Bai, Prof. Y. Qin
Institute of Nanoscience and Nanotechnology
Lanzhou University
Lanzhou 730000, P.R. China
E-mail: qinyong@lzu.edu.cn
Prof. Z. L. Wang
School of Materials Science and Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0245, USA
E-mail: zhong.wang@mse.gatech.edu
[+] W.W. and L.C. contributed equally to this work.

DOI: 10.1002/adma.201104085

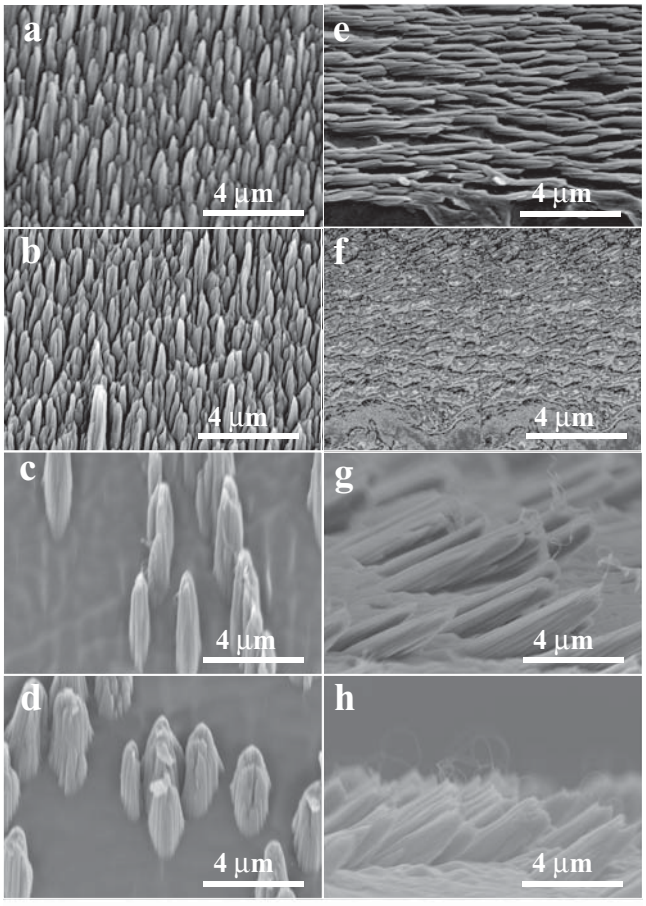

Figure 1. SEM images of PET AONWAs. a–d) Top views. e–h) Side views. From top to bottom: The obliquity of the AONWAs is 10°, 20°, 30°, and 40°. The average thickness of Au is 4 Å and the bombarding time is 1 h.

of NW length. This phenomenon is due to the change of the ions' path during the fabrication process. During the first stage, the positive charges at the NWs' surface will slightly deflect the trajectory of the ions so that they selectively bombard the area near the foot of the NWs. As the bombardment continues, the ions mill off not only the atoms on the substrate film, but also the atoms at the top of the NWs. As a result, the length of NWs will not change obviously when the bombarding time is longer than 1.5 h.

Figure S2 shows SEM images of PET AONWAs fabricated using the same substrate but coated with different thicknesses of Au films (the measurement method is described in the Supporting Information). Control of the deposited Au film can effectively tune the density of NWs from 2×10^5 to 5×10^5 wires/mm^2 when the thickness of the Au film is less than 2.4 Å. The density remains almost the same when the average thickness of the Au film is larger than 2.4 Å. A surface coating of less than 2.4 Å Au thickness leads to a low density of NWs. When the thickness is larger than 2.7 Å, the whole PET surface is covered by continuous Au film. Ar^+ ions firstly bombard off the thinner area of Au film, and the remaining discontinuous Au film acts as a shadow mask for the fabrication of PET NWs. This kind of shadow mask obviously will not change with Au film thickness, so the density of the NWs almost does not change with the thickness for thickness greater than 2.4 Å. Besides Au, other metals, such as Ag, Al, Cu, and Cr, can also be used as a shadow mask to fabricate AONWAs (Figure S3), which will benefit the large scale production of AONWAs at a low price.

