

Superhydrophobic and Superoleophilic Nanoparticle Film: Synthesis and Reversible Wettability Switching Behavior

Xia Zhang,^{*,†} Yonggang Guo,[‡] Pingyu Zhang,^{*,†} Zhishen Wu,[†] and Zhijun Zhang[†]

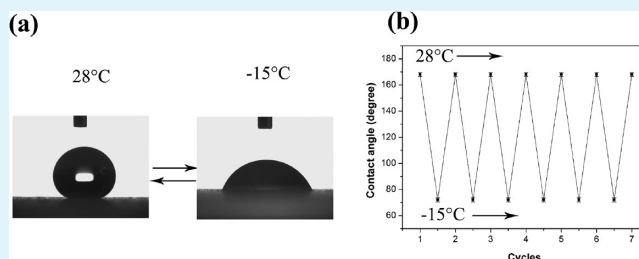
[†]Laboratory of Special Functional Materials, Henan University, Kaifeng 475001, China

[‡]School of Mechanical and Electrical Engineering, Henan University of Technology, Zhengzhou 450007, China

S Supporting Information

ABSTRACT: The present work describes a one-step facile spray deposition process for the fabrication of superhydrophobic and superoleophilic nanoparticle film. The film shows fast response wettability transition between superhydrophobicity and hydrophilicity. The reversible superhydrophobicity to hydrophilicity switching can be easily carried out by adjusting the temperature. The film also demonstrates oil uptake ability and can selectively adsorb oil floating on water surface. Furthermore, the film surface shows the antifouling performance for organic solvents, which can self-remove the organic solvents layer and recover its superhydrophobic behavior. The advantage of the present approach is that the damaged film can be easily repaired by spraying again.

KEYWORDS: superhydrophobic, superoleophilic, spray, reversible wettability, antifouling



INTRODUCTION

Smart surface with reversible switchable wettability behavior under external stimuli have received particular attention because of their potential applications in self-cleaning surfaces, microfluidic tools, and so on.^{1–6} According to environmental variations, such as solvents treatment,⁷ temperature treatment,^{8–10} light illumination,^{11–16} and pH control,¹⁷ surface chemical and/or morphology of stimuli-sensitive materials can be changed, which results in the change of surface wetting behavior. However, the reversible wettability transitions triggered by above-mentioned approaches require a long time, even several weeks,¹² which makes the switching less useful. Furthermore, these approaches require either special equipment or complex process to work. Hence, it would be highly desirable to realize the wettability transition by a convenient and time-saving method.^{18,19} The work described below has accomplished this goal. Using one-step facile spray deposition process, we fabricated transparent nanoparticle film with fast wetting reversible transition by the alternation of different temperature.

As a convenient and versatile method, the spray deposition is applicable for a variety of substrates and is not limited to small areas. Actually, the spray deposition is the most mature technology with high throughput and is the current choice in the modern surface-coating industry.^{20,21} Herein, we fabricated transparent film by spraying SiO₂ suspension on virtually any substrates and drying at ambient environment. The film demonstrates superhydrophobicity as well as superoleophilicity. The film also shows oil or organic solvent uptake ability and it can easily remove oil or organic contaminants from water surface. The advantages of the present approach include the

cheap and fluorine-free raw materials, an industrial implementation method, and easy reparability and applicability so as to make a great application potential in practice.

EXPERIMENTAL SECTION

Hydrophobic SiO₂ nanoparticles used in this study were chemically modified by using chlorotrimethylsilane (TMCS). The fabrication process and more detailed information for hydrophobic SiO₂ are shown in Supporting Information. Poly(dimethylsiloxane) vinyl terminated was obtained from Alfa Aesar Company. In a typical synthesis, 0.8 g of hydrophobic SiO₂ nanoparticles were dispersed in 20 mL of tetrahydrofuran (THF), followed by the addition of 0.2 g of poly(dimethylsiloxane) vinyl terminated and stirred magnetically for 30 min. Then, the suspension was sprayed onto glass substrate with air gas (0.4 MPa) and dried under room temperature for about 5 min until the mixed solvent evaporated completely. The thickness of the film was estimated in the range of 4–6 μm (see Figure S3 in the Supporting Information). It is important to point out that the present film is not substrate-limited and it can be fabricated on different engineering material surface, such as stainless steel, copper, aluminum alloy with good results.

