New Approach to Fabricate an Extremely Super-amphiphobic Surface Based on Fluorinated Silica Nanoparticles

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ABSTRACT: Superoleophobic surfaces possessing static contact angles greater than $140°$ with organic liquids are extremely rare. A simple approach has been developed to fabricate an extremely superamphiphobic coating material based on fluorinated silica nanoparticles resulting contact angles of water and diiodomethane at $167.5°$ and $158.6°$, respectively. The contact angle of diiodomethane at $158.6°$ is substantially higher than the highest literature reported value we know of at $110°$. In addition, this developed film also possesses extremely high contact angles with other organic liquids such as soybean oil ($146.6°$), decahysronaphthalene ($142.5°$), diesel fuel ($140.4°$), and xylene ($140.5°$). This developed superamphiphobic organic–inorganic hybrid film possesses unique liquid repellency for both water and organic liquids that can be used as functional coatings on numerous substrates by a simple coating process. © 2008 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 46: 1984–1990, 2008
**Keywords:** biomimetic; composites; fluorination; hybrid; nanoparticles; super-amphiphobic

INTRODUCTION

Liquid repellency is an important property for a solid surface in many industrial and biological applications.[1–6] Lotus leaves naturally repel water and have inspired development of many synthetic water-repellent surfaces. Numerous studies have suggested that the superhydrophobic character of the lotus leaf surface is attributable to a combination of surface chemistry and roughness on multiple scales. However, a liquid with a markedly lower surface tension spreads rapidly across the lotus leaf leading to a contact angle of

$\sim 0°$,[7] and there are few approaches to fabricate superamphiphobic surfaces.[8] The wettability of a surface is determined by a combination of its chemical properties and topographical microstructures. The chemical modification of a surface can alone lead to water contact angles of up to $120°$ by using fluoropolymeric coatings or silane layers.[9] However, it is still insufficient to produce a superamphiphobic surface, which usually requires the contact angles of water larger than $150°$. One method to improve the liquid repellency of a surface is to combine a suitable chemical structure (low surface energy) with a topographical microstructure (roughness). Previous attempts included preparing a fractal surface,[10] plasma treating polymer surfaces,[11,12] functionalizing roughened substrates with perfluoroalkyl groups,[13] preparing gel-like roughened polymers through solvent

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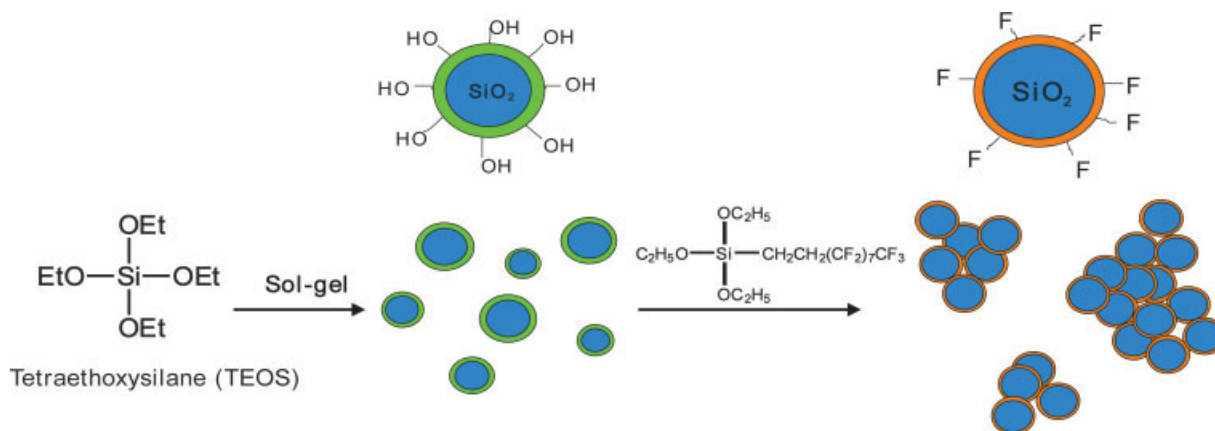
Scheme 1. Preparation of the fluorinated silica nanoparticle. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

processing,[14] phase separating polymer blends,[15] densely packing aligned carbon nanotubes,[16–18] self-assembling monolayers of *n*-alkanoic acids on electrochemical deposition copper films,[19] and other approaches.[20]

