

Facile Transformation of a Native Polystyrene (PS) Film into a Stable Superhydrophobic Surface via Sol–Gel Process

Shengyang Yang, Su Chen,* Yuan Tian, Cang Feng, and Li Chen

State Key Laboratory of Material-Oriented Chemical Engineering and College of Chemistry and Chemical Engineering, Nanjing University of Technology, No. 5 Xin Mofan Road, Nanjing 210009, P. R. China

Received November 14, 2007

Revised Manuscript Received December 8, 2007

Wettability of surfaces with liquids is a very important property of materials that is governed by both the chemical composition and the geometry of solid surfaces.^{1,2} Recently, the construction of superhydrophobic surfaces with a water contact angle (CA) larger than 150° have attracted great investigative efforts because of their importance in fundamental research and industrial applications.^{3,4} Up to now, a variety of elegant techniques have been rapidly proposed for constructing superhydrophobic materials, such as etching (chemical etching⁵ and plasma etching⁶), post treating,⁷ chemical/physical vapor deposition (CVD/PVD),⁸ densely packed aligned carbon or polymer nanotubes,⁹ sol–gel processing,¹⁰ and others,¹¹ to tailor surface topography and

to enhance hydrophobicity via coating a fabricated rough surface with a hydrophobic thin layer or monolayer. In addition, to date, a large number of materials have been used to prepare superhydrophobic surfaces, including inorganics (such as ZnO¹² and SiO₂¹³), organic polymers (such as polypropylene¹⁴) and their hybrids.¹⁵ Unfortunately, in many cases, the reported approaches employ either expensive materials, such as carbon nanotubes¹⁶ and semi- or per-fluorinated materials,^{10a,11a} or complicated procedures,^{6a,10a} thereby limiting the applications of superhydrophobic surfaces.

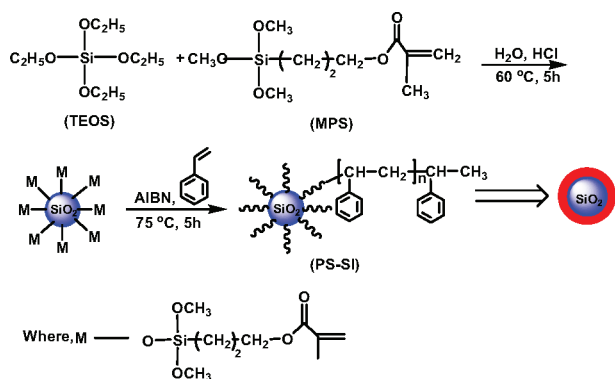
For the purpose of more practical applications, many works are focused on undemanding methods and low-cost materials. Erbil et al.¹⁴ reported a simple and inexpensive method for preparing a gel-like porous superhydrophobic surface of polypropylene. Xie and his co-workers¹⁷ facilely obtained a bionic superhydrophobic surface by PP (polypropylene)–PMMA (polymethylacrylmethacrylate) block copolymer without any low-free-energy modification. Lee et al.¹⁸ fabricated aligned polystyrene (PS) nanofibers by using nanoporous anodic aluminum oxide as a replication template in a nanoimprint pattern transfer process. Jiang's group¹⁹ synthesized a superhydrophobic aligned PS nanotube layer by a simple template-wetting method. In our previous work, we developed a convenient and inexpensive approach for formation of a series of superhydrophobic surfaces via the reaction of metal salts and alkanethiols.²⁰ Here, we desire to demonstrate a straightforward procedure to fabricate a durable superhydrophobic organic–inorganic (PS/SiO₂) hybrid coating without the use of any complex instruments and rigorous experimental conditions. Also, the utilization of this procedure to generate superhydrophobic surfaces has not been described.

Sol–gel process is undoubtedly one of the simplest and the cheapest techniques for the fabrication of materials starting from a chemical solution that reacts to produce colloidal particles. Schematic representation for the formation of PS/SiO₂ sol nanocomposite hybrids (PS-SIs) is shown in Scheme 1. Initially, we fabricated MPS-grafted colloidal silica sols by the synthetic route which can be described as follows: first, the reaction mixture were prepared by mixing tetraethyl orthosilicate (Si(OC₂H₅)₄, TEOS, reagent grade) and methacryloxypropyltrimethoxysilane (MPS, reagent grade) with *N,N'*-dimethylformamide (DMF) ([TEOS]/[MPS] = 10:1

* To whom correspondence should be addressed. Tel. & Fax: 86-25-83587194. E-mail: chensu@njut.edu.cn.

