J Mater Sci (2010) 45:460–466
DOI 10.1007/s10853-009-3962-1

Novel superhydrophobic and highly oleophobic PFPE-modified silica nanocomposite

**Yu Gao · Yangen Huang · Shijun Feng ·
Guotuan Gu · Feng-Ling Qing**

Received: 18 June 2009 / Accepted: 5 October 2009 / Published online: 21 October 2009
© Springer Science+Business Media, LLC 2009

Abstract Superhydrophobic and highly oleophobic surface with micro-nanoscale binary structure (MNBS) was fabricated on the glass substrates with nano-silica modified by perfluoropolyether (PFPE) derivative. It was found that the formation of the MNBS and the modification of nano-silica by functionalized PFPE can be achieved simultaneously. The reaction time for preparing the fluorinated silica from nano-silica and functionalized PFPE plays an important role in the water and oil repellency of the coating surface. The maximum static water contact angle of this coating surface was 151.4° and its hysteresis was 2.9°, while for tetradecane it was 132.2° and 20.5°, respectively. Furthermore, the thermal property of the surface was also investigated. The main thermal weight loss proceeded from 241.7 °C and the total weight loss of the fluorinated silica was less than 30% even when heated to 800 °C.

Introduction

In the past decades, researches on designing superhydrophobic (water contact angle (WCA) higher than 150°) and oleophobic (oil contact angle higher than 90°) solid surfaces have been reported extensively due to the potential applications of these artificial surfaces ranging from self-cleaning (building exterior, windshields, and fabrics) to surface friction reducing for microfluidic channels [1–4].

Superhydrophobic surfaces can be achieved by a combination of low surface energy materials and surface micro- and nano-structures [5–8]. In order to create a biomimetic superhydrophobic surface, various approaches have been proposed for the preparation of superhydrophobic surfaces via the construction of an appropriate surface geometry structure [9]. Most of the preparation methods involve strict conditions (such as harsh chemical treatment), complicated processing procedures, and the use of templates. Recently, multistep procedures for preparing superhydrophobic films with dual-size hierarchical structure originated from silica particles have been reported [10, 11]. These methods include two key steps to achieve superhydrophobicity, the fabrication of micro-nanoscale binary structure (MNBS) with silica particles and modification of it by hydrophobic materials. For the sake of extending the application of this technique to a more extensive field, more scalable and achievable methods are desired.

For achieving superhydrophobicity and high oleophobicity, perfluoroalkyl chains (C_nF_{2n+1}, $n = 8$–10) and their derivatives are the most favorable functional groups due to their very low surface energies (less than 20 mJ/m^2) [12]. However, recent studies suggest that molecules containing perfluoroalkyl chain (C_nF_{2n+1}, $n > 8$) are relatively lipophilic and can accumulate in wildlife and human body, which result in a potential risk for human health and

---

Y. Gao · Y. Huang · S. Feng · F.-L. Qing
State Key Laboratory for Modification of Chemical Fibers
and Polymer Materials, College of Chemistry, Chemical
Engineering and Biotechnology, Donghua University,
2999 North Renmin Road, 201620 Shanghai, China

G. Gu
The Key Laboratory of Special Functional Materials,
Henan University, 475001 Kaifeng, China

F.-L. Qing (✉)
Key Laboratory of Organofluorine Chemistry, Shanghai Institute
of Organic Chemistry, Chinese Academy of Sciences,
345 Lengling Road, 200032 Shanghai, China
e-mail: flq@mail.sioc.ac.cn; yangenhuang@gmail.com

environmental concerns [13, 14]. Perfluoropolyether (PFPE) materials exhibited low surface energy, low toxicity, high chemical resistance, and thermal stability, which have attracted increasing attentions for achieving superhydrophobic coatings [3, 15]. Paper sheets treated with PFPE-modified polyurethanes were characterized by high water and oil repellence [16]. Perfluoropolyether-based organic–inorganic hybrids by sol–gel process as functional coatings onto glass substrates were hydrophobic and oleophobic, but the water contact angles and *n*-hexadecane contact angles of the surface can only reach to 100–112° and 64–68°, respectively [17, 18]. This result also indicated that appropriate surface texture is crucial for achieving superhydrophobicity and high oleophobicity.