The surface morphology of the films was examined by using a JSM-6701F field-emission scanning electron microscope (FESEM, JEOL, Japan). The chemical composition of the as-prepared film was investigated using X-ray photoelectron spectroscopy (XPS), which was conducted on a PHI-5702 electron. The water contact angle (CA) and sliding angle (SA) were measured by a DSA100 contact angle instrument (Germany). The average CA and SA values were obtained by measuring the same sample in at least five different positions, and

Received: December 30, 2011

Accepted: February 13, 2012

Published: February 13, 2012

images were captured with a digital camera (Canon, PowerShot A1200).

RESULTS AND DISCUSSION

Herein, TMCS-functionalized SiO₂ nanoparticles have superior dispersibility in organic solvents (DMF, toluene, pyridine, acetone, ethane nitrile, dodecane, etc.) and can form a transparent SiO₂ dispersion solution. The as-prepared SiO₂ nanoparticle film shows superhydrophobicity and superoleophilicity. FESEM images of the as-prepared film surface are shown in Figure 1. The low-magnification image (Figure

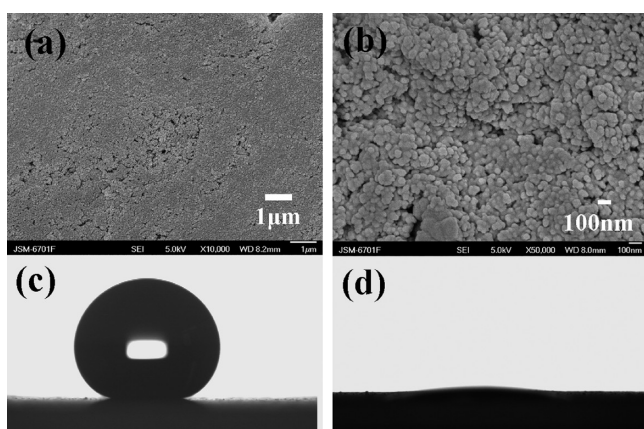


Figure 1. (a, b) FESEM images of the as-prepared film surface with different magnifications. (c, d) Photographs of water and oil droplet shape on the as-prepared film with CA value about 168 and 5°, respectively.

1a) shows the film surface is relatively smooth but has micrometer-scale roughness. In the high-magnification image (Figure 1b), numerous aggregations of nanoparticles with size of 80–100 nm are observed, and nanometer-scale roughness is evident. The water CA on the film surface has a very high value of about 168° (Figure 1c). It is believed that the nanostructure SiO₂ aggregations affect the surface roughness, and on the other hand, hydrophobic SiO₂ nanoparticles change the surface energy of the films. Both of these factors are responsible for inducing superhydrophobic behavior. The XPS spectrum of the as-prepared film surface is shown in Supporting Information (see Figure S4 in Supporting Information). The film also shows

a superoleophilic property. When a drop of oil is dripped on the film surface, it spreads quickly over the surface with the CA value about 5° (Figure 1d).

Figure 2a shows the photographic image of some water droplets floating on the surface at room temperature. The resulting surface is so hydrophobic that water droplets deposited on the surface can exhibit spherical shapes. The sliding angle (SA) is about 2° as shown in Figure 2b, indicating that the water droplet can be moved easily when the surface is slightly tilted. Note that it is not easy to place a water droplet on the film surface. A water droplet (4 μL) suspending on a syringe is difficult to be pulled down to the surface in all cases, even though the droplet is deformed severely (Figure 2c–g).

Rapid wettability transition is a very important characteristic to enable the application of surface in terms of smart devices, such as controlled transportation of fluids, water-proof coatings for moisture-sensitive electronic devices, rapid water motion, and smart membranes.¹³ Herein, the as-prepared films show reversible wettability transition between superhydrophobicity and hydrophilicity. If the as-prepared film was sealed and stored in freezer until the surface temperature dropped down to −15 °C, it would switch from superhydrophobic to hydrophilic. A room temperature droplet, which slipped easily on the SiO₂ nanoparticle film surface at room temperature, started to stick to the cold surface (−15 °C) and had a low CA value (about 71°). However, the film surface was able to restore its superhydrophobicity just by staying at room temperature for only three minutes (Figure 3a). This process had been repeated for several times, and good reversibility of the surface wettability was observed, as shown in Figure 3b.

