Science of Advanced Materials
Vol. 5, pp. 1–6, 2013
(www.aspbs.com/sam)

Surface Engineering Method to Fabricate a Bendable Self-Cleaning Surface with High Robustness

Weiwei Wu[1,†], Li Cheng[1,†], Miaomiao Yuan[1,2,†], Suo Bai[1], Zhiyang Wei[1], Tao Jing[2], and Yong Qin[1,3,*]

[1]*Institute of Nanoscience and Nanotechnology, Lanzhou University, 730000, China*
[2]*School of Basic Medical Sciences, Institute of Pathogenic Biology, Lanzhou University, 730000, China*
[3]*Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences*

ABSTRACT

Self-cleaning is a common phenomenon in natural world and has wide applications in people's real life. Here we report a general surface engineering method to fabricate micro/nano hybrid structure on polymer film, which can be applied to other substrates. The modified polymer surface is superhydrophobic with a water contact angle (CA) of $160 \pm 1°$ and a water sliding angle (SA) of 3°. When bent to two opposite directions, the convex surface and concave surface are still superhydrophobic and exhibit self-cleaning property. Dusts with different sizes can be cleared away from the modified surface by dipping water drops or spraying water mist. The surface engineering method modified surface has ultrahigh robustness. Its perfect multi-scale hierarchical structure and self-cleaning property barely change even after undergoing one hour ultrasonic oscillation. This method is applicable to modify the surfaces of various materials, architectures and devices into self-cleaning surfaces.

KEYWORDS: Self-Cleaning, Superhydrophobic, Wetting Property, Micro/Nano Hybrid Structure, Surface Engineering.

1. INTRODUCTION

Nowadays, various kinds of functional devices play more and more important roles in our daily life. These devices become personal, portable, flexible and multifunctional. However, the fact that their performance degrades with time, especially when their working environment is very dirty, is still a big problem. For solar cell, light sensor etc., the dust covering them is a deadly damage.[1–3] Constantly wiping away of dust will destroy the surface of functional devices. Self-cleaning is a perfect solution to clear away the dust without any damage to devices. Therefore, in order to keep the high reliability of functional devices, it is very valuable to explore an effective surface engineering technology to make their surface self-cleaning.

For self-cleaning structure, two criteria should be met: superhydrophobic property and low adhesive force. Wetting property of a solid surface is usually determined by its chemical composition and geometrical micro/nanostructure.[4] There are two approaches to obtain a superhydrophobic surface. One is by creating a rough surface directly on materials with low surface free energy. The other one is by covering a layer of chemical composition with low surface free energy on an existing rough surface. By now, many methods have been developed to prepare the superhydrophobic surface, for example, roughening fluorinated polymer[5–7] and silicones,[5,8–11] replica of plant leaves,[12] electrodepositing metal nanostructure,[13] patterning metal surface using lithography,[14] electrospinning nanofibers,[15–18] fabrication of aligned one-dimensional micro/nanostructure array[19–24] and coverage of nanoparticles or nanowires on surface.[2,25,26] However, developing a bendable self-cleaning surface with high robustness is still a great challenge. In nature, lotus leaf surface has distinguished self-cleaning property (Fig. 1(a)), which is due to its surface micro/nano hybrid structure. Up to now, although some works have been done to mimic the surface structure of lotus leaf,[12,24,27–30] these bionic structures are still inferior to lotus leaf in self-cleaning property and robustness, notably under a bended status.

Recently, we developed a valuable method (Ar ion bombarding) to *in-situ* fabricate micro-/nanostructure on any flexible polymer substrate.[31] These structures have a super high bonding force with their substrate, which makes it possible to fabricate self-cleaning surface structure with

*Author to whom correspondence should be addressed.
†These authors equally contributed to this work
Email: qinyong@lzu.edu.cn
Received: xx Xxxx xxxx
Accepted: xx Xxxx xxxx

