J Mater Sci (2011) 46:4079–4084
DOI 10.1007/s10853-011-5337-7

# A facile process for preparing superhydrophobic films with surface-modified $SiO_2$/nylon 6,6 nanocomposite

**Yonggang Guo · Qihua Wang · Tingmei Wang**

Received: 17 November 2010 / Accepted: 27 January 2011 / Published online: 10 February 2011
© Springer Science+Business Media, LLC 2011

**Abstract** A superhydrophobic $SiO_2$/nylon 6,6 nanocomposite coating was fabricated by a facile casting process. Compared with the intrinsically hydrophilic pure nylon 6,6, the as-prepared coating displayed a superhydrophobic property in the pH range from 1 to 14. It was also found that the resulting water contact angles of the as-prepared surface were always larger than 159°, but the sliding angles had an obvious decrease from about 33.4°–1° as the content of $SiO_2$ nanoparticles increased. In addition, a transition from the transitional superhydrophobic state between Wenzel's and Cassie's state to the Cassie's state was observed.

## Introduction

Many natural surfaces including the lotus leaf exhibit excellent water repellent surface properties with a water contact angle (CA) bigger than 150° [1]. In addition, the sliding angle (SA) is very low [2], producing a surface on which water droplets simply roll off. Surfaces with superhydrophobic properties can usually be achieved by two methods: either creating a rough structure on a hydrophobic material surface [3, 4] or modifying the rough surface with a special low surface energy material [5–7].

Many synthetic strategies have been reported for achieving superhydrophobicity, such as etching and lithography [8, 9], sol–gel processing [10, 11], layer-by-layer and colloidal assembly [12, 13], electrochemical reaction and deposition [14, 15], electrospinning [16, 17], chemical vapor deposition [18], and so on. Up to now, superhydrophobic polymer nanocomposite coatings have been reported widely [3, 19]. Xu and coworkers [20] fabricated micro–nano hierarchically structured nylon 6,6 surfaces by a phase separation method and the wettability of the surfaces changed from superhydrophilicity to superhydrophobility after further modification by low surface energy material. In the previous study, we had successfully prepared water-repellent $SiO_2$/polystyrene nanocomposite coatings via a simple casting method [21, 22]. Herein, we fabricated a superhydrophobic surface-modified $SiO_2$/nylon 6,6 nanocomposite coating based on hydrophilic nylon 6,6. The adding of surface-modified $SiO_2$ nanoparticles affected the coating surface energy and surface roughness, in turn influencing the wettability of the coating. Compared with other methods, this casting method is simple and does not need special equipment or rigorous conditions.

## Experimental

### Materials

Neat nylon 6,6 pellets (EPR27) were provided by China Shenma Engineering Plastics Co., Ltd. The surface-modified $SiO_2$ nanoparticles with diameters about 70 nm, named as DNS-3, were directly supplied by Henan Provincial Research Center for Engineering and Technology of Nanomaterials. They were modified with single-layer

---

Y. Guo · Q. Wang (✉) · T. Wang
State Key Laboratory of Solid Lubrication, Lanzhou Institute
of Chemical Physics, Chinese Academy of Sciences,
Lanzhou 730000, People's Republic of China
e-mail: wangqh@lzb.ac.cn

Y. Guo
Graduate School, Chinese Academy of Sciences,
Beijing 100039, People's Republic of China

organic carbon-chain by grafting silane ligands in situ in aqueous solution [23]. Unmodified $SiO_2$ nanoparticles (Wacker N20) were supplied by Wacker Chemie AG.

### Preparation of superhydrophobic $SiO_2$/nylon 6,6 nanocomposite coating

In a typical synthesis, 2.0 g of nylon 6,6 was dissolved in 40 mL formic acid ($HCOOH \geq 88\%$). Then, surface-modified $SiO_2$ nanoparticles were dispersed in the above solution with a weight percent to nylon 6,6 of 25, 30, 35, 40, and 45%, respectively and stirred magnetically for at least 72 h. To prepare a coating, about 50 μL of the mixture solution was cast on a glass slide at ambient temperature and dried at 40 °C in an oven about 1 h until the solvent evaporated completely. In addition, pure nylon 6,6 and untreated nano-$SiO_2$/nylon 6,6 films were prepared with the same method. The influence of drying temperature on the changes of CAs was also studied.