The observation is a signature of a so-called Cassie–Wenzel transition²² and the schematic model of the transition is shown in Figure 3c. Indeed, a similar effect has been reported for condensing water vapor onto a nanostructured surface or by cooling the substrate below the dew point.^{23,24} Here also, it seems that a transition from the Cassie to the Wenzel regime due to water vapor condensation on the surface affects the wetting property of the nanoparticle film.²⁴ When the subfreezing film is placed in ambient environment, the humidity in the air will condense to the subfreezing surfaces, and change the surface chemical composition, resulting in the film hydrophilic. After several minutes, water molecules adsorbed on the surface volatilize gradually with the increase of the surface temperature, and the surface recovers to its

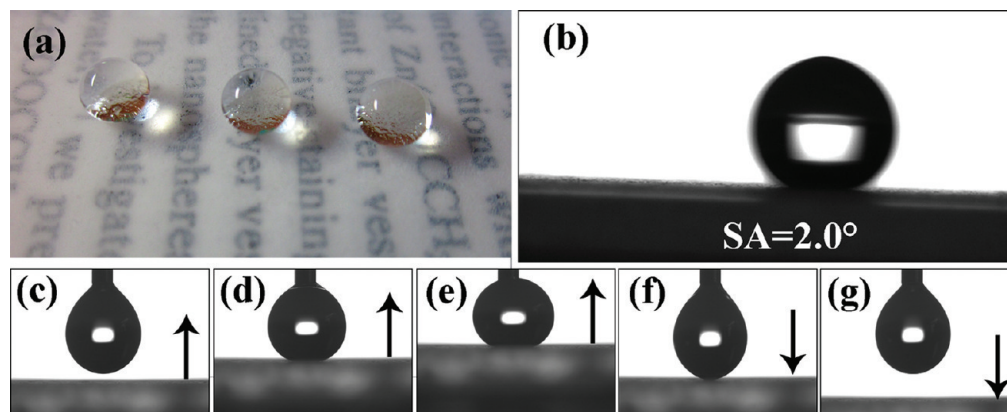


Figure 2. (a) Optical image of several water droplets on the as-prepared film surface. (b) The sliding angle image with value about 2°. (c–g) Approach, contact, deformation, and departure processes of a water droplet suspending on a syringe with respect to the coating surfaces. The arrows represent the moving direction of the substrate.

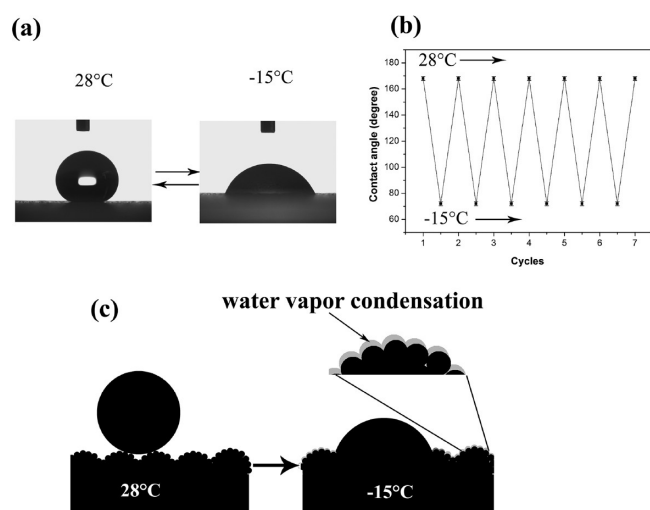


Figure 3. (a) Photographs of water droplet shape on the film surface before and after cooling. (b) Reversible superhydrophobic–hydrophilic transition of the as-prepared films under different temperature. (c) Schematic model of transition from the Cassie to the Wenzel regime.

superhydrophobic state. This reversible switching proceeds by the adsorption and desorption of moisture on the film surfaces at different temperature. It is expected that the water vapor condensation changes the surface chemical composition, and the content of OIs will increase, resulting in the surface hydrophilic.