Because of its mild operative conditions, sol-gel process[21] has been employed to prepare the inorganic network from liquid precursors such as metal alkoxides and organic oligomers, preferably with suitable reactive groups. In fact, the covalent bonding between organic and inorganic components can lead to the formation of a crosslinked structure in which the organic and inorganic moieties are phase separated on a micro- or nanoscale, but the resulting material is macroscopically uniform. Perfluoropolyether-based organic–inorganic hybrids prepared by sol-gel process possess a strong hydrophobic and oleophobic character and have been applied as functional coatings onto glass

substrates.[22] However, there are few reports that have revealed the superamphiphobic character for organic–inorganic hybrids prepared from sol-gel reaction. In this context, we discovered that the silica nanoparticles prepared by sol-gel process modified with 1H,1H,2H,2H-perfluorodecyltriethoxysilane (PFTS) possessing extremely superamphiphobic character. In addition, these fluorinated silica nanoparticles can be used as functional coatings to prepare water- and oil-repellent glasses or other substrates by simple coating process.
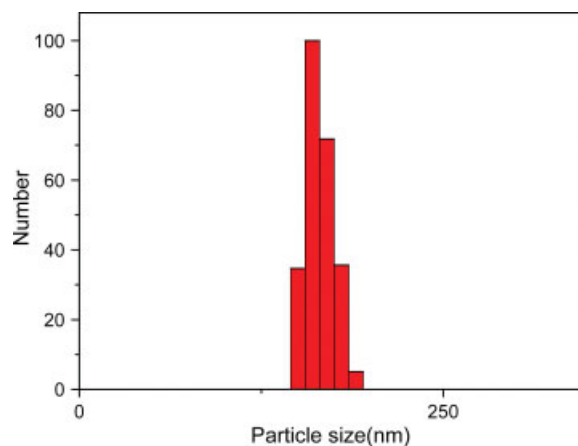
EXPERIMENTAL

Materials

All chemicals were used as received. Tetraethoxysilane (TEOS) was supplied by the Aldrich
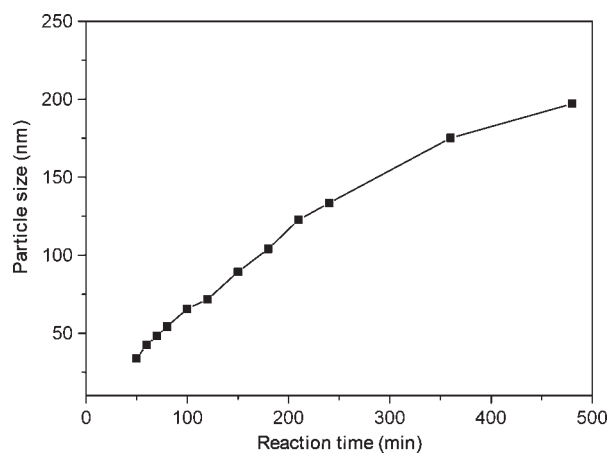
Figure 1. Relation between silica nanoparticle size and sol-gel reaction time.

Figure 2. Hydrodynamic diameter distribution of the silica nanoparticle after being fluorinated. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Chemical Company. PFTS was supplied by the Degussa Chemical Company. Isopropyl alcohol (IPA) and ammonium hydroxide (28 wt %) were supplied by the Tedia Chemical Company.