- (1) (a) Barthlott, W.; Neinhuis, C. *Planta* **1997**, *202*, 1. (b) Neinhuis, C.; Barthlott, W. *Ann. Bot.* **1997**, *79*, 667.
- (2) (a) Wenzel, R. N. *Ind. Eng. Chem.* **1936**, *28*, 988. (b) Cassie, A. B. D.; Baxter, S. *Trans. Faraday Soc.* **1944**, *40*, 546.
- (3) (a) Blosssey, R. *Nat. Mater.* **2003**, *2*, 301. (b) Lafuma, A.; Quéré, D. *Nat. Mater.* **2003**, *2*, 457. (c) Gao, X.; Jiang, L. *Nature* **2004**, *432*, 36.
- (4) (a) Sun, T. L.; Feng, L.; Gao, X. F.; Jiang, L. *Acc. Chem. Res.* **2005**, *38*, 644. (b) Wang, S.; Feng, L.; Jiang, L. *Adv. Mater.* **2006**, *18*, 767. (c) Ma, M. L.; Hill, R. M. *Curr. Opin. Colloid Interface Sci.* **2006**, *11*, 193.
- (5) (a) Zhang, X.; Shi, F.; Yu, X.; Liu, H.; Fu, Y.; Wang, Z. Q.; Jiang, L.; Li, X. Y. *J. Am. Chem. Soc.* **2004**, *126*, 3064. (b) Shi, F.; Wang, Z.; Zhang, X. *Adv. Mater.* **2005**, *17*, 1005. (c) Yu, X.; Wang, Z. Q.; Jiang, Y. G.; Shi, F.; Zhang, X. *Adv. Mater.* **2005**, *17*, 1289. (d) Zhao, N.; Shi, F.; Wang, Z. Q.; Zhang, X. *Langmuir* **2005**, *21*, 4713.
- (6) (a) Oner, D.; McCarthy, T. J. *Langmuir* **2000**, *16*, 7777. (b) Shiu, J. Y.; Kuo, C. W.; Chen, P.; Mou, C. Y. *Chem. Mater.* **2004**, *16*, 4.
- (7) (a) Khorasani, M. T.; Mirzadeh, H. *J. Appl. Polym. Sci.* **2004**, *91*, 2042. (b) Khorasani, M. T.; Mirzadeh, H.; Kermani, Z. *Appl. Surf. Sci.* **2005**, *242*, 339.
- (8) (a) Wu, Y.; Sugimura, H.; Inoue, Y.; Takai, O. *Chem. Vap. Deposition* **2002**, *8*, 47. (b) Liu, H.; Feng, L.; Zhai, J.; Jiang, L.; Zhu, D. B. *Langmuir* **2004**, *20*, 5659. (c) Zhu, L. B.; Xiu, Y. H.; Xu, J. W.; Tamirisa, P. A.; Hess, D. W.; Wong, C. P. *Langmuir* **2005**, *21*, 11208.
- (9) (a) Li, H.; Wang, X.; Song, Y.; Liu, Y.; Li, Q.; Jiang, L.; Zhu, D. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 1743. (b) Feng, L.; Li, S.; Li, H.; Zhai, J.; Song, Y.; Jiang, L.; Zhu, D. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 1221.
- (10) (a) Nakajima, A.; Fujishima, A.; Hashimoto, K.; Watanabe, T. *Adv. Mater.* **1999**, *11*, 1365. (b) Tadanaga, K.; Kitamuro, K.; Matsuda, A.; Minami, T. *J. Sol–Gel Sci. Technol.* **2003**, *26*, 705. (c) Shirlcliffe, N. J.; McHale, G.; Newton, M. I.; Perry, C. C. *Langmuir* **2003**, *19*, 5626.
- (11) (a) Tsujii, K.; Yamamoto, T.; Onda, T.; Shibuichi, S. *Angew. Chem., Int. Ed.* **1997**, *36*, 1011. (b) Bico, J.; Marzolin, C.; Quéré, D. *Europhys. Lett.* **1999**, *47*, 220. (c) Genzer, J.; Efimenko, K. *Science* **2000**, *290*, 2130. (d) Jiang, L.; Zhao, Y.; Zhai, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 4338.