### Characterization

The morphology of the products was determined by using a scanning electron microscopy (SEM) (JSM-5600LV). The chemical compositions of the films were analyzed with VGESCALAB210 X-ray photoelectron spectroscopy (XPS). Sessile water CA and SA were acquired using a DSA-100 optical contact-angle meter (Kruss Company, Ltd., Germany) at room temperature (30 °C). CAs were determined using the Laplace–Young fitting algorithm. Average CA values were obtained by measuring the sample at five different positions. Images were captured with a Sony digital camera (Sony, Ltd., Japan). So did research on how water CA changed with different pH values of aqueous solution.

## Results and discussion

The smooth nylon 6,6 plastic surface has a water CA of 75.9 ($CA < 90°$, hydrophilic material) [20]. In the experiment, a porous film was obtained when the pure nylon 6,6 solution was cast-coated on a glass slide and dried at 40 °C in an oven about 1 h until the solvent evaporated completely (Fig. 1). The water CA changed from about 18°–3.2° in about 5 s (Fig. 1c–f). Obviously, the solvent (formic acid) was evaporated and the coating formed a porous roughness, which made the pure nylon 6,6 coating superhydrophilic. However, an interesting wetting phenomenon was observed by combining surface-modified $SiO_2$ nanoparticles and nylon 6,6. Figure 2 shows the microstructure of the as-prepared nanocomposite coating with 40% modified $SiO_2$. It is clear that the as-prepared surface is made of many irregular island-like pillars of radius 50–100 μm, and spacing 50–100 μm, on which the $SiO_2$ nanoparticles aggregate together to form microstructures. From enlarged SEM image (Fig. 2b), we find that the as-prepared surface is covered with micro particles in the size from a few hundred nanometers to several micrometers. Figure 2c–g shows the approach, contact, deformation, and departure processes of a 5-μL water droplet suspending on a syringe with respect to the nanocomposite surface. It can be seen that the coating surface is so hydrophobic that water droplets can hardly stay on.

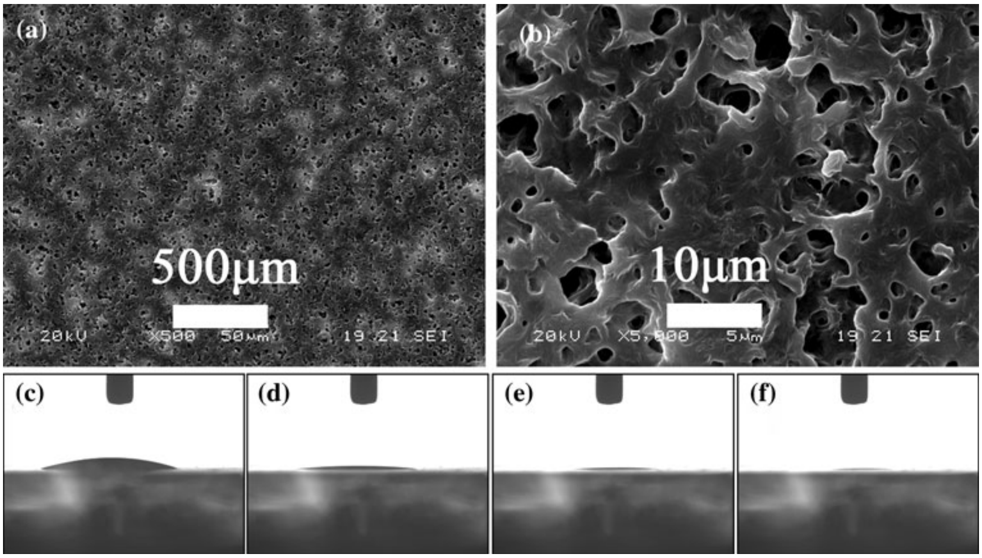

**Fig. 1** SEM images of **a** Pure nylon 6,6 coating and **b** magnified image. Photo **c**–**f** shows the changes of a 5-μL water droplet on the as-prepared coating in about 5 s