Figure 2a depicts a proposed mechanism of formation of oblique NWs. At the beginning, an insulating polymer film is covered with a layer of discontinuous Au granular thin film. Just as reported before,[15] under Ar^+ ion bombardment, these Au nanoparticles act as a shadow mask to protect the polymer film underneath, which leads to hilly structures on the polymer film. After a period of Ar^+ ion bombardment, the Au nanoparticles disappear (Figure 2b), and the hilly structure is positively charged (experimentally proved as described above). When successive Ar^+ ions move through the hilly structure, they will be repulsed by those positive charges, as shown in Figure 2a. To further prove this deflecting effect of accumulated surface positive charges on the motion trajectory of bombarding Ar^+ ions, a p-type semiconductor polymer PEDOT (poly(3,4-ethylenedioxythiophene)) was selected as a film for fabricating AONWA. First, PEDOT thin film was spin-coated on a Si wafer with a good conductance, and Ar^+ ions bombarded it at 20° incident angle to the PEDOT film plane. As shown in Figure 2c, there are only some parallel gullies and few NWs on the film surface. For comparison, PEDOT was spin-coated on an insulating PET substrate. After ion bombardment, PEDOT AONWA could be obviously observed (Figure 2d). The different phenomena in the two experiments arise for the following reasons. Si can transfer away some of the positive charges on the PEDOT film, and the path of succeeding Ar^+ ions is difficult to alter. However, because of the insulation of the PET sheet, the accumulated positive charges on the PEDOT surface cannot be transferred away and will deflect the motion trajectory of incoming Ar^+ ions. Therefore, an insulating substrate is necessary for an electropositive surface and further formation of an AONWA. Because of the deflecting effect, the top of the hilly structure will be bombarded off more slowly than its bottom part, and NWs are formed (Figure 2a). At the same time, because Ar^+ ions are accelerated with a high voltage of 4000 V, they gain high velocity with kinetic energy of 4000 eV, which makes them basically retain their incident direction and etch PET obliquely. If the accelerating voltage is as low as 600 V, as used in inductively coupled plasma (ICP) reactive ion etching processes, single Ar^+ ions cannot etch polymer to form NWs.[16] On the other hand, if the kinetic energy of the Ar^+ ions is too large and the ion beam is focused, they will bombard off anything when they hit the substrate.[14] In summary, our method utilizes a shadow mask, the slight deflection effect of positive charges on incident Ar^+ ions, and the high velocity and directivity of Ar^+ ions to anisotropically etch material to form oblique NWs. Adjusting the incident angle of the Ar^+ ions to the substrate plane allows AONWAs to be fabricated and the NWs' oblique direction to be altered. Besides PET, other materials can also be made into AONWAs. Kapton AONWAs can be fabricated on Kapton film (Figure S4) using a similar procedure. The oblique NWs show perfect alignment and uniform length and diameter.

An in situ fabricated AONWA on polymer sheet is a typical anisotropic textured surface. A similar structure is the basis for gecko[17] and water strider locomotion,[18] butterfly wing water