- (12) (a) Feng, X. J.; Feng, L.; Jin, M. H.; Zhai, J.; Jiang, L.; Zhu, D. B. *J. Am. Chem. Soc.* **2004**, *126*, 62. (b) Huang, L.; Lau, S. P.; Yang, H. Y.; Leong, E. S. P.; Yu, S. F. *J. Phys. Chem. B* **2005**, *109*, 7746.
- (13) (a) Han, J. T.; Xu, X. R.; Cho, K. *Langmuir* **2005**, *21*, 6662. (b) Daoud, W. A.; Xin, J. H.; Tao, X. M. *J. Am. Ceram. Soc.* **2004**, *87* (9), 1782.
- (14) Erbil, H. Y.; Demirel, A. L.; Avci, Y.; Mert, O. *Science* **2003**, *299*, 1377.
- (15) Han, J. T.; Zheng, Y.; Cho, J. H.; Xu, X.; Cho, K. *J. Phys. Chem. B* **2005**, *109*, 20773.
- (16) Sun, T. L.; Wang, G. J.; Liu, H.; Feng, L.; Jiang, L.; Zhu, D. B. *J. Am. Chem. Soc.* **2003**, *125*, 14996.
- (17) Xie, Q. D.; Fan, G. Q.; Zhao, N.; Guo, X. L.; Xu, J.; Dong, J. Y.; Zhang, L. Y.; Zhang, Y. J.; Han, C. C. *Adv. Mater.* **2004**, *16*, 1830.
- (18) Lee, W.; Jin, M. K.; Yoo, W. C.; Lee, J. K. *Langmuir* **2004**, *20*, 7665.
- (19) Jin, M. H.; Feng, X. J.; Feng, L.; Sun, T. L.; Zhai, J.; Li, T. J.; Jiang, L. *Adv. Mater.* **2005**, *17*, 1977.
- (20) Chen, S.; Hu, C. H.; Chen, L.; Xu, N. P. *Chem. Commun.* **2007**, 1919.

Scheme 1. Schematic Illustration of the Preparation Route to Form the PS-SIs


mol/mol), followed by stirring the mixture for 4 h until it was homogeneous. Then, the reaction of the mixture occurred at 60 °C for 5 h after adding deionized water and little hydrochloric acid solution (36 wt%) ([TEOS]:[H₂O]:[DMF]=1:6:4 mol/mol). Finally, the MPS-grafted colloidal silicate suspensions were formed and immediately purified through dialysis against water.

Subsequently, we prepared PS-SIs via free-radical polymerization using MPS-grafted colloidal silicate, styrene monomer, azoisobutyronitrile (AIBN) initiator, and DMF. Styrene monomer (20 g, Aldrich), AIBN (0.04 g, AIBN = 0.02 wt %), and 40 g of DMF containing 1.4 g of nanosized MPS-grafted silica sol (SiO₂ = 0.7 wt %) were mixed in a round-bottom flask at room temperature for 30 min. The mixtures were then reacted at 75 °C for 5 h under a nitrogen-protected atmosphere, and the prepared solution was coated on clean glass slides in the next procedure.

Figure 1 shows a typical transmission electron microscope (TEM) image of the as-prepared PS-SIs surface on which geometrical structures of cocklebur-like morphology have been demonstrated. The disperse nanocomposite particles, which are regular in shape and display a narrow particle size distribution (~120 nm), have distinct with PS chains grafted onto the surface of the nanosilica cores. The inset magnification image clearly displays the size of MPS-functionalized silica cores ranges from 40 to 80 nm, and that of PS shell is about 30 nm. The result nicely coincides with our suggested mechanism and indicates the dispersibility of the PS-covered silica nanoparticles in polymeric matrices is well-enhanced.

