



## A Silica-Sol-Based Fortified Structure with Superhydrophobic Coating for Harsh Conditions

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Although numerous bio-inspired superhydrophobic coatings have been extensively studied in the last decades, most of them suffer from low chemical stability and mechanical weakness, which severely limit their extensive applications. Herein, a silica-based, superhydrophobic, highly stable and mechanically durable coating was prepared via a facile, energy-saving strategy. Modified silica nanoparticles, were fortified with silane coupling agent and spray-deposited on substrates, forming a superhydrophobic, self-cleaning coating with high water contact angle (CA = 159.0°), as well as low rolling angle (RA ≈ 3°). The protective coating showed high chemical stability that endured various harsh conditions, such as wide temperature range (−18 to 250 °C), extreme pH (1 to 13), weeks of exposure under sunlight, etc. Moreover, the coating exhibited superior mechanical robustness that could resist the attack of shear force in vigorous ultrasonication for 7 hours. In addition, repetitive scratching with a steel blade could not undermine the protective coating (CA > 150°). It is believed that the present strategy is a potent candidate for facile fabrication of superhydrophobic surface coatings, which have promising applications on extreme conditions in both household and industry.

**KEYWORDS:** *Silica-Sol, Silane Coupling Agent, Superhydrophobicity, High Stability, Harsh Conditions.*

### INTRODUCTION

Superhydrophobicity is a naturally developed phenomenon<sup>1,2</sup> that has attracted worldwide interest for its extensive applications.<sup>3–5</sup> Superhydrophobic surfaces play an important role in industry and our daily life, especially in biomedical applications,<sup>6</sup> e.g., protein adsorption,<sup>7</sup> drug delivery,<sup>8</sup> and medical diagnostics.<sup>6</sup> Rational design of these materials in constructing a stable air layer at the material surface, which imparts itself to a lot of unique properties, and then explores biomedical applications through in depth utilization of superhydrophobicity. Various biomimetic materials coated superhydrophobic have recently been reported by a number of researchers.<sup>9–12</sup> Jiang et al.<sup>3</sup> fabricated a self-pumping dressing by spraying the prepared sol solution onto the fibre medical gauze, in which dressing could pump the biological fluid from the

hydrophobic side to the hydrophilic side uni-directionally, effectively pumping out the excess biological fluid around the wound and accelerating wound healing pace. He et al.<sup>13</sup> fabricated highly transparent and superhydrophobic coatings with extremely low bacterial adhesion via spray-coating hydrophobic silica sol and CuO nanoparticles. Moreover, Zeng et al.<sup>14</sup> fabricated aluminum surfaces of varying roughness by modifying the sandblasting pressure and then decorating with polydimethylsiloxane to reduce the surface energy.

Although many superhydrophobic coatings have been artificially developed, e.g., layer-by-layer assembly,<sup>15,16</sup> sol-gel strategy,<sup>17–19</sup> plasma etching,<sup>20,21</sup> lithographic patterning,<sup>22,23</sup> chemical vapor deposition,<sup>24,25</sup> electrochemical deposition,<sup>26,27</sup> template-based synthesis<sup>28,29</sup> and so on, they usually suffer from practical difficulties in terms of chemical, mechanical,<sup>30–32</sup> and thermal stability,<sup>33</sup> which severely limit their feasibility in practical uses. For example, it has been reported that 10 min ultrasonication may break down a super-amphiphobic coating, resulting in a rapid decrease of contact angle and an increase of the contact angle hysteresis.<sup>34</sup> Therefore, the mechanical

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strength, durability and stability of the coating in food industry or biomedicine, must be taken into consideration simultaneously. Meanwhile, the coatings are expected to be ecologically and economically friendly for the sake of environmental sustainability, requiring inexpensive raw materials, facile processes and low energy consumption. However, the durability against damage from extreme conditions from state-of-art superhydrophobic coatings have been less well studied in scientific aspect.<sup>35</sup>

In this work, we present an easy and efficient approach to prepare robust, superhydrophobic surface coatings by a sol-gel process at room temperature. In brief, chemically modified silica sol was spray-deposited on glass substrates, forming a superhydrophobic protective surface coating with no need of pre- or post-treatments. More importantly, as stated above, the obtained surface coating exhibited long-term mechanical durability while keeping superhydrophobic and self-cleaning properties after long-time ultrasonication and even blade-scratching. The coating has also been proven to be viable under harsh practical conditions, such as  $-18$  to  $250$  °C, pH 1–13, and sunlight resistance for several weeks. Therefore, the present process is recognized as a potent strategy to be applied in the fabrication of protective surface coatings, making it a promising candidate for human health and industrial instruments.