Preparation of Fluorinated Silica Nanoparticles

About 2.0 g of TEOS were added to 21 mL IPA and mixed until a homogeneous solution was obtained. Then 0.8 g ammonium hydroxide (28 wt %) was added under vigorous stirring and refluxed at 60 °C. Finally, PFTS was added to terminate the reaction until the time of sol-gel reaction was 100 min.

Fabrication of Super-Amphiphobic Surfaces

Superamphiphobic coating on a glass slide was performed through spin-coating process. Fluorinated silica nanoparticles dispersed in IPA as 10 wt % mixture was spin-coated on a glass slide ($100 \times 100 \times 1$ mm^3) at 1500 rpm for 45 s.

Dynamic Light Scattering

The size and distribution of silica nanoparticles and fluorinated silica nanoparticles were measured by dynamic light scattering (DLS). DLS measurement was performed on a Brookheaven 90 plus model equipment (Brookheaven Instruments Corp., USA) with a He-Ne laser with a power of 35 mW at 632.8 nm. The temperature was controlled at 20 °C, and the measurement was done at an angle of 90°.

Scanning Electron Microscopy

The microstructure of the fluorinated silica nanoparticle films was characterized using a JOEL JSM 6500-F scanning electron microscopy (SEM) instrument.

Atomic Force Microscopy

Atomic force microscopy (AFM) images were acquired using a Veeco MultiMode scanning probe microscope. Damage to both the tip and the sample surface was minimized by employing the AFM in the tapping mode. The values of root-mean-square (rms) roughness were calculated over scan area of 10 μm $\times$ 10 μm.
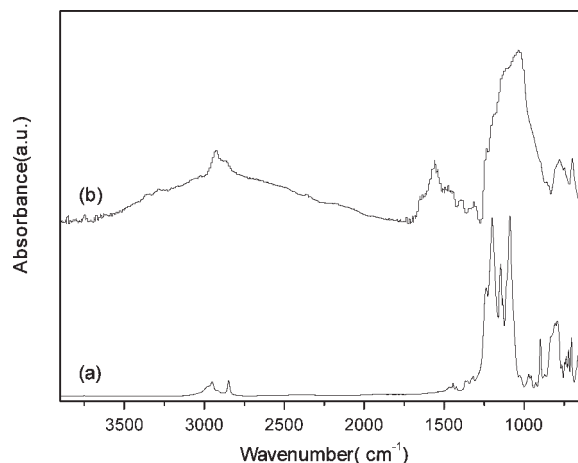
Figure 3. The infrared absorption spectra of the (a) 1H,1H,2H,2H-perfluorodecyl-triethoxysilane and (b) the silica gels with treatment of 1H,1H,2H,2H-perfluorodecyltriethoxysilane.

Fourier Transform Infrared Spectroscopy

All infrared spectra were recorded at using a Nicolet Avatar 320 Fourier transform infrared spectroscopy (FTIR) spectrophotometer, 32 scans were collected with a spectral resolution of 1 cm^{-1}. Infrared spectrum of the polymer film was determined with the conventional potassium bromide (KBr) plate method. The sample was prepared by casting the IPA solution directly onto a KBr plate.

Electron Spectroscopy for Chemical Analysis

Chemical composition in the substrate surface was analyzed using a VG Scientific Microlab 310F spectrometer using a monochromatic Al Ka X-ray source (1486.6 eV photons) and the vacuum in the analysis chamber was maintained at about 10^{-9} Torr or lower.