Adv. Mater. **2012**,
DOI: 10.1002/adma.201104085

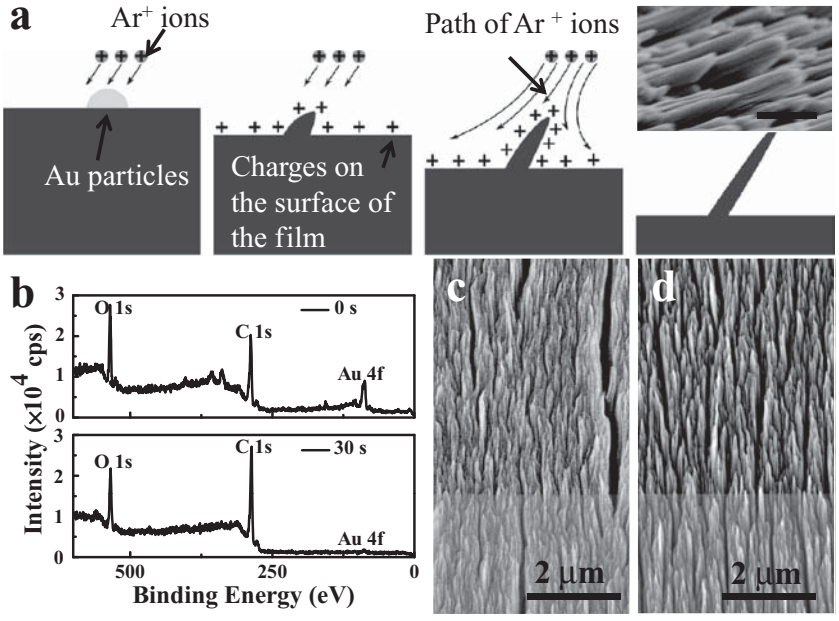

Figure 2. Formation mechanism of NWs. a) Schematic of oblique NW formation. Inset: A typical SEM image of oblique PET NWs; scale bar represents 2 μm. b) XPS spectra of PET sheet coated with Au film before (upper panel) and after 30 s etching (lower panel). c) PEDOT oblique NWs on Si substrate. d) PEDOT oblique NWs on PET thin film. The average thickness of Au is 4 Å and the bombarding time is 1 h.

repellency,[3] plant pollination,[19] and so on. Inspired by natural structures, Mahadevan et al. successfully demonstrated ratchet motion of a soft gel rod driven by asymmetric wave-form vibration.[20] Is there any possibility of transporting objects using an anisotropic nanostructured film under random vibration? Because of its good mechanical properties, we selected PET sheet covered with an in situ fabricated AONWA to directionally transport a similar macroscopic PET sheet and PS microsphere driven by music vibration. Two AONWA-covered PET sheets of size 0.6 cm × 0.8 cm were bent to a "vee" shape and placed face to face horizontally. As illuminated by the NW collision model (see Supporting Information), the intercrossed oblique NWs will move up and down under music vibration, and induce a backward velocity component in the plane of the sheet, which will make the sheets move in opposite directions. When the lower PET sheet is fixed to a base board, the upper sheet will be moved along one direction. If we define the NWs' direction as the direction from its bottom to top projected onto the substrate sheet's plane, the upper sheet moves along the NWs' direction on the lower PET sheet. Even when the sheets are tilted 3.6° with respect to the horizontal plane (**Figure 3**a), the upper PET sheet can be transported upward for a distance of 0.24 cm along the slope of the lower PET sheet. From the time-lapse frames shown in Figures S5a–e and supplementary movie S1, the upper PET sheet obviously moves relative to the lower one. The curve of transported distance of the upper PET sheet versus time is shown in Figure 3c. It can be fitted with a linear relationship with the coefficient of determination (R^2) equal to 0.9722, which means the upper PET sheet climbs up the slope with a uniform velocity. Experimentally, it took 24 s for the upper PET sheet to move 0.24 cm. This time is larger than the value calculated from the NW collision model. The difference may arise for the following reasons. First, the movement of the PET sheet is not continuous in the experiment. During the process of applying a vibration through music, only high amplitude vibration of the base board can make the PET sheet move. That is to say, the PET sheet moves only part of the whole time the music is playing. Second, the gradient in our experiment makes the upward motion more difficult than horizontal motion. Generally speaking, the design for directional transport of the PET sheet is successful. Based on directional transport by AONWA, by patterning the substrate with a path of AONWAs there is the potential to make a vibration-powered shuttle modified with AONWA to transport medicine or other substances, just like magnetic nanopropellers.[21]

According to the NW and microsphere collision model (see Supporting Information), when a microsphere is put on a PET sheet covered with an AONWA, the microsphere will constantly rebound in the opposite direction to the NWs under vibration.