## EXPERIMENTAL REAGENTS AND INSTRUMENTS

### Materials

Tetraethoxysilane (TEOS),  $\gamma$ -(2,3-epoxypropoxy) propyltrimethoxysilane (KH-560), ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) and ethanol were purchased from Sino Pharm Chemical Reagent Co. in analytical grade. 1H,1H,2H,2H-Perfluorodecyltriethoxysilane (HDFTES,  $\text{C}_{16}\text{H}_{19}\text{F}_{17}\text{O}_3\text{Si}$ , 98%), fumed silica ( $\text{SiO}_2$ , diameter 7–40 nm) and methylene blue (MB, analytical grade) were obtained from Sigma-Aldrich. All chemicals were used without further purification.

### Preparation of Fluorinated Silica Sol

The silica sols were prepared following the Stöber method with slight modification. In brief, TEOS was mixed with anhydrous ethanol, deionized water and saturated ammonia solution. The volume ratio was set at 1:10:0.15:0.25. The clear solution was stirred at  $60$  °C for 4 hours in a closed glass container and then added with appropriate HDFTES, followed by stirring for 1 hour to increase the hydrophobicity.

### Hydrolysis of Silane Coupling Agent (KH-560)

Silane coupling agent KH-560 was mixed with deionized water and anhydrous ethanol at a volume ratio of 1:10:5. The solution was stirred at  $50$  °C for 45 minutes. After

hydrolysis, the solution was mixed with silica sol for spray-coating in the next step. The preparation schematic of silica sol is shown as Figure 2.

## Fabrication of Superhydrophobic Coatings by Spray Coating

Glass slides were cleaned with ultrasonication in ethanol and deionized water for 30 minutes, followed by air-drying at  $90$  °C in the oven. The mixture composed of fluorinated silica sols, hydrolyzed KH-560 (4:1 volume ratio, in Fig. 6(c)) and silica nanoparticles (equal concentration to the silica sol) was deposited onto the glass slides by spray-coating at  $70$  °C. The prepared coatings were then heated under vacuum for 3 hours (at  $150$  °C) in order to remove the residues and fortify the silanization.

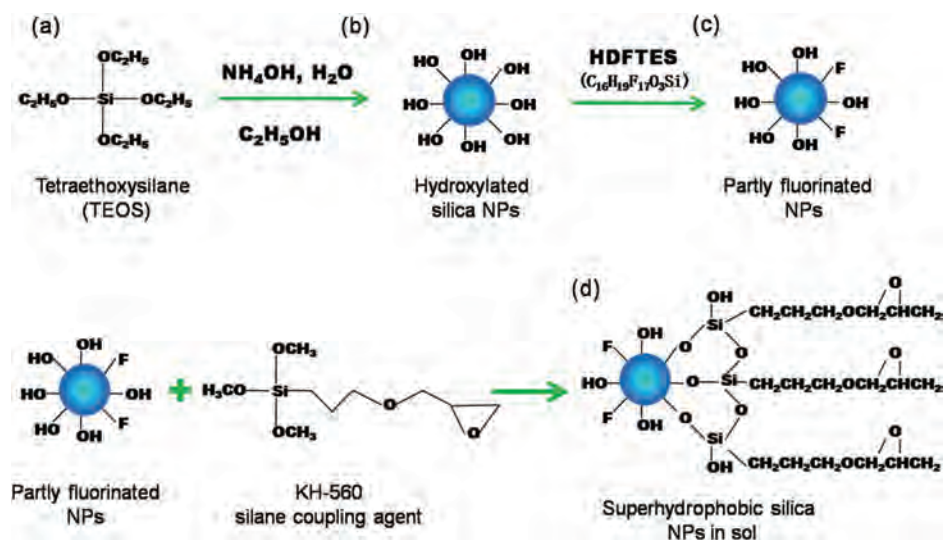
## Characterization of Silica Coatings

The surface morphology of the coating was investigated using scanning electron microscopy (SEM) via Leo 1530 field-emission gun SEM, at an accelerating voltage of 8 kV. X-ray photoelectron spectra (XPS) were obtained on an ESCALAB250xi spectrometer equipped with a focused monochromatic Al X-ray source (1486.6 eV). Surface roughness analysis was conducted on an Atomic force microscopy (AFM, Dimension<sup>®</sup> Icon<sup>™</sup>, Germany) using  $\text{Si}_3\text{N}_4$  probe. The optical transparency for the coating on glass slides was determined by transmittance measurement using UV-Vis spectroscopy (Shimadzu, UV2600), with scanning wavelength from 300 nm to 800 nm, and scanning step was 1 nm. The CA and RA for the coated glass substrate was measured using a contact angle goniometer (Findatek, Model 100SB) with  $5$   $\mu\text{L}$  DI water droplet under laboratory ambient conditions. The CA and RA for every specimen was measured at least five times and the obtained average value was used for subsequent data analysis.