In this work, we wish to report a new coating material with dual-size hierarchical structure which could be prepared by modification of nano-silica particles with low surface energy and low toxic chains PFPE via a simple procedure. The formation of the MNBS and the modification with functionalized perfluoropolyether were achieved simultaneously. The superhydrophobic and highly oleophobic surface was fabricated on the glass substrates. The surface morphology was characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The surface chemical composition was determined by FT-IR spectra and X-ray photoelectron spectroscopy (XPS) analyses. The wetting property of the coating surface was determined by static and dynamic contact angle measurements.

Experimental

Materials

All reagents and solvents were used as received or purified using standard procedures [19]. Tetraethoxysilane (TEOS), 3-aminopropyltriethoxysilane (APS), and triethylamine were purchased from Sinopharm Chemical Reagent Co. Ltd. Acyl fluoride-end functionalized perfluoropolyether (AF-PFPE) was obtained from Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. The molecular structure of the AF-PFPE can be represented by the following formula: $CF_3CF_2CF_2OCF(CF_3)CF_2OCF(CF_3)COF$.

Characterization

The structural and surface morphology of the coating on glass substrate was characterized by a JSM-5600LV SEM (JEOL, Japan). AFM was carried out by using a NanoScope IV instrument (Veeco Instruments Inc, USA) to determine the values of roughness factor (R, $R = 1 + \mathrm{Sdr}$, Sdr is the ratio between the interfacial and projected areas) [20]. Thermogravimetric (TG) analyses were carried out under nitrogen atmosphere with a heating rate of 10 °C/min by using a TG 209 F1 apparatus (Iris, Germany). FT-IR spectra were recorded on a FT-IR spectrometer (Avatar 380) using KBr crystal in the infrared region 4000–600 cm^{-1}.

To confirm the presence and the chemical composition of the PFPE-modified nano-silica (PFPE-NS) coating surface, the X-ray photoelectron spectroscopy (XPS) analysis was carried out by using XPS spectroscope (XPS, XSAM800, Kratos, UK) with a monochromatic Al Kα X-ray source (1486.6 eV photons), operated at 180 W (12 kV and 15 mA) and a pressure of 2×10^{-7} Pa. The survey spectra and the detailed C1s spectra were obtained at a photoelectron take-off angle (α, with respect to the sample surface) of 20°.

The sessile drop method was used for static contact angle measurements at ambient temperature with an automatic video contact-angle testing apparatus (DataPhysics OCA 40 apparatus, DataPhysics Instruments GmbH; Germany). The probe liquids were water, *n*-tetradecane, and *n*-dodecane. The average CA value was determined by measuring three to five different positions of the same sample with 5 μL of water and 3 μL of oil each time. The CA hysteresis angle was calculated by $\theta_A - \theta_R$, where θ_A is the advancing contact angle and θ_R is the receding contact angle. The advancing and receding angle were measured by the same instrument at ambient conditions.

Synthesis of PFPE-modified nano-silica particles (Scheme 1)

The amino-functionalized silica nanoparticles with a Z-average diameter of 105 nm were prepared according to the Stöber method [10]. To a three-necked flask equipped with a condenser and a dropping funnel was added a mixture of absolute ethanol (200 mL) and ammonia (25%, 15 mL); after heating to 60 °C, TEOS (6 mL, 26.9 mmol) was added dropwise with stirring and the mixture was stirred at 60 °C for 5 h. Then a solution of APS (1.0 mL, 4.3 mmol) in ethanol (10 mL) was added dropwise. The mixture was stirred at 60 °C for further 12 h under nitrogen atmosphere. The precipitated nanoparticles were separated by centrifugation and washed with ethanol three times. The white powder was dried in vacuum at 50 °C for 16 h. The existence of amino groups at the surface of silica nanoparticles was examined by the ninhydrin test [10, 21]. The average particle size was measured on Zetasizer Nano ZS Particle Sizer (Malvern Instruments Ltd., UK).

The modification of nano-silica particles with AF-PFPE was conducted in a 50 mL three-necked flask in two steps: (i) dispersing amino-functionalized nano-silica particles

(0.1 g) in anhydrous Freon 113 (15 mL) by ultrasonic vibration for 1 h; and (ii) adding triethylamine (0.2 g, 2 mmol) and AF-PFPE (1.0 g, 2 mmol) dropwise under refluxing. PFPE-modified nano-silica (PFPE-NS **1** and **2**) can be obtained by controlling the reaction time as 2 and 12 h, respectively. All of the products were separated by centrifugation and washed with water and Freon 113 three times.