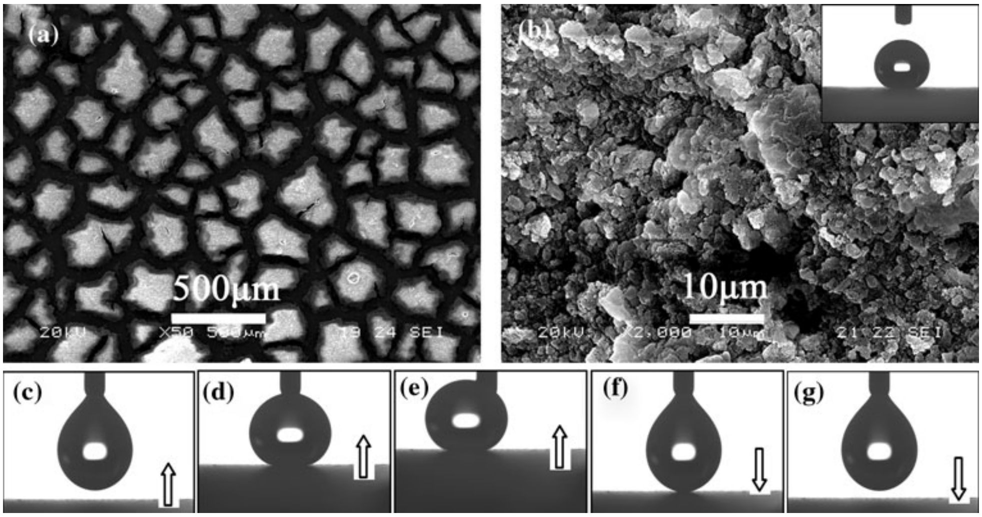

**Fig. 2** SEM images of **a** surface-modified $SiO_2$/nylon 6,6 nanocomposite coating with 40% modified $SiO_2$ and **b** magnified image. The *inset* is the corresponding profile of a water droplet on the surface. Photo **c**–**g** shows the approach, contact, deformation, and departure processes of a 5-μL water droplet suspending on a syringe with respect to the coating surfaces. The *arrows* represent the moving direction of the substrate

The droplets may easily and completely depart from the surface, even though severe deformation occurs in this case. The XPS results (Fig. 3) clearly show that the elements such as O, C, and N are found in the pure nylon 6,6 and modified $SiO_2$/nylon 6,6 nanocomposite films. The peak located at 399.1 eV is attributed to the $N_{1s}$ of nylon, which is consistent with the accepted binding energy value for $N_{1s}$ in nylon [24]. But compared with the pure nylon 6,6 film (Fig. 3a), the peaks of $Si_{2p}$ and $Si_{2s}$ appear in the XPS spectrum of the modified $SiO_2$/nylon 6,6 nanocomposite film (Fig. 3b), indicating $SiO_2$ and nylon 6,6 coexist on the surface.

The influence of the $SiO_2$ weight percent on the wettability of nanocomposite coating was investigated. It was found that when the weight percent of $SiO_2$ was not greater than 25%, the nanoparticles could not cover the substrate homogeneously. But if the weight percent was too high (such as 50%), the adhesion of the nanocomposite film was reduced making the coating easy to separate from the substrate. Considering the two factors, the weight percent of $SiO_2$ nanoparticles was chosen between 25 and 45%. The variation of average water CA and SA at different weight percent of $SiO_2$ nanoparticles is shown in Fig. 4. It can be seen that the CA value efficiently increases from 159.1° to 163.9° as the weight percent of silica increases from 25 to 45%. When the weight percent of silica becomes larger than 40%, the values of the CA reach