## RESULTS AND DISCUSSION

### Reaction Mechanism in Preparation of Superhydrophobic Coating

The schematic procedure for the superhydrophobic coating is depicted in Figure 2. During the preparation of coating solution, the reactions for modified silica sol are described in Figure 1 in Supporting Information. Pure silica sol is easy to agglomerate as a promising candidate for preparing superhydrophobic coating, which then acquires high surface roughness and extremely low surface energy. Moreover, there are still many hydrophilic hydroxyl residues on the surface (Fig. 2(b)). It was found that the hydrolysis product of  $\gamma$ -(2,3-epoxypropoxy) propyltrimethoxysilane (KH-560) formed a composite sol via hydroxyl dehydration condensation on the surface of silica, which ameliorated the dispersion and hydrophobicity of the particles.<sup>40</sup> After coating on glass substrates, the modified silica sol



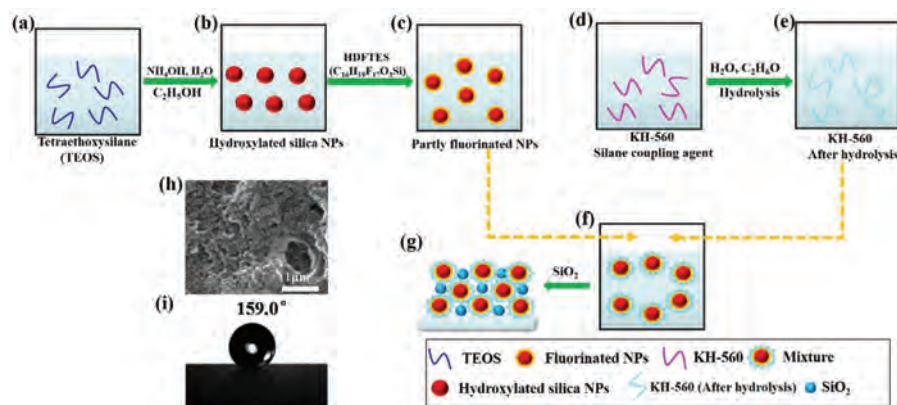
**Figure 1.** Schematic for modification of silica sol.

tightly adhered onto the substrate due to the film-forming property of KH-560, promoting adhesion between the composite sol and substrate surface. Besides, with the help of KH-560, cracks were minimized during heat treatment and integrity and stability of superhydrophobic coating were also greatly improved.

### Wettability of Prepared Coating

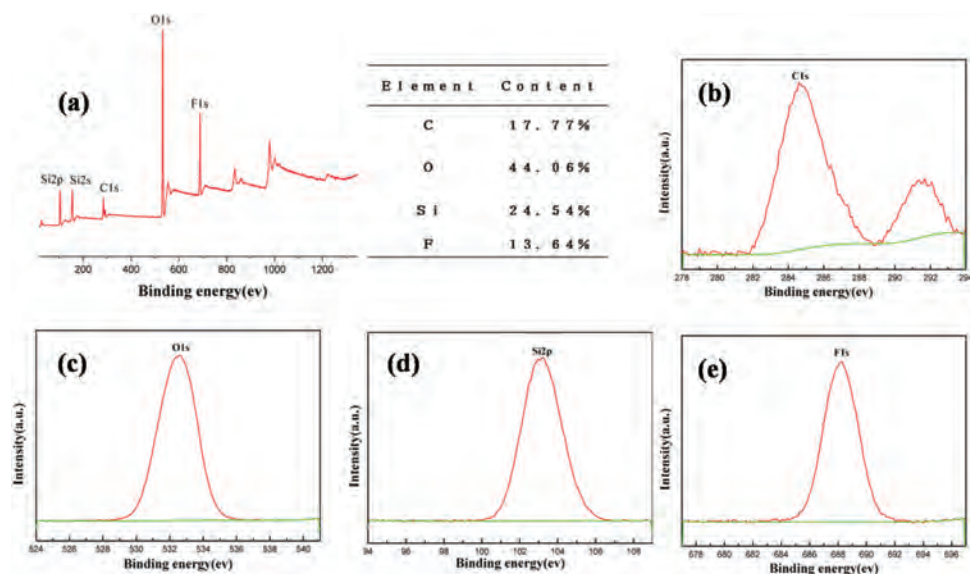
The static contact angle (CA) and surface morphology of the coatings were investigated as shown in Figure 4. After fluorination by 1H,1H,2H,2H-Perfluorodecyltriethoxysilane (HDFTES), the silica sol exhibited superhydrophobicity with CA of  $154^\circ$ . However, the  $\text{SiO}_2$  particles were not distributed homogeneously on the substrate, making them easy to agglomerate and disorderly distributed on the substrate to form surface roughness (Fig. 4(a)). On the contrary, the  $\text{SiO}_2$  particles wrapped