Contact Angle Measurement

The static contact angles of the fluorinated silica nanoparticle films were determined by contact angle goniometry at 25 °C using a Krüss GH-100 goniometer interfaced with image-capture software by injecting a 5 μL liquid drop. To obtain reliable contact data, at least three droplets were dispensed at different regions of the same piece of film, and at least two pieces of film were used to obtain reliable contact angle data.
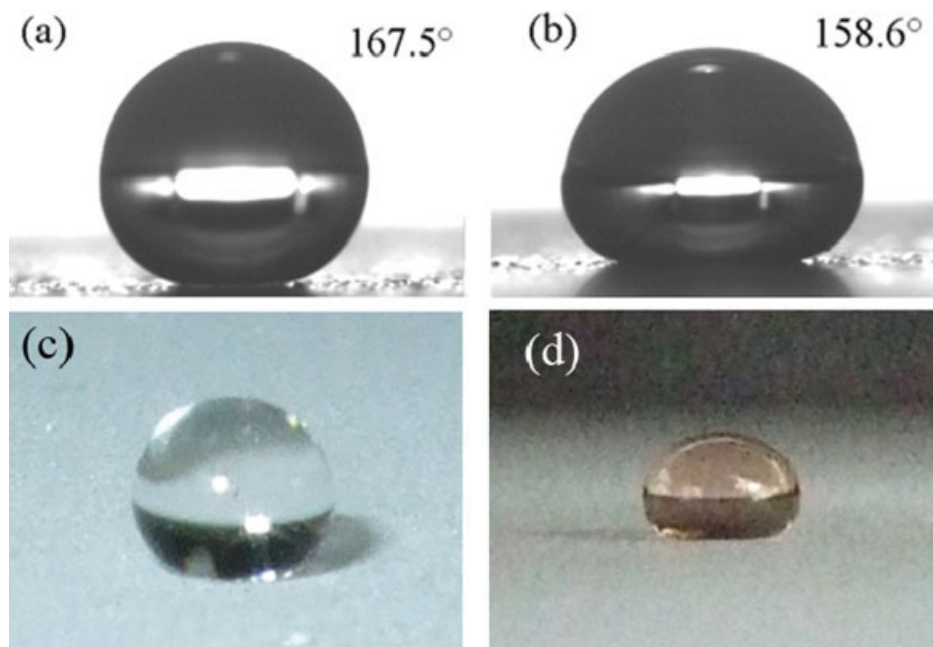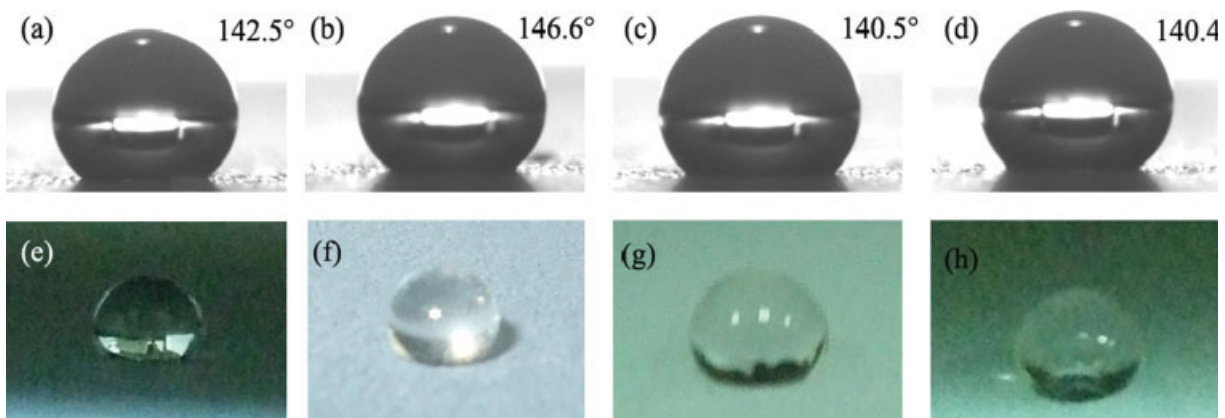
Figure 4. Liquids on fluorinated silica nanoparticle film (a) 5 μL water, (b) 5 μL diiodomethane optical images of liquids, (c) water, (d) diiodomethane.