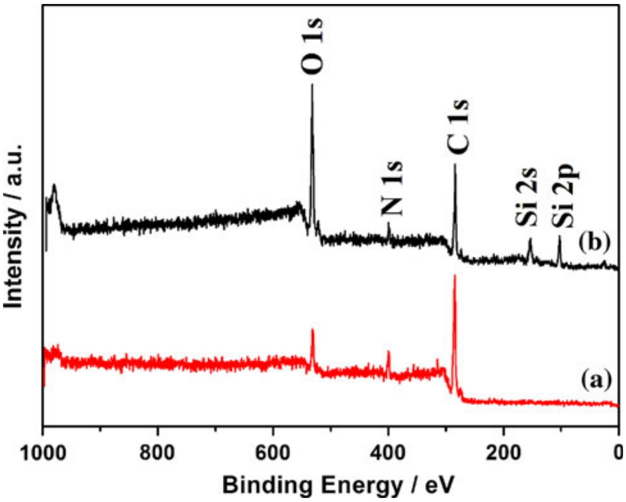

**Fig. 3** XPS spectra of *a* pure nylon 6,6 and *b* surface-modified $SiO_2$/nylon 6,6 nanocomposite film

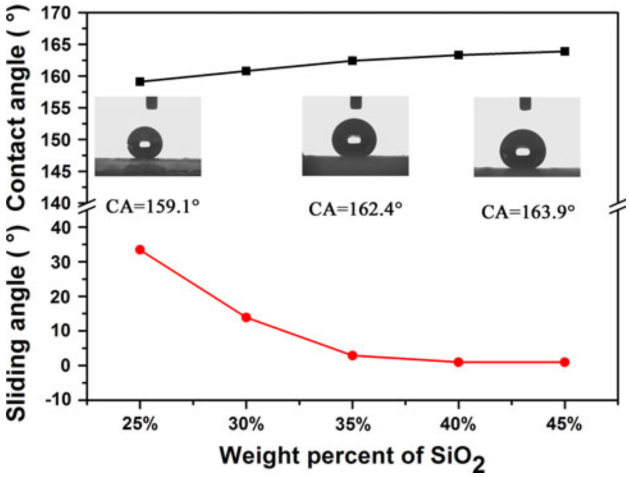

**Fig. 4** The variation of average water contact angle and sliding angle at different weight percent of $SiO_2$ nanoparticles. The *inset* is the corresponding profile of a water droplet on the surface

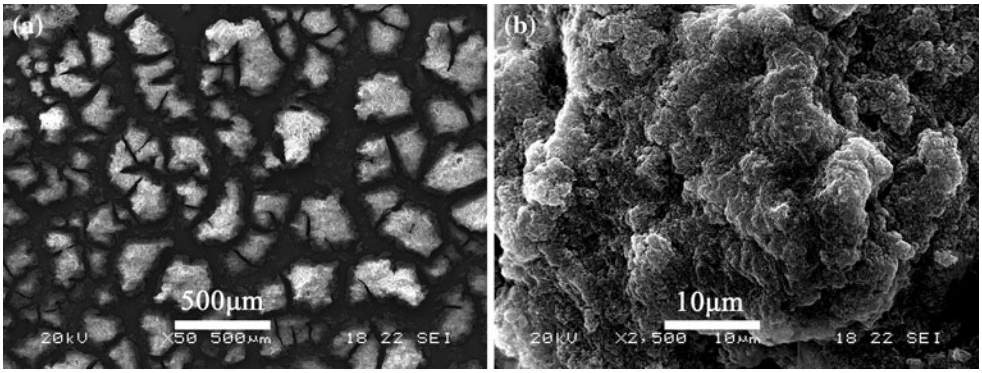

**Fig. 5** SEM images of **a** unmodified $SiO_2$/nylon 6,6 nanocomposite coating and **b** magnified image

almost constant. This observation can be further confirmed by the SA test. The SA change has the reverse trends. In other words, the addition of $SiO_2$ leads to the decrease of SAs.