by the KH-560 were dispersed uniformly as shown in Figures 4(b) and (e). The coatings were intact, flat and well-adhered on the substrate, without observable cracks on the surface under scanning electron microscopy. However, CA of the coatings decreased to  $127.5^\circ$  after silane coupling, as shown in Figure 4(b). The reason for this was that the surface roughness was remarkably decreased after silica nano-particles had been encapsulated by KH-560. Fumed silica nanoparticles (SNs) were then introduced in the mixture in order to increase both the surface roughness and toughness. As shown in Figures 4(c) and (f), the coating regained superhydrophobicity (CA =  $159^\circ$ ) from water-adhesive to water-repellent after the addition of SNs by forming hierarchically rough structure that consisted of hierarchical micro-scale roughness and nanostructures, which were observed in the atomic force microscopy (AFM) image as well. The average surface roughness



**Figure 2.** (a–b) Preparation of silica sol, (c) fluorinated. (d–e) Hydrolysis of silane coupling agent (KH-560). (f) The mixture composed of fluorinated silica sols and hydrolyzed KH-560. (g) Fabrication of superhydrophobic coatings (the mixture of fluorinated silica sols, hydrolyzed KH-560, and silica nanoparticles). (h) SEM image of superhydrophobic coatings. (i) Coating with high water contact angle (CA =  $159.0^\circ$ ).





**Figure 3.** Elements scans of coated surfaces, (a) XPS spectra of superhydrophobic coatings; the content of each element is inserted (b) C (c) O (d) Si (e) F.

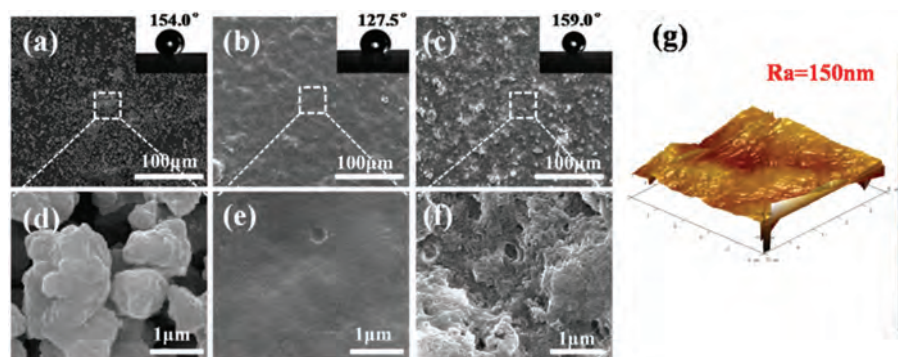
measured from AFM images was  $\sim 150$  nm for the final coating (silica sol/KH560/SNs, Fig. 4(g)). Above analyses indicated that the high surface roughness was essential in controlling surface wettability.

As stated above, the superhydrophobicity is a synergetic effect of surface roughness and its composition. In order to understand the contribution of the surface chemistry, the interfacial composition of silica sol/KH560/SNs coating was examined through X-ray photoelectron spectroscopy (XPS) analysis, and C, O, F and Si were the major components (Fig. 3), with a fluorine content of 13.64%. A high fluorine concentration endows the coating with a low surface energy. In combination with hierarchical micro- and nanoscopic structures, the superhydrophobicity of the coating is promised. The average CA for the coatings was achieved  $159^\circ$  (Fig. 4(c) inset).