Preparation of coatings with PFPE-NS (1, 2)

Microscope glass substrates were cleaned in a boiling Piranha solution, i.e., H_2SO_4 (98%): H_2O_2 (30%) = 7:3 (V/V), for 90 min and then rinsed with deionized water and blown dry with nitrogen gas. The PFPE-NS (**1**, **2**) dispersed in Freon 113 by ultrasonic vibration was deposited on the glass substrate by manual dip-coating. After a period of 30 min at room temperature under the ventilator hood, samples were subjected to a thermal post-treatment at 120 °C for 2 h.

Results and discussion

Preparation of the PFPE-NS

In this work, we prepared the superhydrophobic coating material by a simple procedure as shown in Scheme 1. Firstly, the amino functionalized silica nanoparticles were prepared according to the Stöber method. The size distribution by number of the amino functionalized silica particles is shown in Fig. 1. It indicated that more than 70% of particles are less than 100 nm in diameter. Then the modification of the silica nanoparticles by PFPE chains was conducted by the reaction of AF-PFPE and amino functionalized silica particles in Freon 113 using triethylamine as catalyst. PFPE-NS (**1**) and (**2**), with different surface morphology, were obtained by controlling the reaction time of modification as 2 and 12 h, respectively.

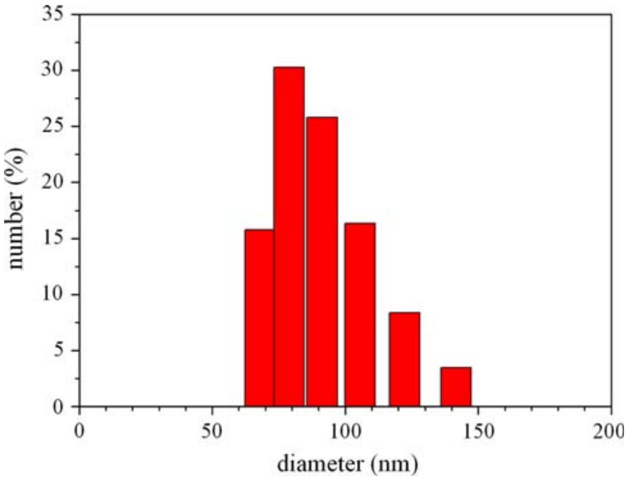
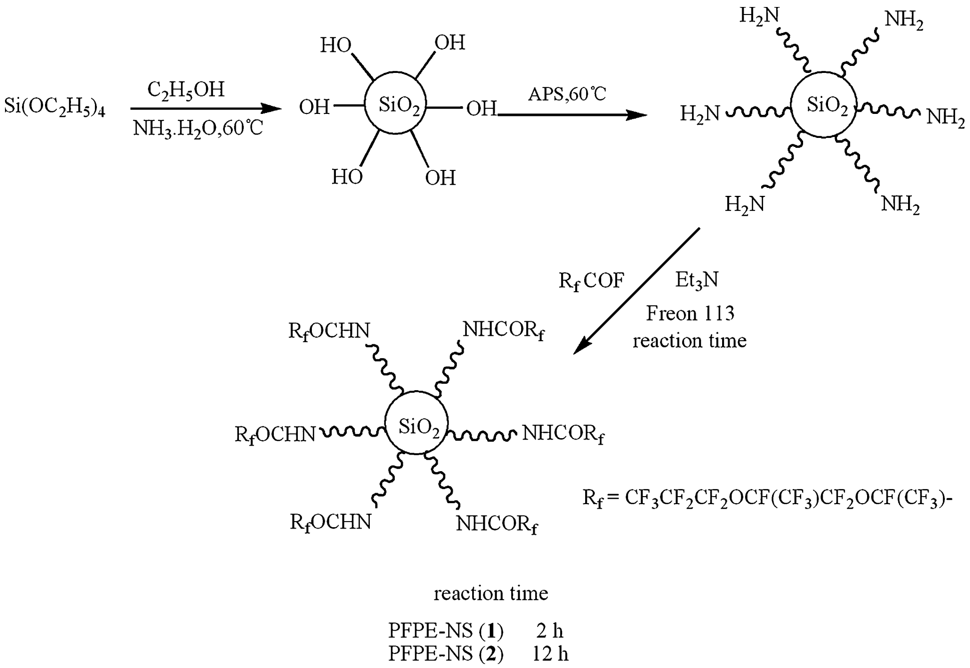