ARTICLE

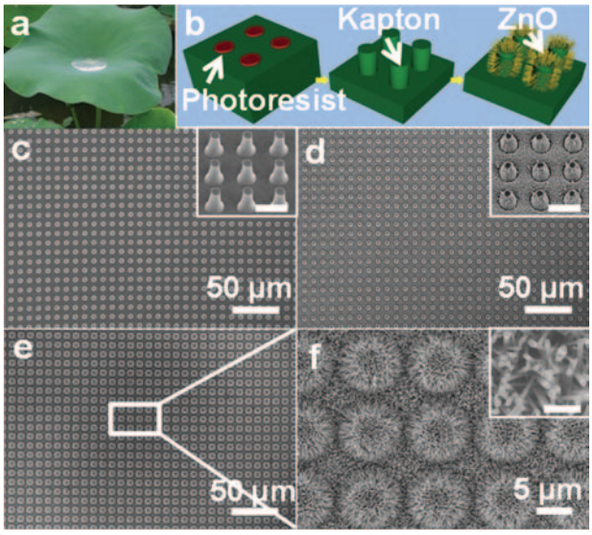

Fig. 1. (a) Photograph of a lotus leaf. (b) Sketch of the fabrication process. Kapton micropillars are fabricated using photoresist micropillars as mask. Then, ZnO nanowires re grown on them. (c)–(f) Top view SEM images. (c) Photoresist micropillar array. (d) Kapton micropillar array. The insets in figures (c) and (d) are 30° tilted high-magnification SEM images (the scale bars are both 10 μm). (e) *in-situ* fabricated Kapton micropillar/ZnO nanowires hierarchical structure. (f) A high magnification SEM image of figure (e). The inset is a top view high-magnification SEM image (the scale bar is 500 nm).

high robustness. In this paper, we utilize this technology and further develop a surface engineering method to fabricate a bendable self-cleaning surface with high robustness. This kind of hierarchical surface coated with oleic acid has ultrahigh stability and excellent mechanical property, and keeps its outstanding self-cleaning property even when it is under bended status and ultrasonic environment. Both water droplets and mist can clear away nanosize or larger dusts from the surface.

2. EXPERIMENTAL DETAILS

All the solvent and raw materials are analytically level purity and used without any further purification. The Kapton film is purchased from DuPont Company. The whole fabrication process is depicted as following three steps (Fig. 1). First, photoresist micropillars is fabricated on Kapton film using photolithography method as shown in the left image of Figure 1(b). Second, Kapton micropillars are *in-situ* fabricated on Kapton film's surface under the protection of above photoresist micropillars (the middle image of Fig. 1(b)). At last, dense ZnO nanowires arrays are grown on Kapton micropillars, and their surfaces are modified by oleic acid.

Fabrication of Polymer micropillars. First, a piece of Kapton film with thickness of 250 μm (DuPont Company) is cleaned with acetone, alcohol and deionized water in sequence to remove all contaminants on its surface. Then, clean air is used to blow them dry. Second, Kapton film is spin coated with AZ-P1350 positive photoresist with thickness of 5 μm at a speed of 6000 revolutions per minute (rpm) for 60 seconds. After that, the polymer substrate is baked at 100 °C for 90 seconds. Later on, it is patterned using a mask aligner under 365 nm ultraviolet of 3 mw/cm^2 for 60 seconds and developed using NaOH aqueous solution (3.5 g/l). Third, the Kapton film covered with photoresist micropillars is placed into an Ar ion milling machine (Gatan Dual 600). Ar ion beam is used to bombard the film surface at 4 kV and 0.2 mA along its normal direction for 4 hours. The residual photoresist on the top of polymer micropillars are removed by ultrasonic cleaning in alcohol.

Growth and surface modification of ZnO nanowires. Magnetron sputtering is used to deposit a layer of 50 nm thick ZnO seedlayer on Kapton film *in-situ* fabricated with micropillars. Then the film is immersed into a precursor solution at 95 °C for 6 hours. The precursor solution consists of 20 mM $Zn(NO_3)_2$ and 20 mM hexamethylenetetramine (HMTA). After growth, the film is rinsed with deionized water. After baking it in oven for 1 hour, the film is immersed in oleic acid overnight. At last, it is rinsed to obtain self-cleaning surface.