In order to investigate the influence of the surface-modified $SiO_2$ nanoparticles on the wettability of the coating, the unmodified $SiO_2$ nanoparticles were used to prepare nanocomposite coating with the same method. Figure 5 shows the SEM images of unmodified $SiO_2$/nylon 6,6 nanocomposite coating. Comparing Fig. 5a with Fig. 2a, the surfaces show the similar morphology. From the magnified image (Fig. 5b), it can be seen that the $SiO_2$ nanoparticles aggregate together to form a rough surface. Surprisingly, compared with the water-repellent nanocomposite coating (Fig. 2), the case is just contrary. A water droplet spreads rapidly and wets the surface within 0.5 s and the CA is nearly zero, showing the superhydrophilic property. This extreme wetting behavior can be attributed to the three factors: hydrophilic carbonyl and amide groups of nylon, hydrophilic hydroxyl group of unmodified $SiO_2$, and the rough structure. The understanding of how the surface roughness affects wettability can be explained by the equation derived by Wenzel, $\cos\theta_a = r\cos\theta$, where $\theta$ represents the inherent CA of the smooth surface, $\theta_a$ is the apparent CA of the rough surface and $r$ is defined as the surface roughness [25]. According to Wenzel's equation, on a rough but chemically homogeneous surface, the surface roughness always enhances the underlying wetting characteristics. In other words, it drives a hydrophobic surface to more hydrophobic and a hydrophilic surface to more hydrophilic.

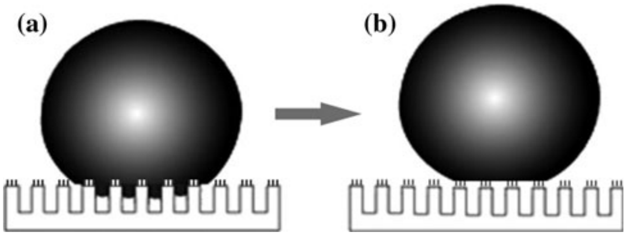

**Fig. 6** Two states of the as-prepared superhydrophobic surfaces. **a** The transitional superhydrophobic state between Wenzel's and Cassie's states; **b** Cassie's state

Though the resulting water CA of the as-prepared surface was always larger than 159°, the SA varied from 33.4° to 1° with further increasing the weight percent of modified $SiO_2$. That is, the CA of the as-prepared coating achieves its maximum and the SA gets its minimum. So we have obtained two superhydrophobic surfaces with a larger adhesion when the weight percent of $SiO_2$ is 25%, and a smaller adhesion when the weight percent of $SiO_2$ increases to above 35%, respectively. In general, there are two superhydrophobic states on a rough surface: Wenzel's state [25] and Cassie's State [26]. The former represents a wet-contact mode of water and rough surface, where water droplets pin the surface and cannot slide on the surface. The latter represents a nonwet-contact mode and water droplets can roll off easily owing to their low adhesive force. However, when the weight percent of modified $SiO_2$ was 25%, the prepared coating in this experiment was superhydrophobic but the water droplets slid away with tilting to 33.4°. That means it is in a state between Wenzel's model and Cassie's model (Fig. 6a). When the weight percent of $SiO_2$ is above 35%, the SA is so low that water droplets can hardly stay on the as-prepared coating, indicating which is in a Cassie's state (Fig. 6b). Noting that this phenomenon was in accordance with Jiang's research, in which six different CA states for superhydrophobic surfaces were brought forward [27–29]. In this article, the variation of SA indicated that a transition from the transitional superhydrophobic state between Wenzel's and Cassie's state to the Cassie's state had occurred as the weight percent of silica was increased (Fig. 6).

Interestingly, the as-prepared surface showed superhydrophobic properties in the pH range from 1 to 14, indicating that the pH of the aqueous solution had little or no effect on the wettability of the surface with 40% modified $SiO_2$. Figure 7 shows the relationship between pH and water CAs on the superhydrophobic surfaces. It is clear that