RESULTS AND DISCUSSION

The process of preparation of fluorinated silica nanoparticles is shown in Scheme 1 and the DLS and FTIR were carried out to confirm the character of the fluorinated silica nanoparticle. The relationship between the average silica nanoparticle size and sol-gel reaction time is shown in Figure 1, the silica nanoparticle size increases as sol-gel time is increased. After the addition of the PTFS to terminate sol-gel reaction, the sizes of the fluorinated silica nanoparticles are found at 165 nm

as shown in Figure 2. The multifunctional groups of the terminal agent induce some aggregation of those fluorinated silica nanoparticls; therefore, the size of the fluorinated silica nanoparticles is significantly larger than the original silica nanoparticles. Figure 3 shows the infrared absorption spectra of the (a) PFTS and (b) the silica gels treated with PFTS. According to previous report,[23] absorption peaks at 1000–1400 cm^{-1} are attributed to the fluorocarbon molecules, the bands at 3200–3800 cm^{-1} are assigned to silanol groups, and the bands below 1100 cm^{-1} are


Figure 5. Five microliter liquids on fluorinated silica nanoparticle film (a) decahydronaphthalene, (b) soybean oil, (c) diesel fuel, (d) xylene and optical images of liquids, (e) decahydronaphthalene, (f) soybean oil, (g) diesel fuel, (h) xylene.
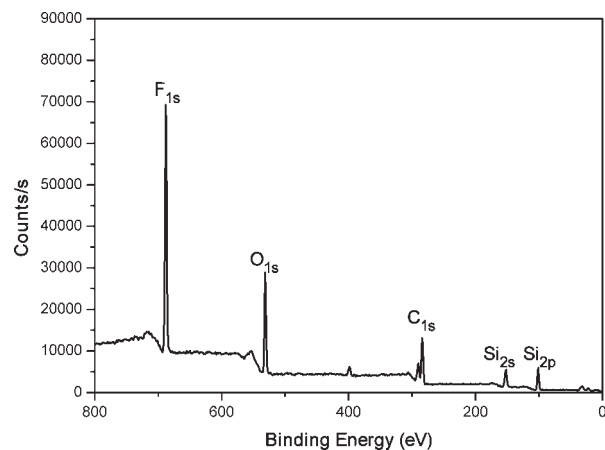
Figure 6. ESCA spectrum of the fluorinated silica nanoparticle film.

attributed to the vibrations of both Si—O—Si bonds and polyfluorocarbon chain. From Figure 3, it is obvious that the silica gels are coated with PFTS.