Characterization of wetting and self-cleaning property. CA and SA are measured by DSA100 from Krüss, Hamburg, Germany. Pictures of self-cleaning behavior are taken with a camera equipped on the probe station (TK-C9211EC/LEADTEX VC100, JVC). We use a deionized water droplet of 5 μL as an indicator. All the CAs and SAs are characterized for 3 times.

3. RESULTS AND DISCUSSION

Our surface engineering method of fabricating micro/nano hierarchical structure consists of two processes: *in-situ* fabrication of micropillars on substrate, and subsequent growth and chemical modification of ZnO nanowires on these micropillars, which is schematically shown in Figure 1(b). First, a layer of positive photoresist is spin-coated on a clean Kapton film. After baking, photolithography and developing, periodic arranged photoresist micropillars as shown in Figure 1(c) are obtained. They are very uniform in morphology, size and spacing distance. At the bottom of this micropillar, the diameter and spacing distance are both 5 μm, which is similar to the papillae of lotus leaf in nature.[27,32] Then, Kapton film with photoresist micropillars is bombarded with Ar ion beam to *in-situ* fabricate Kapton micropillars. The exposed parts of Kapton film are bombarded away and the area protected by photoresist micropillars exists, which is similar to the fabrication of oblique PET nanowires.[32] As a result, the polymer micropillars are obtained after removing the residual photoresist in alcohol solution. The pattern of photoresist micropillars is well transferred onto Kapton film surface as shown in Figure 1(d). The diameter and

spacing distance of *in-situ* fabricated Kapton micropillars can be controlled by changing the pattern of photolithography mask. The height of micropillars can be longer by increasing Ar ions' bombarding time. Finally, a thin layer of 50 nm thick ZnO seedlayer is coated on above Kapton micropillars' surface using magnetron sputtering, and subsequently ZnO nanowires are grown on this surface with hydrothermal method.

Figure 1(e) is a low magnification scanning electron microscope (SEM) image of *in-situ* fabricated Kapton micropillars/ZnO nanowires hierarchical structure. It shows that all Kapton micropillars are covered with ZnO nanowires array, and the hierarchical structure is uniform in large area. This kind of special hierarchical structure allows air to be trapped between its surface and above water droplet, which benefits to the large contact angle and superhydrophobic property.[33] To further characterize the morphology of ZnO nanowires, a high magnification SEM image of the surface is observed (Fig. 1(f)). The length of ZnO nanowires is about 2.5 μm. The inset of this figure is a higher magnification SEM image. It can be verified that their diameter is about 50 nm. The hexagonal top surface indicates that the ZnO nanowires possess a wurtzite structure and their growth direction is along *c*-axis.

Considering that there are monolayers of hydroxyl (–OH) moieties existing at the surface of the as-grown ZnO nanowires,[34] oleic acid that contains the carboxyl (–COOH) group can be used to modify ZnO surface. Oleic acid forms a self-assembled monolayer on ZnO surface, and its alkyl chains cover the ZnO surface completely as shown in Figure 2. This makes ZnO surface at a low surface free energy state and hydrophobic. As a result, the Kapton surface covered with Kapton micropillar/ZnO nanowires hierarchical structure has a good self-cleaning property after the oleic acid modification on the ZnO surface.

To characterize the superhydrophobic property of a surface engineering method modified Kapton film, the water contact angle and sliding angle on the surface are measured (Fig. 3). As shown in Figure 3(a), the surface of this film is macroscopically nonwetting using a water droplet of 5 μl as indicator. Figure 3(b) is a typical optical microscope image, which shows that the CA on flat Kapton film reaches $160 \pm 1°$. Through carefully adjusting the angle between the sample stage and horizontal plane, the sliding angle is measured to be about 3°. Furthermore, the wetting property of water on a surface engineering method modified surface is measured when it is bent to a convex and concave shape, mimicking the surfaces of many living hydrophobic organisms. By placing a droplet of water on the vault with curvature of 0.19 1/mm (Fig. 3(c)), the CA is measured to be as high as $159 \pm 1°$ (Fig. 3(d)). The sliding angle is so small that the droplet moves away immediately from the surface as soon as it is dipped on the surface. In addition, as shown in Figure 4, the water