Fig. 1 The size distribution by number of the amino-functionalized silica particles

Chemical structures of the PFPE-modified silica

As shown in Fig. 2a, the characteristic absorption bands of N–H (3340 cm^{-1}) and C–H (2940 cm^{-1}) indicated the achievement of amino functionalization of the nano-silica. The existences of amino groups were also confirmed by

Scheme 1 Preparation of PFPE-NS (**1** and **2**)



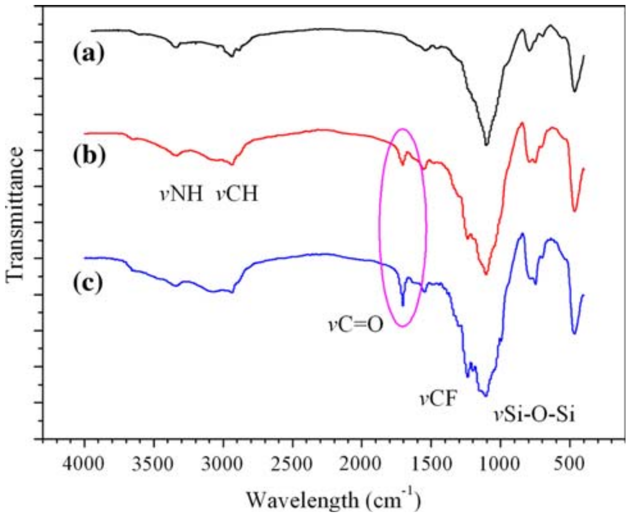


Fig. 2 FT-IR spectra of amino nano silica particle, PFPE-NS (**1**) and (**2**). (*a*) amino nano silica particle; (*b*) PFPE-NS (**1**); (*c*) PFPE-NS (**2**)

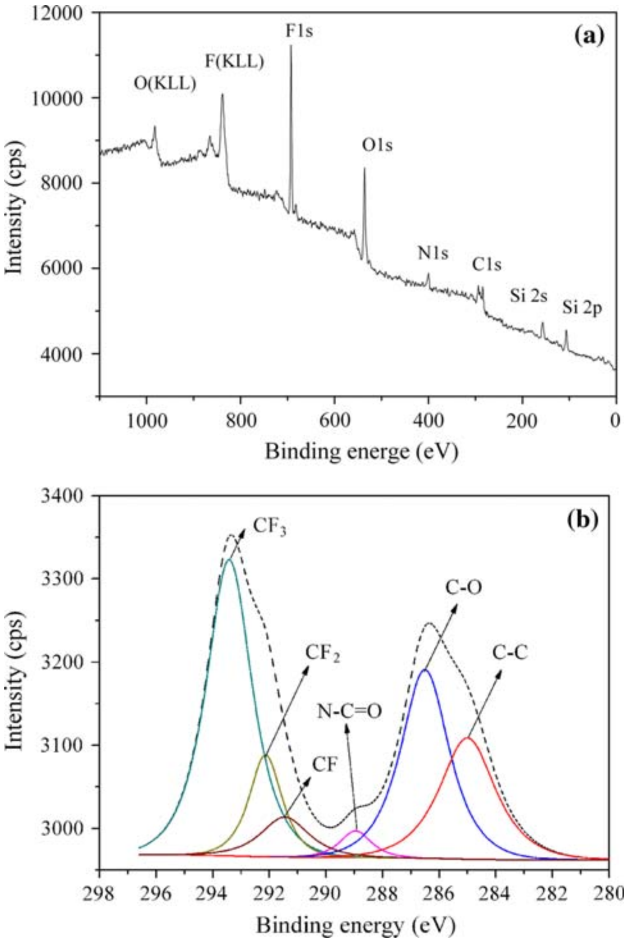


Fig. 3 XPS spectra of the coating surface of PFPE-NS (**2**)

positive results of ninhydrin test. The appearance of characteristic absorption bands of C=O (1700 cm^{-1}) and C–F (1240 cm^{-1}) for the PFPE-modified silica particles illustrated that the AF-PFPE has reacted with the amino groups of nano-silica (Fig. 2b, c). The much weaker absorption peak intensity of C=O (1700 cm^{-1}) of PFPE-NS (**1**) than that of PFPE-NS (**2**) suggests that less AF-PFPE has reacted with amino nano-silica when the reaction time was only 2 h.