Static contact angle analyses were applied to characterize the hydrophobicity and oleophobicity of the organic–inorganic hybrid film. As shown in Figure 4, the static contact angles of water and diiodomethane are 167.5° and 158.6° (sliding angles were less than 3°). According to previous reports,[22,24] the highest static contact angles for water and diiodomethane for thin films prepared by sol-gel process are 146.8° and 110°. In addition, the static contact angles of other organic liquids, soybean oil, decahydronaphthalene, diesel fuel, and xylene are 146.6°, 142.5°, 140.4°, and 140.5° as shown in Figure 5. Contact angle measurements reflect the characteristics of the interface between coating film and the probe liquid, including both thermodynamic interactions and surface roughness. Thermodynamic interactions are related to the composition of the surface but contact angle analysis does not give direct information about relative concentration of different atoms; therefore, an independent evaluation of
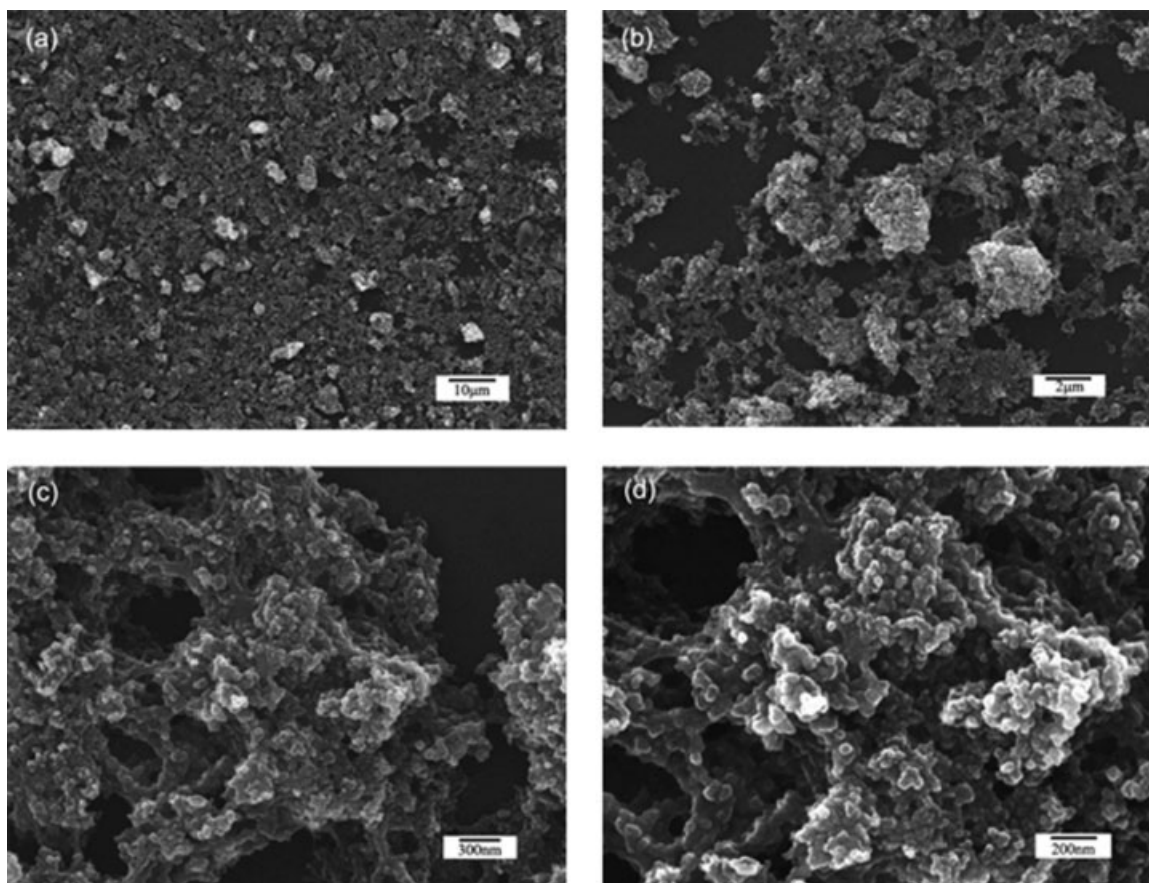
Figure 7. SEM images with different magnification of fluorinated silica nanoparticle film. (a) 1 k, (b) 5 k, (c) 30 k, (d) 50 k.
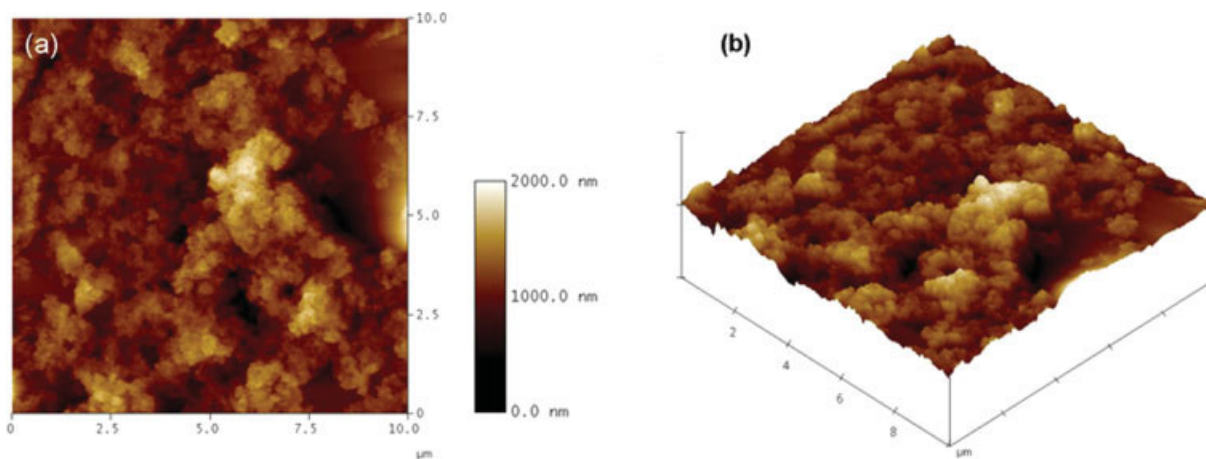
Figure 8. AFM images of (a) fluorinated silica nanoparticle film (b) 3D image of fluorinated silica nanoparticle film. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