To compare the water contact angle of native PS film with that of the PS-SI hybrid film, we prepared these two kinds of samples by spin-coating the corresponding solution onto clean glass substrates, and drying them only at room temperature. Figure 2 shows the scanning electron microscope (SEM) images of prepared samples and the shapes of water droplets on the surfaces are inserted. Compared with the CA (84°) on the native PS film (Figure 2a), the CA value of the translucent PS-SI hybrid film (SiO₂ = 0.7 wt %) reaches to 106°, indicating that the well-dispersed spherical silica nanoparticles formed on the surface enhanced the roughness and its hydrophobicity (Figure 2b). On the other hand, the MPS-grafted silica nanoparticles may yield hydrophobic functionalized methacrylate groups on the surface

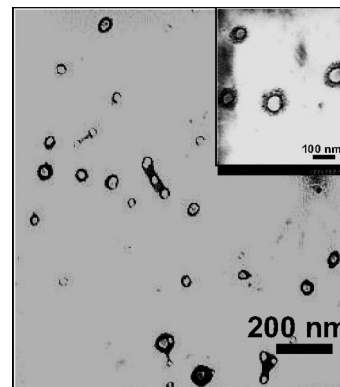


Figure 1. TEM images of cocklebur-like PS-SIs (SiO₂ = 0.7 wt %) with low and high magnifications.

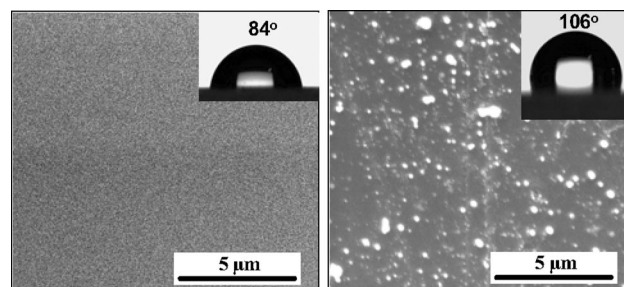


Figure 2. SEM images of the surfaces of (a) native PS and (b) PS-SIs (SiO₂ = 0.7 wt %). Inset: Water drop profile in CA measurement (5 µL droplet size) on corresponding surfaces.

of silica, resulting in a decreased of the surface energy of the system. Therefore, the solvent resistance of PS-SI hybrids was reinforced by the synergistic action between PS and silica nanoparticles.

Obviously, the hydrophobicity of PS-SI film precedes the native PS film; however, it is still insufficient to be classified as superhydrophobic.^{1,2} We employed surface etching technologies (SET) to create the rough surface by pure tetrahydrofuran (THF) solution and dodecanethiol solution to mimic the lotus surface. PS-SI was dissolved in DMF to a concentration of 30 wt % and the diluent hybrids were directly spin-coated on a clean glass substrate. Then, the substrate was dried at 85 °C under reduced pressure conditions. The substrate coated with PS-SIs (SiO₂ = 0.7 wt %) was sprinkled by 1 mL tetrahydrofuran (THF) three times and dried in an ambient environment. The other hybrid film was prepared as previously described, slantwise immersed in a dodecanethiol (DDT) solution during 5 min sonication, followed by subsequent rinsing with plenty of ethanol and then dried under an ambient environment. The SEM images of the rough surfaces of PS-SIs film (SiO₂ = 0.7 wt %) after treatment are shown in Figure 3. As seen in Figure 3a, by dip-etching THF on the top of the surface at ambient temperature, the film surface revealed a random distribution of “platelike” pores with the diameter ranging from about 300 nm to 5 µm. Because THF is a nonsolvent for silica but a good solvent for PS, we suppose that the big pores are derived from the region containing lower concentration of nanosilica in the PS matrix, which are attributed to the etching effect of THF. On the contrary, the small pores are derived from the region containing relative higher