The surface chemical composition of PFPE-NS (**2**) coating was analyzed by XPS analysis. As shown in Fig. 3a, Si 2s, Si 2p, C 1s, N 1s, O 1s, F 1s peaks were detected at around 150, 100, 285, 400, 535, and 690 eV, respectively. The C1s XPS high-resolution spectrum with five subpeaks stands for five kinds of carbon bonds, shown in Fig. 3b. The bands at 293.4, 292.0, 291.4, 288.7, 286.5, and 285.0 eV are attributed to –CF_3, –CF_2, –CF, N–C=O, C–O, and C–C, respectively [17, 22, 23].

The XPS quantification in atomic concentration has been carried out taking into account the individual peak areas and the corresponding atomic sensitivity factors (ASF). The relative atomic concentration of *i* element (C_i) can be calculated using the equation:

$$C_i = \frac{I_i/\mathrm{ASF}_i}{\sum_j I_j/\mathrm{ASF}_j} \qquad (1)$$

The ASF values provided here for Si 2p, C 1s, N 1s, O 1s, and F 1s are 0.29, 0.25, 0.42, 0.66, and 1.00, respectively. The calculated atom concentrations of F and C in the outermost surface are 35.77 and 15.14%, respectively. The atomic ratio of F/C is 2.36 which is significantly higher than the corresponding bulk atomic ratio (F/C, 1.4) of PFPE-NS (**2**), indicating a strong surface enrichment of fluorine. Furthermore, the atomic ratio of F/C (2.36) more than 2 means the CF_3 side groups are mainly oriented to the surface.

Surface morphology

The SEM images of PFPE-NS (**1** and **2**) are shown in Fig. 4. As can be seen from Fig. 4a, the average diameter of the PFPE-NS (**1**) is about 100 nm, which is coincident with the data in Fig. 1. It can be found that the small silica nanoparticles were coagulated to form micro-nanoscale binary structure (MNBS) when the reaction time of modification is 12 h (Fig. 4b).

As shown in Fig. 5b, the AFM images of PFPE-NS (**2**) coating also indicates that the MNBS was formed when the reaction time was 12 h. The surface of each micro-scale or sub-micro-scale protuberance is embedded with hundreds of nano-scale particles. While PFPE-NS (**1**) coating has only nano-structure as shown in Fig. 5a. This result suggests that the fluorinating reaction time plays a significant role in the formation of MNBS. The silica in the