Considering both superhydrophobic and superoleophilic properties of the film, we fabricated the films on filter paper to separate the oil from water. It was found that the films were able to selectively absorb a broad range of organic solvents or oil while completely repelling water. As shown in images a and b in Figure 4, when the filter paper coated with superhydrophobic films was immersed into water, it strongly repelled water and remained dry after being taken out. However, when

there was a layer of silicone oil on the water surface, the modified filter paper selectively adsorbed the oil as soon as it touched the oil surface (Figure 4c, d). Surprisingly, the as-prepared films also demonstrated the antifouling property for organic solvents with relatively low boiling point, such as hexane, toluene, chloroform, ethanol, and acetone. When a droplet of organic solvent was placed onto the film surface, it wetted the whole surface instantly with the CA value about 0° (Figure 5a). But after about 30 s, the organic layer evaporated

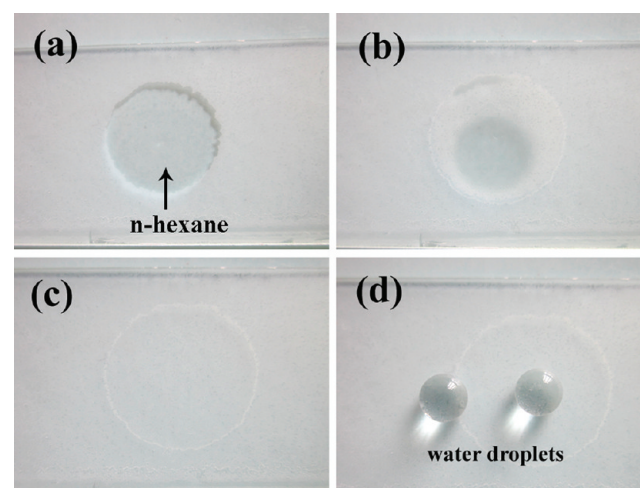


Figure 5. Photographs demonstrating the antifouling property for organic solvent with relatively low boiling point. (a) Spreading of a n-hexane droplet (4 μL) on the coating surface; (b, c) n-Hexane droplet almost disappears after 30 s; (d) placement of a water droplet on the coating surface, demonstrating the recovery of superhydrophobicity.

and disappeared completely (Figure 5b, c). After that, the surfaces restored its superhydrophobic wetting behavior (Figure 5d). Video S1, included as a part of the Supporting Information, shows how quickly the surface can self-remove the organic solvent layer and recover its superhydrophobic

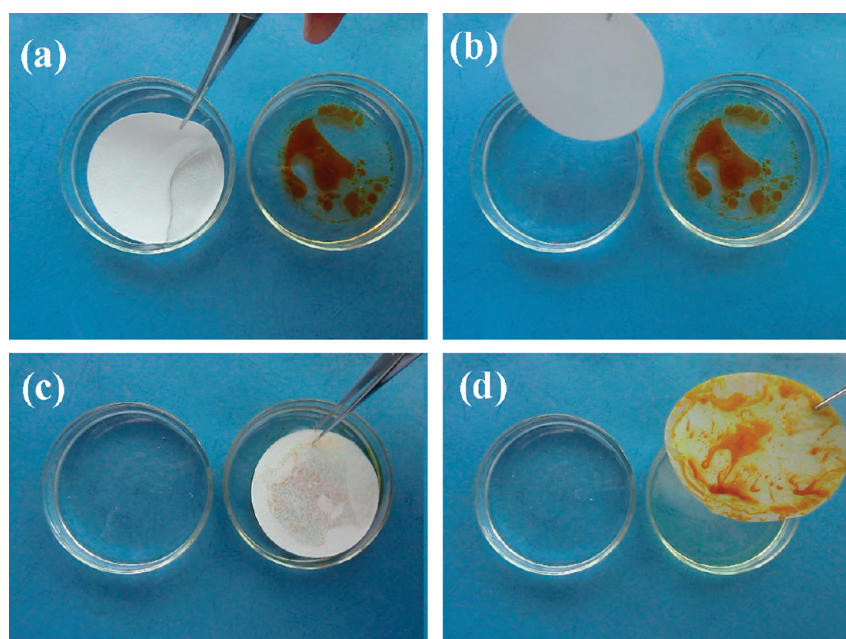


Figure 4. Removal of silicone oil from water surface.

behavior. It is clear that the nanostructured SiO₂ film can not be destroyed during the evaporation process of low boiling point solvents. As far as the high boiling point solvents, the case is just contrary. The solvents wetted the film surface quickly with a low CA value (less than 5°) and could not evaporate all the time.