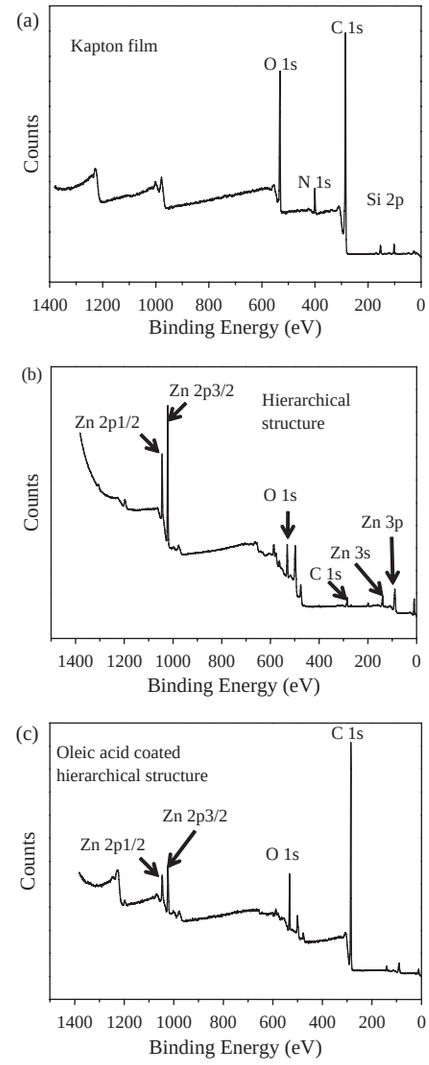

Fig. 2. X-ray photoelectron spectroscopy (XPS). (a) The Kapton film. (b) The polymer micropillars/ZnO nanowires hierarchical structure. (c) The oleic acid coated Polymer micropillars/ZnO nanowires hierarchical structure.

droplet can be dragged by the needle tip to move freely on the surface and can be lifted up by the needle tip easily, which further indicates the very small adhesive force between water droplet and surface. Figures 3(e) and (f) are photographs and an enlarged cross sectional image of a water droplet placed on a concave surface with curvature of 0.35 1/mm, respectively. Because the radius of curvature of the bended concave surface is too small to be comparable with the water droplet, the CA is difficult to be measured precisely. It is obvious that the surface still keep non-wetting. Figure 5 displays the superhydrophobic property of the surface more clearly. When the droplet falls down onto the concave surface, the drop moves between left and right sides quickly, this implies that the surface has good superhydrophobic property and small adhesive force to water. Thus, the surface engineering method modified

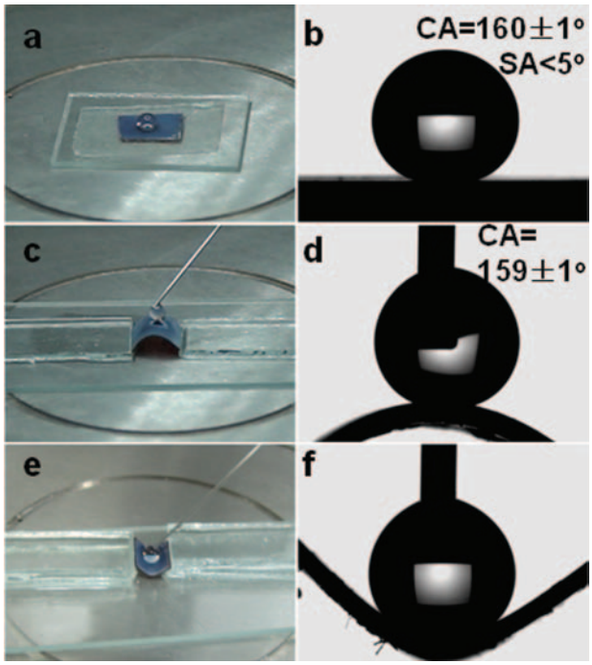

Fig. 3. Water droplet wetting property and sliding angle on the surface engineering method modified Kapton surface with different bended status. (a)–(b) Water droplet on a flat surface. (c)–(d) Water droplet on a convex surface. (e)–(f) Water droplet on a concave surface.