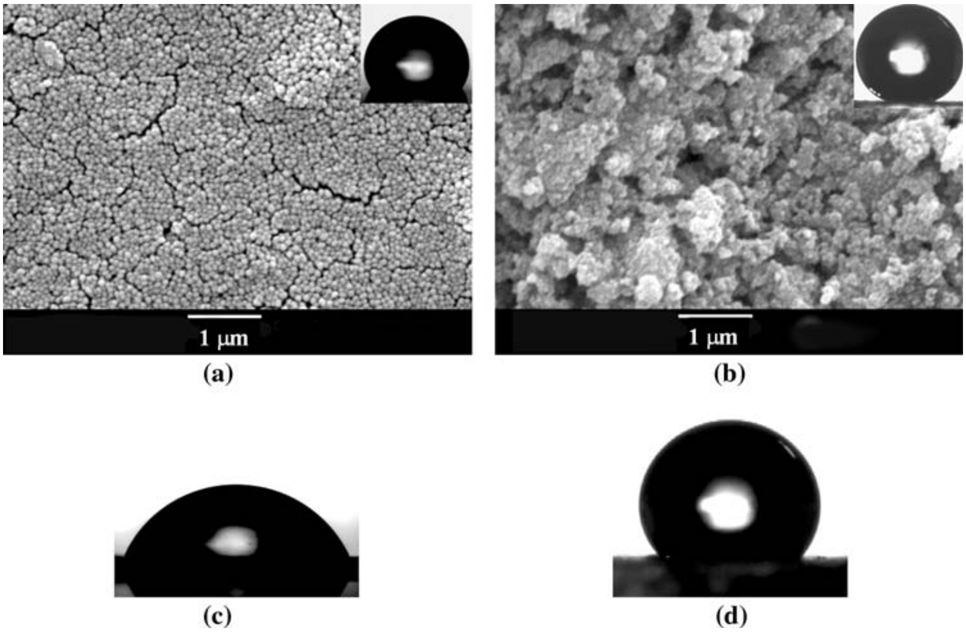


Fig. 4 SEM images of the coating surfaces and photos of water drops on the corresponding samples, **a** PFPE-NS (**1**), **b** PFPE-NS (**2**); Photos of *n*-tetradecane drops on the coating surfaces, **c** PFPE-NS (**1**), **d** PFPE-NS (**2**)

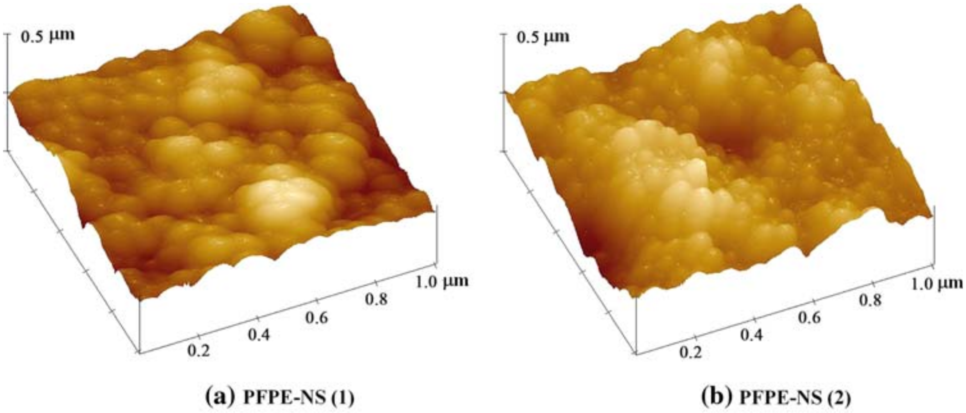
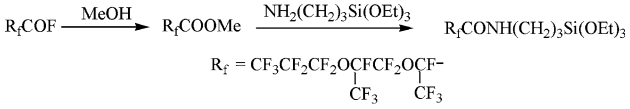


Fig. 5 AFM images of the coating surfaces of PFPE-NS (**1** and **2**)

nano-range has a tendency to undergo coagulation to form large micron-sized aggregates in the reaction system. It is probably that the coagulation of nano-silica caused the formation of micro-scale or sub-micro-scale protuberances when the reaction time is enough.

It is reported that even a material with the lowest surface energy (6.7 mJ/m^2 for a surface with regularly aligned closest-hexagonal-packed –CF_3 groups) gives a water contact angle of only around 120° [24]. Yarosh et al. [25] synthesized similar organofluorosilicon compounds according to Scheme 2.



$$R_fCOF \xrightarrow{MeOH} R_fCOOMe \xrightarrow{NH_2(CH_2)_3Si(OEt)_3} R_fCONH(CH_2)_3Si(OEt)_3$$

$$R_f = CF_3CF_2CF_2O\underset{CF_3}{\underset{|}{C}}FCF_2O\underset{CF_3}{\underset{|}{C}}F-$$

Scheme 2 Synthesis of organofluorosilicon

When the compound was used to treat specimens of construction materials, the WCA was only 130°, which did not achieve the superhydrophobic effect due to the lack of roughness. So a proper surface roughness is necessary for achieving higher hydrophobicity. In our work, the introduction of the MNBS resulted in the WCA as 151.4° and WCA hysteresis as only 2.9°. Furthermore, the tetradecane and dodecane contact angle achieved to 132.2° and 113.9°, respectively, which were much higher than 90°.