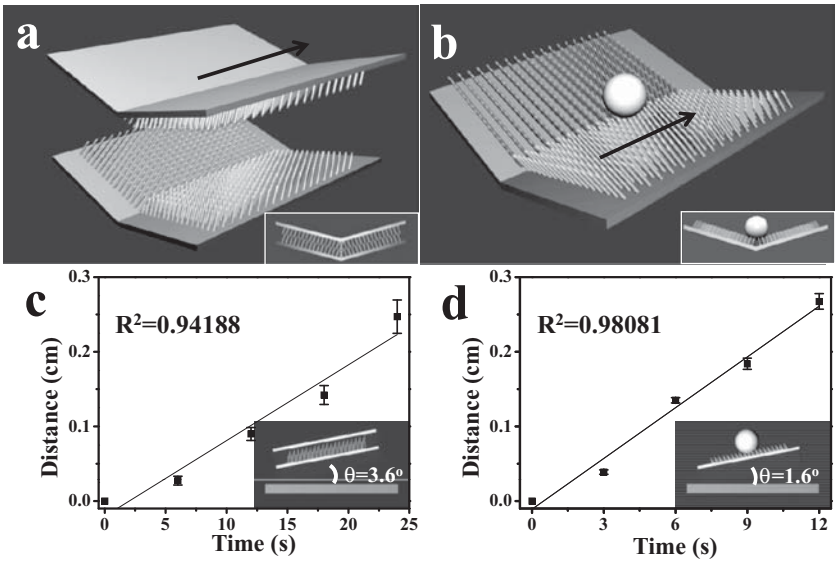

Figure 3. Directional transport of PET sheet and a PS microsphere along a slope. a,b) Sketches of transport for PET sheet (a) and a PS microsphere (b). The arrows indicate the direction of movement of the film and microsphere on the bottom PET sheet. c,d) Distance moved by PET sheet (c) and PS microsphere (d) as a function of time along a slope with obliquity θ as shown in the insets in (c) and (d).

In our experiment, a PS microsphere was placed on the PET sheet covered with AONWA as depicted in Figure 3b. Under vibration caused by the same music as used in the previous experiment, the PS microsphere climbed up a 1.6° slope of an AONWA-covered PET sheet along the opposite direction to the direction of the NWs, as indicated by the arrow (Figure 3b, Figure S5 f–j, and supplementary movie S2). As shown in the Figure 3d, the displacement and time can be fitted to a linear relationship with $R^2 = 0.9835$. If the PS microsphere is put on a horizontal PET sheet covered with AONWA, the PS microsphere moves in the opposite direction to the NW direction until it leaves the sheet, but if the microsphere is placed on a horizontal PET sheet covered with vertical NWs or randomly aligned NWs, or even a horizontal smooth PET sheet, the PS microsphere just moves randomly around its initial position under vibration and will not move away from PET sheet. Therefore, under conditions without liquid and with vibration, surface modification with AONWA is a feasible way to remove all kinds of dust, such as PS microspheres, from an object's surface. As a result, engineering a surface with AONWA has great potential to accomplish directional transport of micro/nanometer-scale substances and self-cleaning without liquid.

Asymmetric surface structures always exhibit anisotropic wetting.[8,22–28] Similar to other asymmetric structures, the surface covered with an AONWA has a large difference in contact angle (CA) of a water drop in the four in-plane directions. Without any surfactant treatment of the AONWA, the CA of 56.8° along the NW's direction is obviously larger than the CA of 84.5° in the opposite direction (**Figure 4**a). The AONWA has almost the same CAs of 115.3° and 118° along the two directions perpendicular to the NWs' direction (Figure 4b). At the same time, with the increase of the AONWA's obliquity, the difference of CAs along the NWs' parallel and antiparallel directions decreases, which means the anisotropic wetting property of AONWA for water decreases with increasing obliquity. These phenomena may be determined by the unique surface geometry and the intrinsic contact angle of the liquid on the PET sheet.[8] This property offers further insights that could lead to modifications of the wetting property of asymmetric surfaces.