surface maintains its superhydrophobic property and small sliding angle at different curvature, which can be ascribed to that large amount of ZnO nanowires decorated on the microstructure trap air between them. If the surface is only covered with micropillars, the value of sliding angle increases when the polymer film becomes convex.[35]

A superhydrophobic surface with low adhesive force always leads to self-cleaning property, which is well known as lotus leaf effect. Water droplets with different sizes such as rain, dew and frog can clean the lotus leaf surface when they roll on the surface. Here, as shown Figure 6, we characterize the self-cleaning properties of a surface engineering method modified Kapton surface by

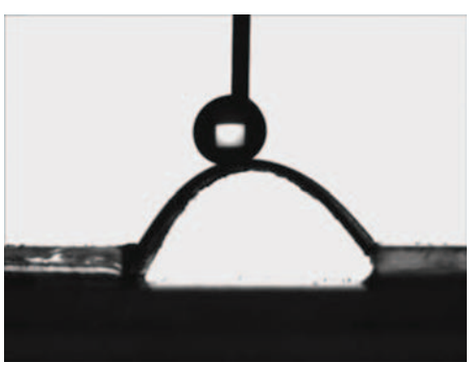

Fig. 4. Wetting and anti-adhesive property on a convex surface engineering method modified surface.

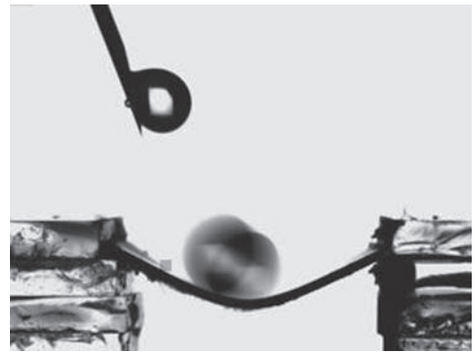

Fig. 5. Wetting and anti-adhesive property on a concave surface engineering method modified surface.

using big droplet and water mist to imitate the heavy rain and fog. Furthermore, it is also demonstrated that both microscale and nanoscale dust pollution such as silica microparticle (Fig. 6) and Zinc nanopowder (Fig. 7) can be cleaned by water droplet or mist.

Figure 6(a) is the photographs of flat Kapton film covered with silica particles at different stages after dripping water droplets. As indicated by the arrow, silica contaminants are removed thoroughly along the moving path of the water droplet when it rolls off from the surface. After dripping a few droplets of water, the whole surface is cleaned without any contaminant (stage 3 of Fig. 6(a)). When Kapton film is bent into a convex shape, water droplets can still move away silica particles from the surface

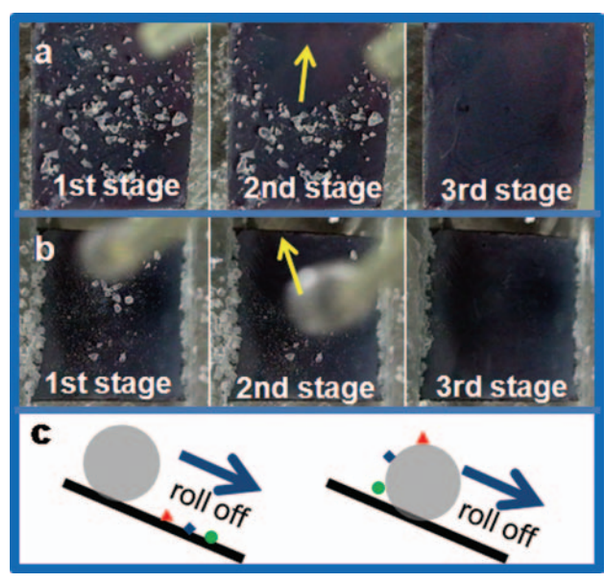

Fig. 6. Pictures of silica on flat Kapton film (a) and convex Kapton film (b) at different stages. The 1st stage is the moment before dripping a water droplet, the 2nd stage is the moment after dripping a water droplet and all silica contaminants have been cleared by water at 3rd stage. The yellow arrows depict the moving path of the water droplet. (c) Schematic of the self-cleaning mechanism. The contaminants are moved away from Kapton surface because the adhesive force between them and water droplet is larger than that between them and the surface.