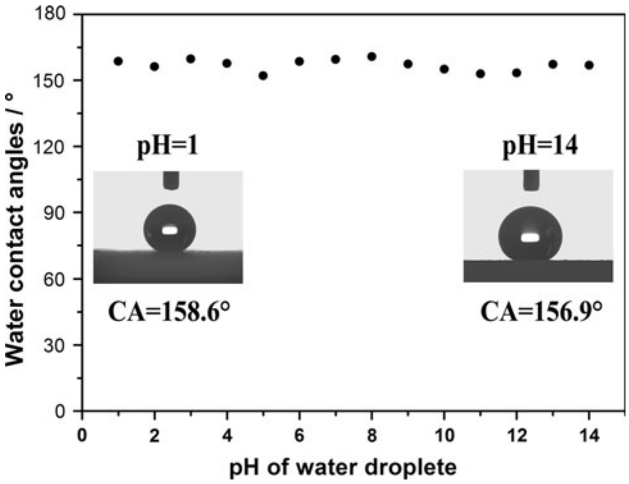

**Fig. 7** Relationship between pH of water droplet and water CAs on the resulting nanocomposite surface with 40% modified $SiO_2$

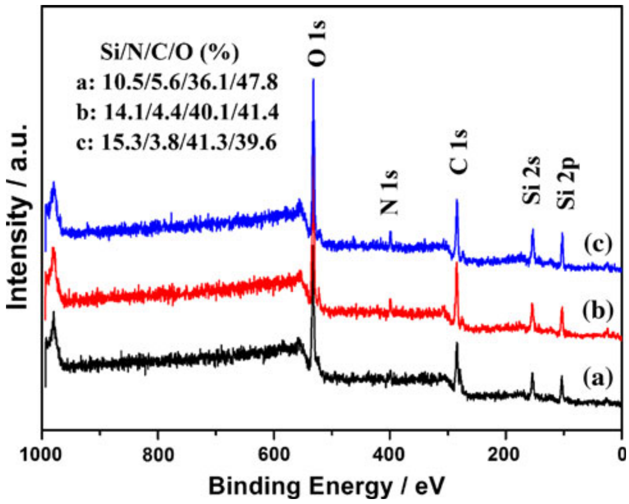

**Fig. 8** XPS spectra of surface-modified $SiO_2$/nylon 6,6 nanocomposite film dried at *a* 20 °C, *b* 40 °C, *c* 60 °C

the water CAs are larger than 150° within experimental time (about 30 s) not only for pure water but also corrosive liquids, such as acidic and basic aqueous solutions. These results are very important for the use of nylon 6,6 as engineering plastics with superhydrophobicity surfaces in the wide pH range of corrosive liquids. Hopefully, such special superhydrophobic properties will greatly extend the applications of nylon 6,6 in many other important industrial fields.

The drying temperatures of the fabrication of nylon 6,6 nanocomposite surfaces were investigated. If the drying temperature was higher than 70 °C, the as-prepared surfaces were easy to shed from the substrate. So the temperature should be limited to 70 °C. When the drying process was carried out at 40, 50, and 60 °C, separately, the results showed that temperature had no apparent influence on the as-formed structure and wettability. But the drying temperatures was lower than 40 °C (such as 20 °C), the as-prepared coating had a water CA of about 140° (>90°, hydrophobic material) but had high adhesive force with water. Figure 8 shows the XPS spectra of modified $SiO_2$/nylon 6,6 nanocomposite coating with addition of 40% $SiO_2$ dried at 20 °C (Fig. 8a), 40 °C (Fig. 8b), and 60 °C (Fig. 8c). It was found that ratio of Si/N/C/O changed from 10.5/5.6/36.1/47.8 to 14.1/4.4/40.1/41.4, and finally to 15.3/3.8/41.3/39.6 as the drying temperature changed from 20 to 40 °C and to 60 °C. It can be seen that the atom concentration of silicon increased obviously, while the atom concentration of nitrogen decreased. As the temperature increased, it can be concluded that $SiO_2$ nanoparticles were brought out to the coating surface by the movement of nylon chain segment. It was the low surface energy modification of $SiO_2$ nanoparticles that affected the wettability of the as-prepared surface.

## Conclusions

In conclusion, we reported an easy way to obtain a superhydrophobic nanocomposite polymer coating using hydrophilic pure nylon 6,6 as original materials. The resulting water CA of the modified surface was always larger than 159°, but the SAs decreased as the content of $SiO_2$ nanoparticles increased. The mechanism was also briefly discussed. The process we used here could be applied to other hydrophilic polymers to produce superhydrophobic surfaces, thereby extending the use of such materials for super wetting applications. Compared with the similar superhydrophobic polymer coatings synthesized by other methods, it is found to be mild, convenient, inexpensive, and efficient.