In summary, a valuable method is described that can be used to fabricate many kinds of AONWAs with controllable obliquity, NW diameter, length, and density. This method is elucidated with a mechanism including shadow mask protection, positively charged surface, and slight deflection of incident ions. The surface structure of AONWAs can be utilized to transport objects with size ranging from a microscopic PS microsphere to a macroscopic PET sheet. In addition, AONWAs show a unidirectional wetting property for water drops, and there is a close relation between the anisotropy of the wetting property and the NWs' obliquity. AONWAs fabricated with our general method are potentially useful for a wide range of applications, including digital microfluidic devices, fluidic diodes, biomimetic mechanical research, drug delivery systems, and self-cleaning without a liquid.

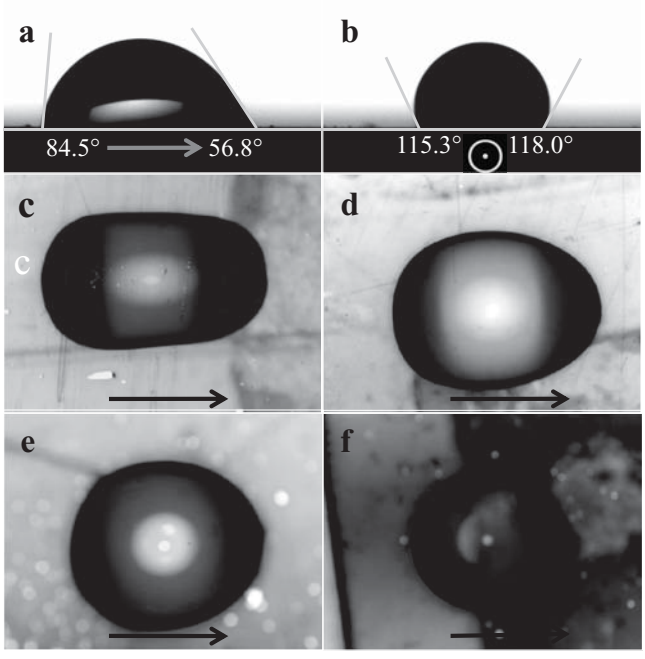

Figure 4. Water wetting property of PET sheets modified with different-obliquity AONWAs. The arrows show the direction of NW growth projected on the PET sheet plane. a) Contact angles along the projection direction. b) Contact angles perpendicular to the projection direction. c–f) Top views of water drops on PET sheets with different-obliquity AONWAs. From c) to f), the obliquity is 10°, 20°, 30°, and 40°, respectively.

Experimental Section

AONWA fabrication: A Gatan Model 600 Dual Ion Milling (Gatan, Pleasanton, CA) was used to fabricate AONWAs. This machine can supply a uniform and highly directional ion beam with adjustable incident angle. Before bombarding, the substrates were first cleaned with acetone, alcohol, and deionized water in sequence in order to remove all surface contaminants. Then, clean air was used to blow them dry. After that, different thickness Au thin films were deposited on the substrate as a shadow mask through magnetron sputtering. The Ar^+ ion beam was created by an ion gun (4 kV, 0.2 mA) filled with argon and its angle of incidence was tuned from 10° to 40° in our experiments.

Measurement of the contact angle: A drop shape analysis system (DSA100 from Krüss, Hamburg, Germany) was used to measure the contact angle. The anisotropic nanostructure film was kept horizontal during the measurement.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

We gratefully acknowledge the financial support from NSFC (No. 50972053, 11034004), NCET (No. NCET-08), the Ph.D. Programs Foundation of the Ministry of Education of China (No. 20090211110026), and the Fundamental Research Funds for the Central Universities (No. lzujbky-2010-k01). We thank Mr. Yingdong Li of Beijing Ion Beam Technology Co. Ltd. for technical support and Dr. Wenwen Hu for helping to establish the NW collision model.