Regarding the real application, the stability of the obtained superhydrophobic surfaces was also investigated. The water CA on the surface still remains larger than 150° after storage three months at ambient temperature, as well as the SA is less than 5°, showing the long-term stability of the film. However, the present film can be easily scratched because there is no strong chemical bonding to substrates and mechanical scratch will dramatically affect the water CA value. This drawback can be easily resolved by spraying again. The damaged films will be repaired by spraying the solution onto the substrates and the reparative films restore its good superhydrophobicity immediately. Importantly, the as-prepared film shows superhydrophobicity in the pH range from 1.0 to 14.0. That is, the water CAs are larger than 150° not only for pure water but also corrosive liquids, such as acidic and basic aqueous solutions. Figure 6

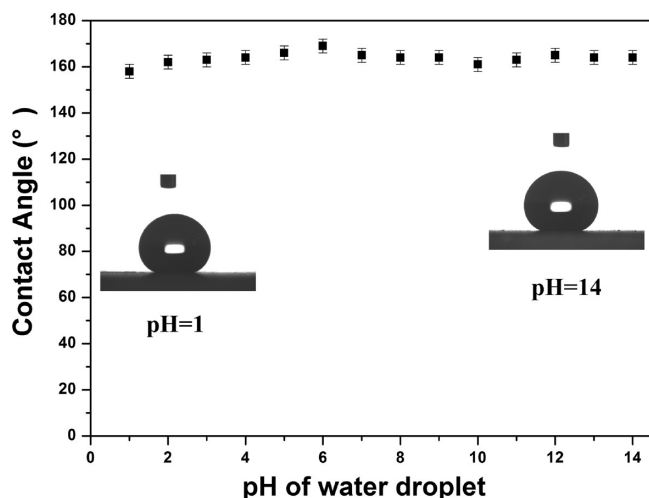


Figure 6. Relationship between pH of water droplet and water CA on the nanoparticle film surface.

shows the relationship between pH and CA on the superhydrophobic surfaces. It is clear that the CA values remain larger than 150° when the pH is varied from 1.0 to 14.0, indicating the pH of the aqueous solution has little or no effect on the wettability of the surface. These results are very important for the application of SiO₂ nanoparticle films in the wide pH range of corrosive liquids.

CONCLUSIONS

The transparent SiO₂ nanoparticle films are fabricated via a simple spray deposition method under ambient conditions. The films show reversible switching between superhydrophobicity and hydrophilicity under different temperature. The films also demonstrate the antifouling property for organic solvents with relatively low boiling point, because low-boiling-point solvents could evaporate easily. It does not need any chemical modification with low-surface-energy materials such as expensive fluorochemicals to realize the superhydrophobicity. The superhydrophobic films can be fabricated on various substrates and the damaged film can be restored to its good

superhydrophobicity immediately just by spraying at any time and almost any where. We expect that this simple and time-saving fabrication technique will make it possible for large-scale production of superhydrophobic and superoleophilic surfaces.

ASSOCIATED CONTENT

Supporting Information

Preparation and characterization of hydrophobic SiO₂ nanoparticles; FESEM image of cross-section view and XPS analysis of the as-prepared transparent film surface; Videos showing the surface antifouling property for the low boiling point solvents. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: zx@henu.edu.cn (X.Z.); pingyu@henu.edu.cn (P.Z.).
Tel: +86-378- 3881358. Fax: +86-378- 3881358.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by National Basic Research Program of China (973 program) (Grant 2007CB607606) and the Innovative Group Foundation from NSFC (Grant 50975077).