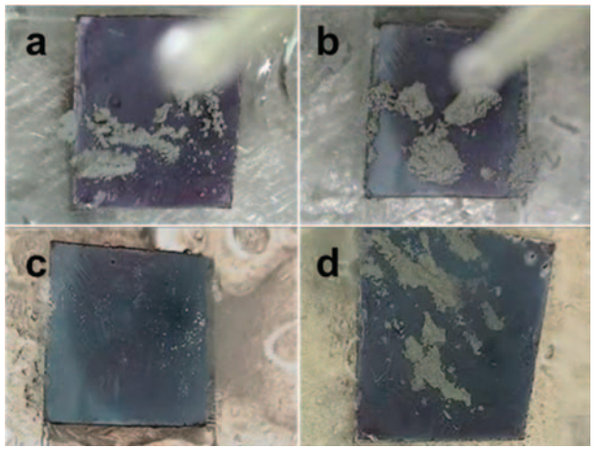

Fig. 7. Self-cleaning property of (a) a flat and (b) a convex surface modified by the surface engineering method for Zn nanopowder under dripping water droplets. Self-cleaning property of the above flat surface for (c) silica particles and (d) Zn nanopowder under spraying water mist.

(Fig. 6(b)). Moreover, if the contaminants of silica particles are replaced with smaller particles (Zn nanopowder), same self-cleaning phenomena of a surface engineering method modified surface under flat and bended status are also observed (Fig. 7), which means any size contaminants can be cleaned from the surface at different bended status just by dipping water droplets. The self-cleaning property of a surface engineering method modified Kapton film surface under different bended status can be ascribed to lotus leaf effect[31] and its structure stability. The contact area between the contaminants and the modified surface is very small. When a droplet contacts the contaminants, the adhesive force between the droplet and the contaminant is much larger than that between the contaminant and the modified surface. Thus, the contaminants is captured and moved away from the surface engineering method modified surface (Fig. 6(c)). On the other hand, the *in-situ* fabrication of Kapton micropillars/ZnO nanowires hierarchical structure ensures the high stability of this structure under a bent status. As a result, the bended Kapton film surface still has very good self-cleaning property.

How small a water droplet can still clean a surface is an important parameter featuring the self-cleaning property because the smaller a droplet is, the more difficult is for it to slide and move away contaminants. Although few studies have focused on this issue, a very small water droplet from a drizzle can make lotus leaf clean in nature. To mimic this phenomenon, water mist is sprayed to a surface engineering method modified surface to characterize its self-cleaning property. As shown in Figure 7(c), water mist forms much smaller droplet, then rolls off from the surface and moves away the contaminants easily. After a period of time, the modified surface with contaminants of silica particles is still cleaned. If the contaminants are smaller Zn nanopowder instead of silica particles, same phenomenon is also observed (Fig. 7(d)).

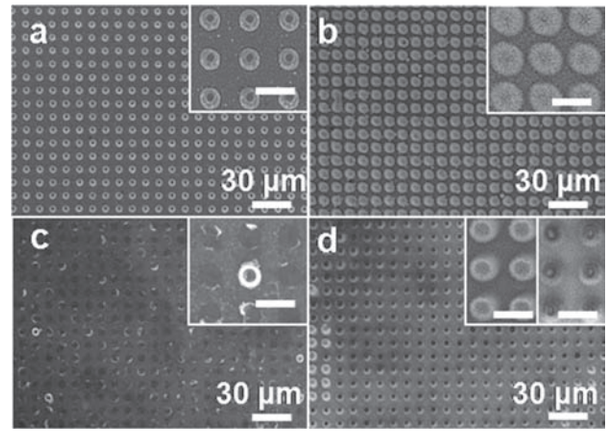

Fig. 8. Surface morphology of a Kapton film after ultrasonication. (a)–(b) SEM images of Kapton micropillars and Kapton micropillar/ZnO nanowires hierarchical structure on the surface, respectively, after ultrasonic processing of the film for 1 hour. (c)–(d) SEM images of photoresist micropillars and photoresist micropillar/ZnO nanowires hierarchical structure on surface, respectively, after ultrasonic processing the film for 10 minutes. The insets are enlarged images and all scales indicate 10 μm.