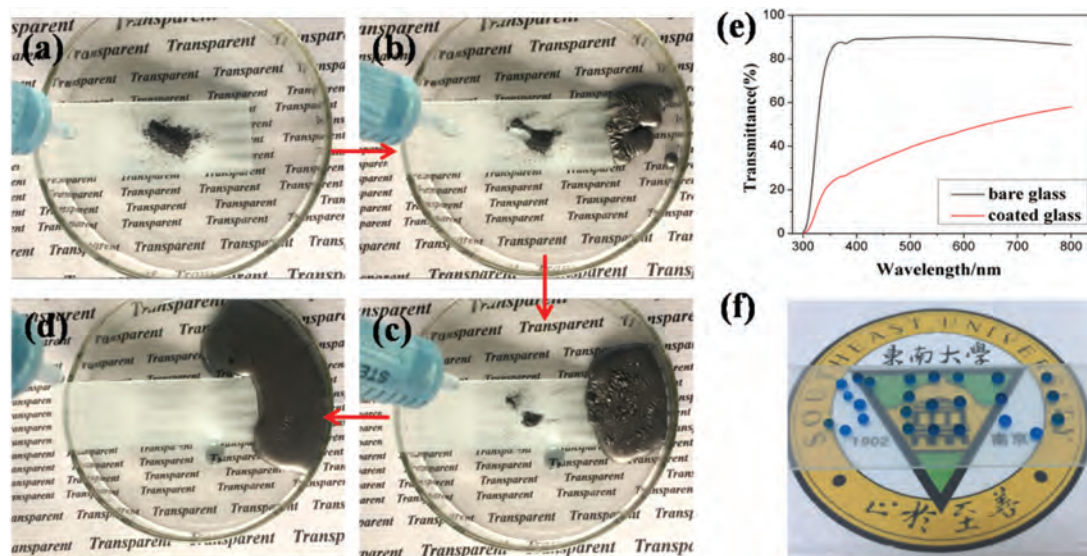
### Self-Cleaning Behavior and Transparency of Prepared Coating

The coating exhibited good self-cleaning property, since measured average rolling angle (RA) was  $\sim 3^\circ$ . As shown in Figures 5(a)–(d), dust from carbon black was spread onto the slightly-tilted, coated glass slides before water droplets were dribbled to the surface, the water quickly slid off and the dusts were wrapped up and swept away, leaving a clean surface. The self-cleaning coating can provide a dustproof, non-adhesive surface in domestic and industrial applications.

In addition to self-cleaning property of the superhydrophobic coating, the optical transparency was also determined through UV-vis transmittance spectroscopy. The transmittance of pristine and coated glass in the range of 300–800 nm wavelength is displayed in Figure 5(e).



**Figure 4.** SEM images of surface morphology and wettability characterization of three compositions of coatings. (a, d) Surficial characterization of spray-deposited fluorinated silica sol film. (b, e) Surficial characterization of spray-deposited fluorinated silica sol/KH560 hybrid film. (c, f) Surficial characterization of spray-deposited fluorinated silica sol/KH560/SNs hybrid film. (g) AFM image of spray-deposited fluorinated silica sol/KH560/SNs hybrid film.



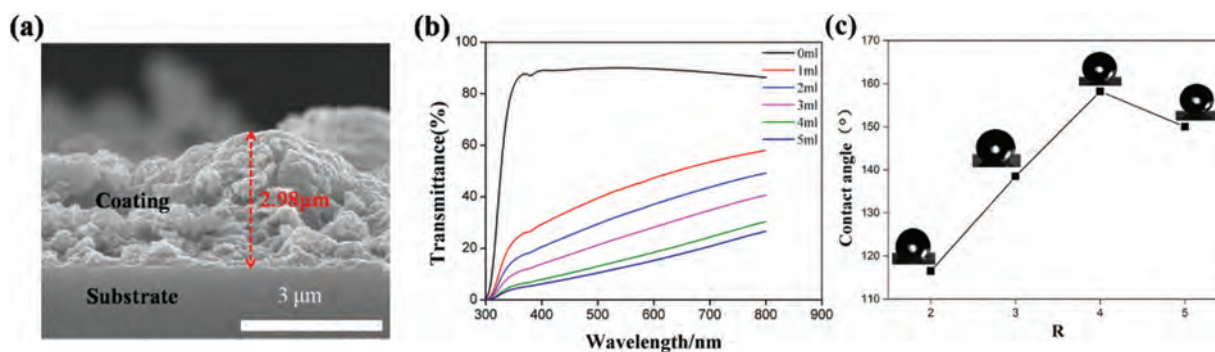
**Figure 5.** (a–d) Evolutional surface process of “self-cleaning” behavior for the superhydrophobic coating on a glass substrate. (e) UV-vis transmittance spectra for coated glass substrates (red) and bare glass substrates (black), respectively. (f) Optical photograph of methylene blue-dyed water droplets on the coated glass surface overlaying printed paper.