**Acknowledgement** This study was supported by the National Science Foundation for Distinguished Young Scholars of China (Grant no. 51025517), the Innovative Group Foundation of NSFC (Grant no. 50721062), and the National 973 project of China (2007CB607606).

## References

1. Neinhuis C, Barthlott W (1997) Ann Bot 79:677
2. Oner D, McCarthy TJ (2000) Langmuir 16:7777
3. Erbil HY, Demirel AL, Avci Y, Mert O (2003) Science 299:1377
4. Sorna Gowri V, Almeida L, de Amorim MTP, Pacheco NC, Souto AP, Esteves MF, Sanghi SK (2010) J Mater Sci 45:2427. doi:10.1007/s10853-010-4210-4
5. Lau KKS, Bico J, Teo KBK, Chhowalla M, Amaratunga GAJ, Milne WI, McKinley GH, Gleason KK (2003) Nano Lett 3:1701
6. Feng L, Song Y, Zhai J, Liu B, Xu J, Jiang L, Zhu D (2003) Angew Chem Int Ed 42:800
7. Feng L, Li S, Li H, Zhai J, Song Y, Jiang L, Zhu D (2002) Angew Chem Int Ed 41:1221
8. Song XY, Zhai J, Wang YL, Jiang L (2005) J Phys Chem B 109:4048

9. Furstner R, Barthlott W, Neinhuis C, Walzel P (2005) Langmuir 21:956
10. Hegde ND, Venkateswara Rao A (2007) J Mater Sci 42:6965. doi:10.1007/s10853-006-1409-5
11. Gao Y, Huang YG, Feng SJ, Gu GT, Qing FL (2010) J Mater Sci 45:460. doi:10.1007/s10853-009-3962-1
12. Zhai L, Cebeci FC, Cohen RE, Rubner MF (2004) Nano Lett 4:1349
13. Ming W, Wu D, van Benthem R, de With G (2005) Nano Lett 5:2298
14. Shirtcliffe NJ, McHale G, Newton MI, Chabrol G, Perry CC (2004) Adv Mater 16:1929
15. Hosono E, Fujihara S, Honma I, Zhou HS (2005) J Am Chem Soc 127:13458
16. Jiang L, Zhao Y, Zhai J (2004) Angew Chem Int Ed 43:4338
17. Zhu MF, Zuo WW, Yu H, Yang W, Chen YM (2006) J Mater Sci 41:3793. doi:10.1007/s10853-005-5910-z
18. Huang L, Lau SP, Yang HY, Leong ESP, Yu SF, Prawer S (2005) J Phys Chem B 109:7746
19. Liu XY, Zhang CC, Hang YC (2004) Macromol Rapid Commun 25:1606
20. Zhang L, Zhang XY, Zhe Z, Wu JJ, Zhao N, Xu J (2010) J Colloid Interface Sci 345:116
21. Hou WX, Wang QH (2007) J Colloid Interface Sci 316:206
22. Guo YG, Jiang D, Zhang X, Zhang ZJ, Wang QH (2010) Appl Surf Sci 256:7088
23. Li XH, Cao Z, Liu F, Zhang ZJ, Dang HX (2006) Chem Lett 35:94
24. Hayn RA, Owens JR, Boyer SA, McDonald RS, Lee HJ (2010) J Mater Sci. doi: 10.1007/s10853-010-5100-5
25. Wenzel R (1936) Ind Eng Chem 28:988
26. Cassie ABD, Baxter S (1944) Trans Faraday Soc 40:546
27. Wang S, Jiang L (2007) Adv Mater 19:3423
28. Feng L, Zhang Y, Xi J, Zhu Y, Wang N, Xia F, Jiang L (2008) Langmuir 24:4114
29. Xia F, Jiang L (2008) Adv Mater 20:2842