Structural robustness is critical important for artificial surface to maintain its special wetting property and low adhesive force. In this study, a surface engineering method modified surface is put into an ultrasonic cleaning bath to check its structural robustness. After one hour ultrasonic vibration, the primary structure (Kapton micropillar) is not damaged (Fig. 8(a)), and the whole Kapton micropillars/ZnO nanowires hierarchical structure has no obvious change too (Fig. 8(b)). As a comparison, we fabricate AZ-P1350 photoresist micropillar array on Kapton film and grew ZnO nanowires on these micropillars, and then put them into ultrasonic bath. Only after ultrasonic vibration of ten minutes, both the primary structure micropillar array and the whole hierarchical structure are damaged severely (Figs. 8(c) and (d)). In fact, most of micropillars have disappeared and only a few are maintained. Thus, on comparing the ultrasonic results of two kinds of micro/nano hierarchical structures, respectively, based on *in-situ* fabricated Kapton micropillars and additional fabricated photoresist micropillars, it emerges that the *in-situ* fabricated microstructure has stronger survivability to sonication and the surface engineering method modified surface has much higher robustness.

4. CONCLUSIONS

In summary, a surface engineering method has been developed to create a robust micropillars/nanowires hierarchical structure on polymer substrate. The surface engineering method modified surface exhibits excellent self-cleaning property with large contact angle of 160° and low sliding angle of 3°. Any size contaminants can be cleaned off from the surface with water droplets or mist no matter whether the surface is flat, convex or concave. The surface

hierarchical structure is so robust that even one hour ultrasonic vibration can not cause any damage to it. This technology of making bendable, robust and self-cleaning surface paves the way to the new self-cleaning structure with excellent mechanical property and high stability.

Acknowledgment: W. W. Wu, L. Cheng, M. M. Yuan contributed equally to this work. Research was supported by Fok Ying Tung education foundation (131044), NSFC (No. 50972053), Ph.D. Programs Foundation of Ministry of Education of China (No. 20090211110026), the Fundamental Research Funds for the Central Universities (Nos. lzujbky-2010-k01, lzujbky-2012-210), Special Talent Funding of Lanzhou University, New Academic Researcher Award for Doctoral Candidates. We thank Dr. J. Zhang, Professor J. Y. Zhang for assistance in characterizing CA and SA. We also thank Mr. Yingdong Li in Beijing Ion Beam Technology Co. Ltd. for technical support.