The coated glass substrates were translucent, with best transparency of  $\sim 60\%$  in the visible region (400–800 nm). The readability of the pattern underneath coated glass substrates reflected their transparency in Figure 5(f), and the superhydrophobicity was also demonstrated by almost sphere, blue-colored water droplets. It is well known that the thickness of the coating plays an important role in the transparency. As shown in Figure 6(a), the thickness of the coating with best transparency was  $\sim 3 \mu\text{m}$ , which can be further reduced in future practice. In addition, the transparency of the coating decreased sharply with increased thickness in Figure 6(b). It is therefore believed that further efforts ought to be made in the future study in order to prepare fully transparent or completely opaque coatings. We further studied the effect of KH-560 content on the superhydrophobicity of the coating in Figure 6(c). In this study, we define a variable  $R$ ,

which represents the meaning of

$$R = \frac{V(\text{fluorinated sol})}{V(\text{KH-560})}$$

the volume ratio of the fluorinated sol to KH-560. As shown in Figure 6(c), When  $R = 4$ , the contact angle for the coating reached maximum ( $\text{CA} = 159^\circ$ ). KH-560 organically combined two kinds of  $\text{SiO}_2$  particles to form a micro-nano hierarchical structure, which was similar to the Cassie model. When  $R < 4$ ,  $\text{SiO}_2$  particles were coated by KH-560, which greatly reduced the surface roughness of the coating. In this case, the coating lost its superhydrophobicity. When  $R < 4$ , KH-560 was too low to combine two kinds of  $\text{SiO}_2$  particles to form a micro-nano bilayer structure. In order to maximize the performance of the superhydrophobic coating, the volume ratio for the fluorinated sol and KH-560 was chosen to be 4.