surface characteristics of the hybrid material was obtained by electron spectroscopy for chemical analysis (ESCA) analysis to elucidate the composition of the outermost layer (2–3 nm) of the coatings. Figure 6 shows ESCA overview scan on the fluorinated silica nanoparticle hybrid film. The calculated relative elemental contents are C(1s):O(1s):F(1s):Si(2p) = 37:19:13:31, implying that a strong surface enrichment of organic phase with respect to the inorganic silica phase (Si and O atoms). It has been reported and accepted that the low surface energy behavior of a fluoro-containing polymer is caused by segregation of the fluorinated segment on the surface and thus creates a hydrophobic surface. As a result, the surface of silica nanoparticle modified by PFTS (the C% and F% for fluorinated silica nanoparticle were 37 and 31%) display the unique hydrophobicity and olephobicity behavior.

The topographical microstructure of a surface is the other important factor to affect the wettability of a surface in addition to its chemical properties. Combination of a suitable chemical structure (surface energy) with a topographical microstructure (roughness) leads to the static contact angles of this organic–inorganic hybrid film greater than 150°. From SEM images shown in Figure 7, this superamphiphobic surface gives a rough surface possessing both micro- and nanoscale binary structures. The root-mean-square roughness of this fluorinated silica nanoparticle film is 280.1 nm calculated from AFM image as shown in Figure 8. Combined micro- and nanoscale binary structures and chemical composition, the static

contact angles for hydrophilic and hydrophobic liquids are larger than 140° with sliding angles less than 3°.

CONCLUSIONS

A simple method has been developed to modify the surface of silica nanoparticles with PFTS using sol-gel process. The coated film of this organic–inorganic hybrid possesses unique liquid repellency for water, diiodomethane, soybean oil, decahydronaphthalene, xylene, and diesel fuel. Furthermore, this extremely superamphiphobic film can be prepared by simple coating process, which could have an impact on a wide range of phenomena, including biofouling by marine organisms, loss of self-cleaning ability of plant leaves in polluted waters, and swelling of elastomeric seals and O-ring.

REFERENCES AND NOTES

1. Aussillous, P.; Que're', D. Nature 2001, 411, 924–928.
2. Feng, L.; Song, Y.; Zhai, J.; Liu, B.; Xu, J.; Jiang, L.; Zhu, B. Angew Chem Int Ed Engl 2003, 42, 800–802.
3. Zhang, J.; Lu, Y.; Huang, W.; Han, Y. Macromol Rapid Commun 2005, 26, 477–480.
4. Tsujii, K.; Yamamoto, T.; Onda, T.; Shibuichi, S. Angew Chem Int Ed Engl 1997, 36, 1011.
5. Youngblood, J. P.; McCarthy, T. J. Macromolecules 1999, 32, 6800–6806.

6. Wang, C. F.; Chiou, S. F.; Ko, F. H.; Chou, C. T.; Lin, H. C.; Huang, C. F.; Chang, F. C. Macromol Rapid Commun 2006, 27, 333–337.