References and Notes

1. Y. B. Park, H. Im, M. Im, and Y. K. Choi, *J. Mater. Chem.* 21, 633 (**2011**).
2. L. Yuan, J. Dai, X. Fan, T. Song, Y. T. Tao, K. Wang, Z. Xu, J. Zhang, X. Bai, P. Lu, J. Chen, J. Zhou, and Z. L. Wang, *ACS Nano* 5, 4007 (**2011**).
3. Y. Liu, A. Das, S. Xu, Z. Lin, C. Xu, Z. L. Wang, A. Rohatgi, and C. P. Wong, *Adv. Energy Mater.* 2, 47 (**2012**).
4. L. Jiang, R. Wang, B. Yang, T. J. Li, D. A. Tryk, A. Fujishima, K. Hashimoto, and D. B. Zhu, *Pure Appl. Chem.* 72, 73 (**2000**).
5. J. L. Zhang, J. A. Li, and Y. C. Han, *Macromol. Rapid. Comm.* 25, 1105 (**2004**).
6. L. B. Xu, W. Chen, A. Mulchandani, and Y. S. Yan, *Angew. Chem. Int. Edit.* 44, 6009 (**2005**).
7. H. Yabu and M. Shimomura, *Chem. Mater.* 17, 5231 (**2005**).
8. M. H. Jin, X. J. Feng, J. M. Xi, J. Zhai, K. W. Cho, L. Feng, and L. Jiang, *Macromol. Rapid. Comm.* 26, 1805 (**2005**).
9. M. T. Khorasani, H. Mirzadeh, and Z. Kermani, *Appl. Surf. Sci.* 242, 339 (**2005**).
10. M. H. Sun, C. X. Luo, L. P. Xu, H. Ji, O. Y. Qi, D. P. Yu, and Y. Chen, *Langmuir* 21, 8978 (**2005**).
11. N. Zhao, Q. D. Xie, L. H. Weng, S. Q. Wang, X. Y. Zhang, and J. Xu, *Macromolecules* 38, 8996 (**2005**).
12. S. M. Lee, H. S. Lee, D. S. Kim, and T. H. Kwon, *Surf. Coat. Tech.* 201, 553 (**2006**).
13. M. E. Abdelsalam, P. N. Bartlett, T. Kelf, and J. Baumberg, *Langmuir* 21, 1753 (**2005**).
14. H. Notsu, W. Kubo, I. Shitanda, and T. Tatsuma, *J. Mater. Chem.* 15, 1523 (**2005**).
15. L. Jiang, Y. Zhao, and J. Zhai, *Angew. Chem. Int. Edit.* 43, 4338 (**2004**).
16. Z. Z. Gu, H. M. Wei, R. Q. Zhang, G. Z. Han, C. Pan, H. Zhang, X. J. Tian, and Z. M. Chen, *Appl. Phys. Lett.* 86, 201915 (**2005**).
17. M. L. Ma, R. M. Hill, J. L. Lowery, S. V. Fridrikh, and G. C. Rutledge, *Langmuir* 21, 5549 (**2005**).
18. A. Singh, L. Steely, and H. R. Allcock, *Langmuir* 21, 11604 (**2005**).
19. X. J. Feng, L. Feng, M. H. Jin, J. Zhai, L. Jiang, and D. B. Zhu, *J. Am. Chem. Soc.* 126, 62 (**2004**).
20. W. Lee, M.-K. Jin, W.-C. Yoo, and J.-K. Lee, *Langmuir* 20, 7665 (**2004**).
21. N. J. Shirtcliffe, G. McHale, M. I. Newton, G. Chabrol, and C. C. Perry, *Adv. Mater.* 16, 1929 (**2004**).
22. X. J. Feng, J. Zhai, and L. Jiang, *Angew. Chem. Int. Edit.* 44, 5115 (**2005**).
23. E. Martines, K. Seunarine, H. Morgan, N. Gadegaard, C. D. W. Wilkinson, and M. O. Riehle, *Nano Lett.* 5, 2097 (**2005**).
24. H. Yan, K. Kurogi, H. Mayama, and K. Tsujii, *Angew. Chem. Int. Edit.* 44, 3453 (**2005**).
25. J. T. Han, S. Y. Kim, J. S. Woo, and G. W. Lee, *Adv. Mater.* 20, 3724 (**2008**).
26. T. Nakanishi, T. Michinobu, K. Yoshida, N. Shirahata, K. Ariga, H. Moehwald, and D. G. Kurth, *Adv. Mater.* 20, 443 (**2008**).
27. L. Feng, S. H. Li, Y. S. Li, H. J. Li, L. J. Zhang, J. Zhai, Y. L. Song, B. Q. Liu, L. Jiang, and D. B. Zhu, *Adv. Mater.* 14, 1857 (**2002**).
28. A. Solga, Z. Cerman, B. F. Striffler, M. Spaeth, and W. Barthlott, *Bioinspir. Biomim.* 2, S126 (**2007**).
29. B. Bhushan, Y. C. Jung, and K. Koch, *Philos. Trans. R. Soc. London, Ser. A* 367, 1631 (**2009**).
30. H. Ko, Z. X. Zhang, K. Takei, and A. Javey, *Nanotechnology* 21, 295305 (**2010**).
31. W. W. Wu, L. Cheng, S. Bai, Z. L. Wang, and Y. Qin, *Adv. Mater.* 24, 817 (**2012**).
32. W. Barthlott and C. Neinhuis, *Planta* 202, 1 (**1997**).
33. A. B. D. Cassie and S. Baxter, *Trans. Faraday Soc.* 40, 546 (**1944**).
34. W. Gopel, *Prog. Surf. Sci.* 20, 9 (**1985**).
35. A. H. Cannon and W. P. King, *J. Micromech. Microeng.* 20, 025018 (**2010**).