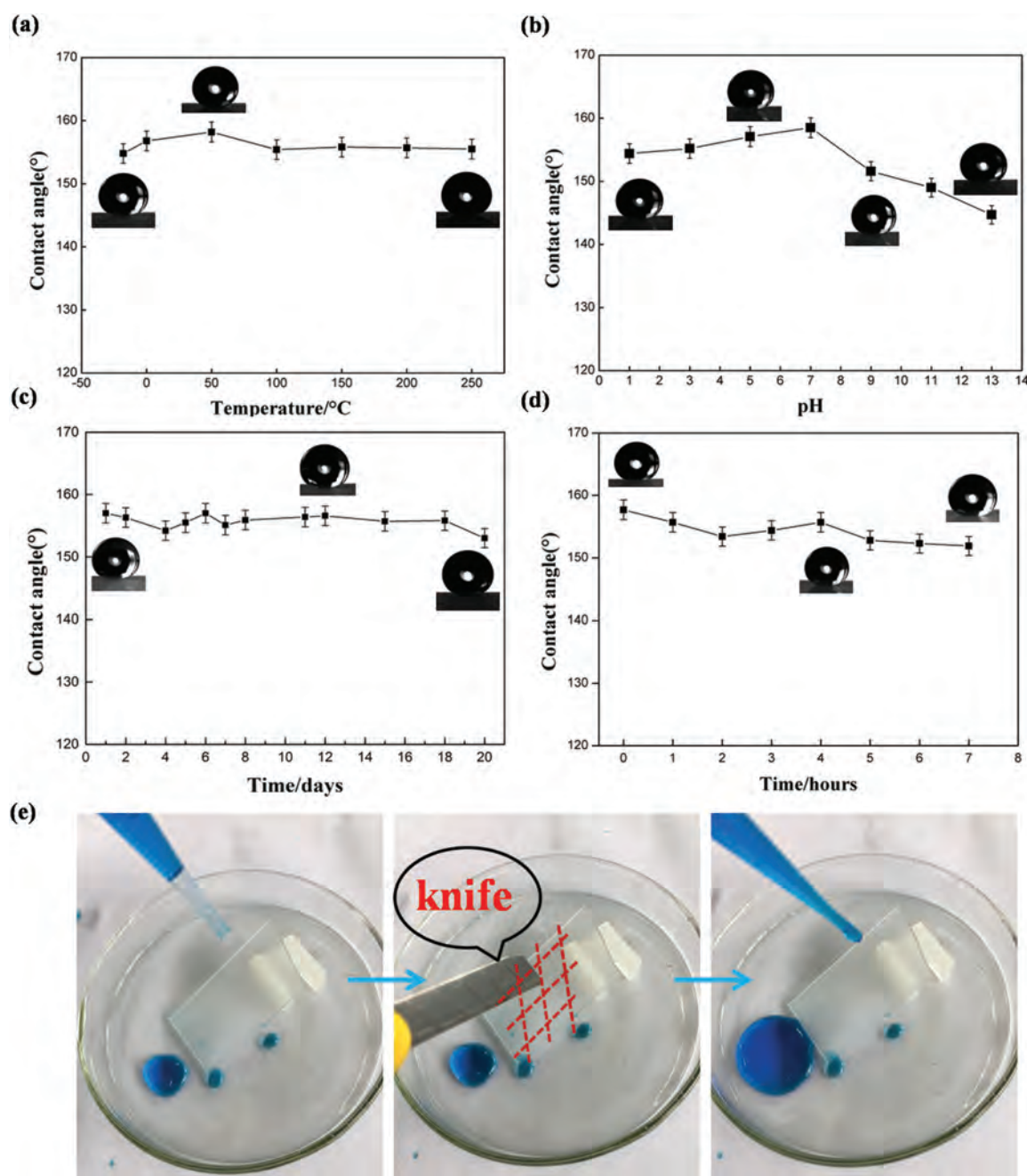


**Figure 6.** (a) SEM images of thickness for the coating with best transparency. (b) Transparency of superhydrophobic coating spray-deposited with different volumes. (c) CA as a function of  $R$  of as-prepared superhydrophobic coatings.

### Long-Term Stability of Superhydrophobic Coating

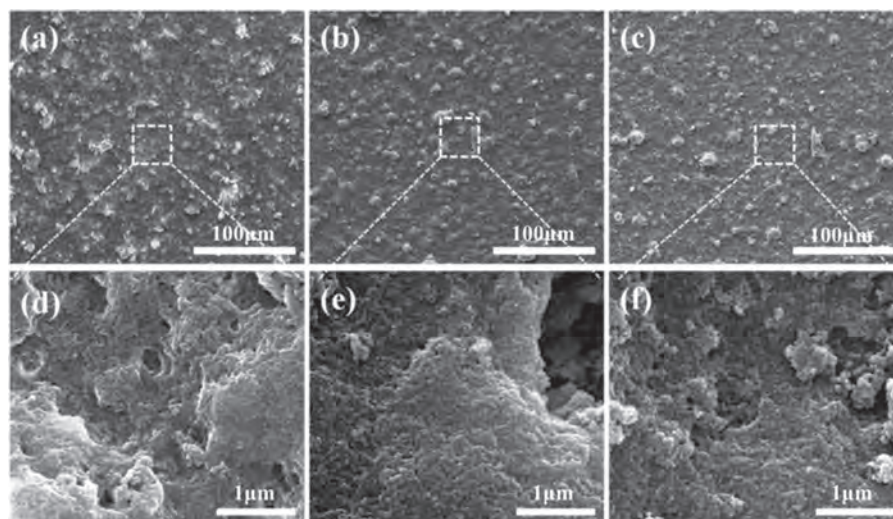
Outdoor applications of superhydrophobic surfaces include mirrors in automobiles, exterior walls of buildings, surfaces of textile, and so on. They often require not only the superior anti-wetting performance, but also call for the long-term stability under various harsh conditions. In the present study, the temperature stability for the coating was

carried out from  $-18$  to  $250$  °C for 2 hours. As illustrated in Figure 7(a), the CA for the coatings changed negligibly after being frozen at  $-18$  °C for 2 hours. No ice was deposited on the surface. Back to room temperature, water droplets still rolled off the surface. After baking at an extremely high temperature of even  $250$  °C for 2 hours, CA remained  $155^\circ$  without any observable change on the coating. The superior thermostability of superhydrophobic



**Figure 7.** Stability of as-prepared superhydrophobic coating under harsh practical conditions. (a) Thermo-treatment from  $-18$  to  $250$  °C for 2 hours. (b) Rinsed in solutions of different pH values (1 to 13) for 1 h. (c) Continuous exposure to sunlight up to 3 weeks. (d) Mechanical durability test by means of ultrasonication, 0–7 h. (e) Destructive attempts on the superhydrophobic coating by scratching with a steel blade water droplets still dropped away automatically (the dotted line illustrated the trace of knife).