REFERENCES

- (1) Shi, F.; Song, Y.; Niu, J.; Xia, X.; Wang, Z.; Zhang, X. *Chem. Mater.* **2006**, *18*, 1365–1368.
- (2) Feng, C.; Zhang, Y.; Jin, J.; Song, Y.; Xie, L.; Qu, G.; Jiang, L. *Langmuir* **2001**, *17*, 4593–4597.
- (3) Qing, G. Y.; Wang, X.; Fuchs, H.; Sun, T. L. *J. Am. Chem. Soc.* **2009**, *131*, 8370–8371.
- (4) Russell, T. P. *Science* **2002**, *297*, 964–967.
- (5) Daniel, S.; Chaudhury, M. K.; Chen, J. C. *Science* **2001**, *291*, 633–636.
- (6) Srinivasan, S.; Praveen, V. K.; Philip, R.; Ajayaghosh, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 5750–5754.
- (7) Lu, X. Y.; Peng, J.; Li, B. Y.; Zhang, C. C.; Han, Y. C. *Macromol. Rapid Commun.* **2006**, *27*, 136–141.
- (8) Gao, J.; Liu, Y. L.; Xu, H. P.; Wang, Z. Q.; Zhang, X. *Langmuir* **2010**, *26*, 9673–9676.
- (9) Song, W. L.; Xia, F.; Bai, Y. B.; Liu, F. Q.; Sun, T. L.; Jiang, L. *Langmuir* **2007**, *23*, 327–331.
- (10) Fu, Q.; Rao, G. V. R.; Basame, S. B.; Keller, D. J.; Artyushkova, K.; Fulghum, J. E.; Lopez, G. P. *J. Am. Chem. Soc.* **2004**, *126*, 8904–8905.
- (11) Yang, J.; Zhang, Z. Z.; Men, X. H.; Xu, X. H.; Zhu, X. T. *Langmuir* **2010**, *26*, 10198–10202.
- (12) Caputo, G.; Cortese, B.; Nobile, C.; Salerno, M.; Cingolani, R.; Gigli, G.; Cozzoli, P. D.; Athanassiou, A. *Adv. Funct. Mater.* **2009**, *19*, 1149–1157.
- (13) Yan, B.; Tao, J. G.; Pang, C.; Zheng, Z.; Shen, Z. X.; Yu, T. *Langmuir* **2008**, *24*, 10569–10571.
- (14) Xia, F.; Jiang, L. *Adv. Mater.* **2008**, *20*, 2842–2858.
- (15) Xia, F.; Zhu, Y.; Feng, L.; Jiang, L. *Soft Matter* **2009**, *5*, 275–281.
- (16) Chen, M.; Besenbacher, F. *ACS Nano* **2011**, *5*, 1549–1555.
- (17) Wang, S. T.; Liu, H. J.; Liu, D. S.; Ma, X. Y.; Fang, X. H.; Jiang, L. *Angew. Chem., Int. Ed.* **2007**, *46*, 3915–3917.
- (18) Zhu, X. T.; Zhang, Z. Z.; Men, X. H.; Yang, J.; Xu, X. H. *ACS Appl. Mater. Interfaces* **2010**, *2*, 3636–3641.
- (19) Zhu, X. T.; Zhang, Z. Z.; Men, X. H.; Yang, J.; Xu, X. H.; Zhou, X. Y. *Appl. Surf. Sci.* **2011**, *257*, 3753–3757.
- (20) Hwang, H. S.; Kim, N. H.; Lee, S. G.; Lee, D. Y.; Cho, K. *ACS Appl. Mater. Interfaces* **2011**, *3*, 2179–2183.

- (21) Wu, W. C.; Wang, X. L.; Liu, X. J.; Zhou, F. *ACS Appl. Mater. Interfaces* **2009**, *1*, 1656–1661.
- (22) Barbieri, L.; Wagner, E.; Hoffmann, P. *Langmuir* **2007**, *23*, 1723–1734.
- (23) Quéré, D. *Nat. Mater.* **2002**, *1*, 14.
- (24) Karmouch, R.; Ross, G. G. *J. Phys. Chem. C* **2010**, *114*, 4063–4066.