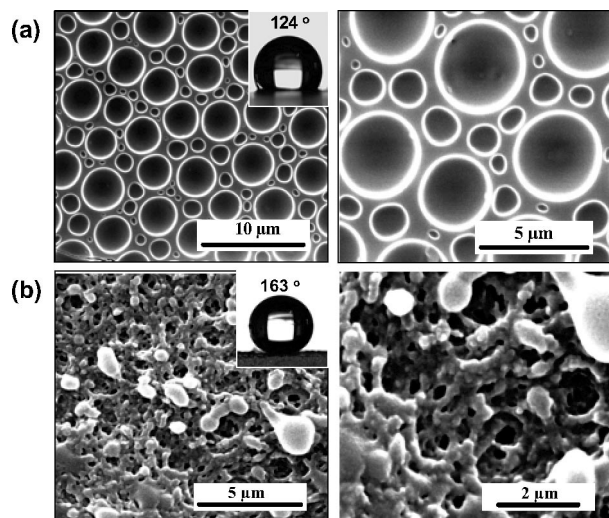


Figure 3. SEM images of the surfaces of PS-SiO₂ film (SiO₂ = 0.7 wt%) (a) dip-etched by THF solution, and (b) treated by dodecanethiol solution with SET. Inset images indicate the CA of a 5 μ L water drop on the corresponding surface.

concentration of nanosilica, which result in the improvement of the chemical resistance of the film. The micrometer-sized pores array together regularly and thus increase the surface roughness. As a result, the water repellency increases sharply with a CA from 106 to 124° (Figure 3a inset). When PS-SiO₂ (SiO₂ = 0.7 wt%) film was immersed in DDT solution under controlled sonication for a short time (about 5 min), the morphology of the as-formed surface was much different (Figure 3b). The film shows an interesting hierarchical structure with dispersed cavities and protuberances in microscale. The size of the microprotuberances ranges from approximately 500 nm to 1 μ m. On the top of the microprotuberances, some nanoparticles (~60 nm) can be obviously observed in the magnified image of the Figure 3b. The reason is that the free PS matrix is gradually dissolved in DDT and the silica nanoparticles remained on the surface and aggregated to form protuberances under the controllable energy of sonication. In this case, the as-prepared hybrid films possess a bionic micro/nanoscales binary structure and exhibit superhydrophobic properties. Air can be adequately trapped among the hierarchical structure and the CA on the surface reaches to 163° (Figure 3b inset), almost twice that on smooth PS surface. Further evidence for the superhydrophobicity of the surface is given by the low tilt angle that reflects the difference between advancing and receding contact angle. The tilt angle on the surface is $4.8 \pm 1.3^\circ$, indicating that water droplets roll off easily.

To further understand the superhydrophobicity of PS-SiO₂ film, it is necessary to explain the air trapped phenomenon theoretically. As proposed in the literature, the relationship between the CA of a smooth PS θ surface and that of a PS-SiO₂ rough surface θ_r is described by Cassie–Baxter eq 1^{2b}

$$\cos\theta_r = f_1\cos\theta - f_2 \quad (1)$$

where f_1 and f_2 are the fractions of solid contact area and air contact area with water, respectively (i.e., $f_1 + f_2 = 1$). It can be deduced from this equation that the fraction of the air (f_2) increases with increasing θ_r . That is to say, the larger air contact fraction will boost the superhydrophobicity of the films. According to the previous data ($\theta_r = 163^\circ$), the value f_2 calculated by eq 1 was about 0.96, which denotes well-superhydrophobic. Also, it indicates that the air trapped in the rough surface by combining micro- and nanostructure is very important to superhydrophobicity, because air that is trapped between the water droplets and the rough film minimized the contact area.

In conclusion, we have successfully prepared superhydrophobic PS-SiO₂ films with a hierarchical structure consisting of macro-cavities and nanotextures through a facile and inexpensive approach. The rough hierarchical micro/nanostructures that contribute to superhydrophobic properties are controlled in the preparation of this type of materials. A parallel approach to that of this investigation constitutes a promising way to fabricate superhydrophobic surfaces via chemically tailor-made design. We anticipate that this procedure can be expanded to a variety of commercial materials other than PS, including polypropylene (PP), polyacrylate (PA), poly(vinyl chloride) (PVC). Practical applications, for instance, in the self-cleaning field, may follow. Hence, systematic research on surfaces of sol–gel polymer nanocomposites continues.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (Grants 20606016, 10676013, 20576053), the Natural Science Foundation of Jiangsu province of China (Grant BK2005119), and the Natural Science Foundation of the Jiangsu Higher Education Institutions of China (Grant 07KJA53009).

Supporting Information Available: Summaries of the various characterizations studies, including the results of Fourier transform infrared spectrometer (FT-IR), atomic force microscope (AFM), and transmission electron microscope (TEM) (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

CM703220R