Surface wetting property

The water and oil contact angles and their hysteresis are listed in Table 1. Compared with PFPE-NS (**1**) coating, PFPE-NS (**2**) has much better water and oil repellency. The measured roughness factor of PFPE-NS (**2**) by AFM

Table 1 Static contact angles and their hysteresis with water (θ_{H_2O}), *n*-dodecane (θ_{DODE}), and *n*-tetradecane (θ_{TETRA}) for the PFPE-NS surfaces

PFPE-NS	Reaction time (h)	Roughness factor	θ_{H_2O} (°)		θ_{TETRA} (°)		θ_{DODE} (°)	
			Static	Hysteresis	Static	Hysteresis	Static	Hysteresis
(**1**)	2	2.2	127.6	10.8	56.9	38.1	9.6	None[a]
(**2**)	12	2.5	151.4	2.9	132.2	20.5	113.9	26.7

[a] The static CA is too small to measure the advancing and receding angle

analysis is 2.5, while that of PFPE-NS (**1**) is only 2.2. The higher roughness is an important factor to achieve the superhydrophobicity and oleophobicity. Qu et al. [26] also obtained the superhydrophobic hybrid film surfaces based on silica and fluoropolymer. They compared the surface morphologies, roughness, and the wettability of the film surfaces containing different structural silica particles and their experimental data showed that the roughness factor of a superhydrophobic coating should be higher than 2.4, which is similar to our result.

The photos of water and oil drops on PFPE-NS (**1**) and PFPE-NS (**2**) surfaces are shown in Fig. 4, as seen in the inset of images a, b, and c, d. PFPE-NS (**2**) achieved not only superhydrophobicity but also highly oleophobicity.

For the MNBS coating, air can be trapped in pore or nano-gaps on pore walls at the films. In this case, Cassie presented a model to describe the wettability as following [27]:

$$\cos\theta^* = f_1 \cos\theta - f_2 \tag{2}$$

where f is the ratio of the actual interface area to the projected area and the subscripts 1 and 2 represent the solid/liquid and air/liquid interface, respectively. The value of f_2 increases with the roughness of the interface. The θ^* is the apparent contact angle for the rough surface, and θ is the intrinsic contact angle for a flat surface. Note that $f_1 = 1 - f_2$, thus Eq. 2 can be rewritten as follows:

$$\cos\theta^* = \cos\theta - f_2(1 + \cos\theta) \tag{3}$$

According to Eq. 3, when θ is fixed, the value of θ^* increases with f_2, that is to say, the value of θ^* increases with the roughness also. The experimental result of the qualitative relationship between CA and the roughness of PFPE-NS coating is in accordance with the theoretical result from Eq. 3.

According to the analyses of the morphology and chemical composition of the coating surface, more AF-PFPE were grafted onto the nano-silica particles and more micro- or submicro-scale structure were formed with the increase of the reaction time, which further resulted in the superhydrophobicity and high oleophobicity of PFPE-NS (**2**). It should be pointed out that only one size of particles was applied in this work, and furthermore, both the formation of the MNBS and the modification with the low free energy compound were achieved simultaneously.

Thermal stabilities of the amino functional and PFPE-modified nano-silicas

The TG curves of the PFPE-NS (**2**) are shown in Fig. 6. Thermal weight losses at different temperatures obtained by using NETZSCH Proteus Thermal Analysis software are summarized in Table 2.

Thermal weight loss below 100 °C represents the desorption of free water or small molecules. As seen in Table 2, the weight loss of the PFPE-modified nano-silica at 100 °C is less than the amino functional one. The main thermal weight loss of both samples occurred in the range

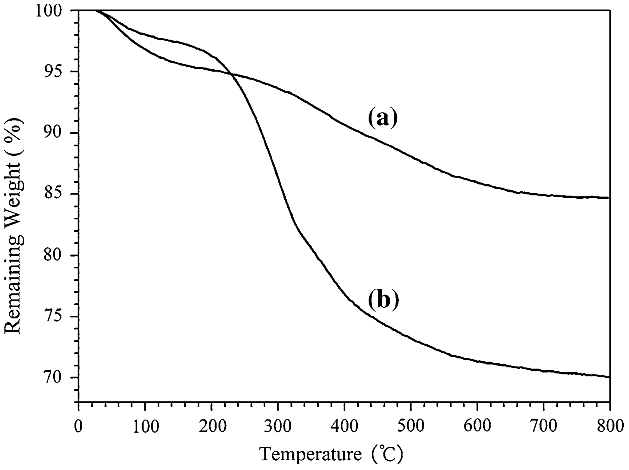


Fig. 6 TG curves of (*a*) amino functional nano silica, (*b*) PFPE-NS (**2**)

Table 2 Thermal weight loss at different temperatures

Temperature (°)	Amino functional nano silica Weight loss (%)	PFPE-modified nano silica Weight loss (%)
100	3.17	1.94
200	4.84	3.68
300	6.34	13.65
400	9.31	23.13
600	14.04	28.63
800	15.30	29.92

from 200 to 600 °C. The total weight loss of the PFPE-modified nano-silica coating is less than 30% even after heating to 800 °C. The decomposition onset temperature of the amino functional silica is 294.9 °C, while the PFPE-modified one is 241.7 °C. Although the decomposition onset temperature of the PFPE-NS (**2**) is decreased slightly for the introduction of imide group, it is still higher than 200 °C, which implies that PFPE-NS (**2**) is suitable for the common application such as construction coating and textile finishing.