7. Barthlott, W.; Neinhuis, C. Planta 1997, 202, 1–8.

8. (a) Coulson, S. R.; Woodward, I. S.; Badyal, J. P. S. Langmuir 2000, 16, 6287–6293; (b) Coulson, S. R.; Woodward, I. S.; Badyal, J P. S. Chem Mater 2000, 12, 2031–2038; (c) Chen, W.; Fadeev, A. Y.; Hsieh, M. C.; Oner, D.; Youngblood, J.; McCarthy, T. J Langmuir 1999, 15, 3395–3399; (d) Tuteja, A.; Choi, W.; Ma, M.; Mabry, J. M.; Mazzella, S. A.; Rutledge, G. C.; McKinley, G. H.; Cohen, R. E. Science 2007, 318, 1618–1622.

9. Shafrin, E. G.; Zisman, W. A. In Contact Angle, Wettability, and Adhesion; Fowkes, F. M., Ed.; Advances in Chemistry Series; American Chemical Society: Washington, DC, 1964; p 145.

10. Onda, T.; Shibuichi, S.; Satoh, N.; Tsujii, K. Langmuir 1996, 12, 2125–2127.

11. Morra, M.; Occhiello, E.; Garbassi F. Langmuir 1989, 5, 872–876.

12. Woodward, I.; Schofield, W. C. E.; Roucoules, V.; Badyal, J. P. S. Langmuir 2003, 19, 3432–3438.

13. Tsujii, K.; Yamamoto, T.; Onda, T.; Shibuichi, S. Angew Chem Int Ed Engl 1997, 9, 36, 1011–1012.

14. Erbil, H. Y.; Demirel, A. L.; Avci, Y.; Mert, O. Science 2003, 299, 1377–1380.

15. Xie, Q.; Xu, J.; Feng, L.; Jiang, L.; Tang, W.; Luo, X.; Han, C. C. Adv Mater 2004, 16, 302–305.

16. Lau, K. K. S.; Bico, J.; Teo, K. B. K.; Chhowalla, M.; Amaratunga, G. A. J.; Milne, W. I.; McKinley, G. H.; Gleason, K. K. Nano Lett 2003, 3, 1701–1705.

17. Feng, L.; Li, S.; Li, Y.; Li, H.; Zhang, L.; Zhai, J.; Song, Y.; Liu, B.; Jiang, L.; Zhu, D. Adv Mater 2002, 14, 1857–1860.

18. Li, H.; Wang, X.; Song, Y.; Liu, Y.; Li, Q.; Jiang, L.; Zhu, D. Angew Chem In Ed Engl 2001, 40, 1743–1746.

19. Wang, S.; Feng, L.; Liu, H.; Sun, T.; Zhang, X.; Jiang, L.; Zhu, D. Chem Phys Chem 2005, 6, 1475–1478.

20. Ishida, H.; Allen, D. J. J Polym Sci Part B: Polym Phys 1996, 34, 1019–1084.

21. Brinker, C.; Scherer, G. Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing; Academic Press: Boston, 1990.

22. (a) Fabbri, P.; Messori, M.; Montecchi, M.; Pilati, F.; Taurino, R.; Tonelli, C.; Toselli, M. J Appl Polym Sci 2006, 102, 1483–1488; (b) Fabbri, P.; Messori, M.; Montecchi, M.; Nannarone, S.; Pasquali, L.; Pilati, F.; Tonelli, C.; Toselli, M. Polymer 2006, 47, 1055–1062.

23. Monde, T.; Nakayama, N.; Yano, K.; Yoko, T.; Konakahara, T. J Colloid Interface Sci 1997, 185, 111–118.

24. (a) Gu, G.; Dang, H.; Zhang, Z.; Wu, Z. Appl Phys A 2006, 83, 131–132; (b) Ameduri, B. B. B.; Moreau, J. J. E.; Moutaabbid H.; Wong M. C. M. J Fluorine Chem 2000, 104, 185–194.