Received: October 24, 2011
Published online:

DOI: 10.1002/adma.201104085

[1] S. N. Gorb, *Proc. R. Soc. London B* **1999**, *266*, 525.
[2] S. N. Gorb, *Int. J. Insect Morphol. Embryol.* **1998**, *27*, 205.
[3] Y. M. Zheng, X. F. Gao, L. Jiang, *Soft Matter* **2007**, *3*, 178.
[4] 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.* **2002**, *14*, 1857.
[5] M. Prakash, D. Quere, J. W. M. Bush, *Science* **2008**, *320*, 931.
[6] J. Yu, S. Chary, S. Das, J. Tamelier, N. S. Pesika, K. L. Turner, J. N. Israelachvili, *Adv. Funct. Mater.* **2011**, *21*, 3010.
[7] N. A. Malvadkar, M. J. Hancock, K. Sekeroglu, W. J. Dressick, M. C. Demirel, *Nat. Mater.* **2010**, *9*, 1023.
[8] K. H. Chu, R. Xiao, E. N. Wang, *Nat. Mater.* **2010**, *9*, 413.
[9] Y. Shen, J. I. Hong, Z. C. Peng, H. Fang, S. Zhang, S. X. Dong, R. L. Snyder, Z. L. Wang, *J. Phys. Chem. C* **2010**, *114*, 21277.
[10] M. K. Choi, H. Yoon, K. Lee, K. Shin, *Langmuir* **2011**, *27*, 2132.
[11] K. Q. Peng, M. L. Zhang, A. J. Lu, N. B. Wong, R. Q. Zhang, S. T. Lee, *Appl. Phys. Lett.* **2007**, *90*, 163123.
[12] M. C. Demirel, S. Boduroglu, M. Cetinkaya, A. Lakhtakia, *Langmuir* **2007**, *23*, 5861.
[13] R. Spohr, G. Sharma, P. Forsberg, M. Karlsson, A. Hallén, L. Westerberg, *Langmuir* **2010**, *26*, 6790.
[14] S. Reyntjens, R. Puers, *J. Micromech. Microeng.* **2001**, *11*, 287.
[15] H. Fang, W. Z. Wu, J. H. Song, Z. L. Wang, *J. Phys. Chem. C* **2009**, *113*, 16571.
[16] J. R. Morber, X. Wang, J. Liu, R. L. Snyder, Z. L. Wang, *Adv. Mater.* **2009**, *21*, 2072.
[17] G. Huber, H. Mantz, R. Spolenak, K. Mecke, K. Jacobs, S. N. Gorb, E. Arzt, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 16293.
[18] J. W. M. Bush, D. L. Hu, M. Prakash, *Adv. Insect Physiol.* **2007**, *34*, 117.
[19] B. Oelschlagel, S. Gorb, S. Wanke, C. Neinhuis, *New Phytol.* **2009**, *184*, 988.
[20] L. Mahadevan, S. Daniel, M. Chaudhury, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 23.
[21] A. Ghosh, P. Fischer, *Nano Lett.* **2009**, *9*, 2243.
[22] J. Drelich, J. L. Wilbur, J. D. Miller, G. M. Whitesides, *Langmuir* **1996**, *12*, 1913.
[23] H. Gau, S. Herminghaus, P. Lenz, R. Lipowsky, *Science* **1999**, *283*, 46.
[24] J. Bico, C. Tordeux, D. Quere, *Europhys. Lett.* **2001**, *55*, 214.
[25] Y. Chen, B. He, J. H. Lee, N. A. Patankar, *J. Colloid Interface Sci.* **2005**, *281*, 458.
[26] R. Seemann, M. Brinkmann, E. J. Kramer, F. F. Lange, R. Lipowsky, *Proc. Natl. Acad. Sci. USA* **2005**, *102*, 1848.
[27] J. Y. Chung, J. P. Youngblood, C. M. Stafford, *Soft Matter* **2007**, *3*, 1163.
[28] H. Kusumaatmaja, R. J. Vrancken, C. W. M. Bastiaansen, J. M. Yeomans, *Langmuir* **2008**, *24*, 7299.