Summary

In summary, a novel superhydrophobic and oleophobic nano-composite was prepared. It was found that the MNBS can be achieved via the coagulation of one size of nano-silica. Thus the formation of the MNBS and the modification with low free energy compound can be realized in one step. In addition, it is worth noting that the low toxic PFPE oligomer was applied as the fluorinating agent, rather than the conventional but controversial long-chain perfluoroalkyl compounds. The results of this research may be of considerable significance both as fundamental and industrial guiding principles.

Acknowledgement We are grateful to the Program for Changjiang Scholars and Innovative Research Team in University (No. IRT0526) and Shanghai Municipal Scientific Committee (08JC1400400) for the financial support.

References

1. Ball P (1999) Nature 400:507
2. Gu ZZ, Uetsuka H, Takahashi K, Nakajima H, Onishi H, Fujishima A, Sato O (2003) Angew Chem Int Ed 42:894
3. Zhang L, Zhou ZL, Cheng B, DeSimone JM, Samulski ET (2006) Langmuir 22:8576
4. Zhang X, Shi F, Niu J, Jiang YG, Wang ZQ (2008) J Mater Chem 18:621
5. Barthlott W, Neinhuis C (1997) Planta 202:1
6. Quere D (2002) Physica A 313:32
7. Bico J, Marzolin C, Quere D (1999) Europhys Lett 47:220
8. Sun TL, Feng L, Gao XF, Jiang L (2005) Acc Chem Res 38:644
9. Feng XJ, Jiang L (2006) Adv Mater 18:3063
10. Ming W, Wu D, Benthem RV, De G (2005) Nano Lett 5:2298
11. Tsai PS, Yang YM, Lee YL (2007) Nanotechnology 18:1
12. Shibuichi S, Yamamoto T, Onda T, Tsujii K (1998) J Colloid Interface Sci 208:287
13. Ellis DA, Mabury SA, Martin JW, Muir DCG (2001) Nature 412:321
14. Lau C, Anitole K, Hodes C, Lai D, Pfahles-Hutchens A, Seed J (2007) Toxicol Sci 99:366
15. Guo ZG, Zhou F, Hao JC, Liu WM (2006) J Colloid Interface Sci 303:298
16. Trombetta T, Iengo P, Turri S (2005) J Appl Polym Sci 98:1364
17. Fabbri P, Messori M, Montecchi M, Nannarone S, Pasquali L, Pilati F, Tonelli C, Toselli M (2006) Polymer 47:1055
18. Fabbri P, Messori M, Montecchi M, Pilati F, Taurino R, Tonelli C, Toselli M (2006) J Appl Polym Sci 102:1483
19. Armarego WLF (2003) Purification of laboratory chemicals, 5th edn. Butterworth-Heinemann, Boston, p 53
20. Qu A-L, Wen XF, Pi PH, Cheng J, Yang ZR (2007) Appl Surf Sci 253:9430
21. Eiselt P, Lee KY, Mooney DJ (1999) Macromolecules 32:5561
22. Vaidya A, Chaudhury MK (2002) J Colloid Interface Sci 249:235
23. Abenojar J, Torregrosa-Coque R, Martínez MA, Martín-Martínez JM (2009) Surf Coat Technol 203:2173
24. Nishino T, Meguro M, Nakamae K, Matsushita M, Ueda Y (1999) Langmuir 15:4321
25. Yarosh AA, Krukovsky SP, Pryakhina TA, Kotov VM, Zavin BG, Sakharov AM (2006) Mendeleev Commun 16:190
26. Qu A-L, Wen XF, Pi P, Cheng J, Yang ZR (2008) J Mater Sci Technol 24:693
27. Liu B, Lange FF (2006) J Colloid Interface Sci 298:899