**Figure 8.** SEM images of surface morphologies for three different types of coatings after acidic/alkaline treatment. (a, d) Surficial characterizations of spray-deposited fluorinated silica sol/KH560/SNs hybrid film without treatment. (b, e) The same film after being treated with HCl (pH = 1) for 1 h. (c, f) The same film treated with KOH (pH = 13) for 1 h.

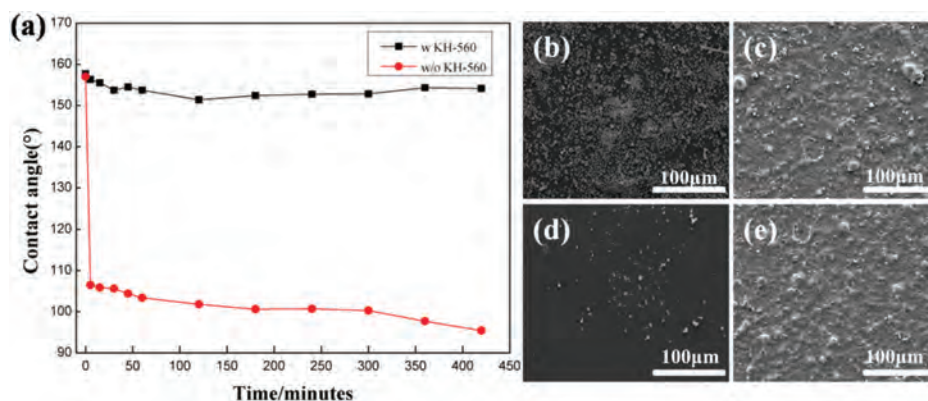
coating suggested that it can meet extendable applications at a wide temperature range of at least from  $-18$  to  $250$  °C.

The endurance of the surface coating in harsh pH variation sometimes determines its applications, especially in industry. The acid- and alkali-resistance for the coating was also evaluated. The coatings were immersed in acidic or alkaline solutions with different pH values for 1 hour. As shown in Figure 7(b), the CAs didn't change in acidic solutions compared to pristine surface at greater than  $150$ ° temperature. On the contrary, the performance of the coating slightly deteriorated after alkaline treatment. The reason is that KH-560 has weak acidity, which partially reacted with the alkaline substance in the solution. However, the intactness of the coating and hierarchical structure were maintained (Fig. 8). The CA therefore remained above  $140$ ° even at a pH of 13 (Fig. 7(b)). It is therefore believed that the present superhydrophobic coating is

viable and stable enough in most of industrial and domestic conditions.

It is noteworthy that, light, especially sunlight, can significantly deteriorate the long-term stability of any coatings, since different wavelength fractions in the sunlight have thermal effect that cause direct beam damage and/or induce oxidizing agents such as ozone. The present superhydrophobic coating has been continuously exposed to sunlight up to three weeks. The performance of the coating was satisfying with little change of the CAs observed (Fig. 7(c)). The performance indicated that the coating has sufficient stability under long-term sunlight exposure.

Having proven that the silica coating is stable in most harsh conditions such as temperature, pH and sunlight exposure, the durability towards physical damage caused by external force has also been taken into consideration. Two different means, ultrasonication and scratch with a sharp blade were employed in the present study.



**Figure 9.** (a) CA as a function of ultrasonication time for as-prepared superhydrophobic coatings without and with silane coupling agent (KH-560). (b) Coating without KH-560 before ultrasonication. (c) Coating with KH-560 before ultrasonication. (d) Coating without KH-560 after ultrasonication for 7 h. (e) Coating with KH-560 after ultrasonication for 7 h.

**Table I.** Stability of superhydrophobic coating in previous studies.

Major components	Procedure description	Thermal resistance	Acid-base resistance	Sunlight irradiation	Ultrasonic destruction	Blade scratching	Ref.
Candle soot and PDMS	High-temperature calcination and CVD modification	−5–475 °C	N.A.	N.A.	N.A.	N.A.	[36]
Silica and TMS	Spin coating	N.A.	N.A.	2000 h outdoor exposure	N.A.	N.A.	[37]
Silica	Dip coating	N.A.	N.A.	N.A.	2 h	N.A.	[38]
Silicone oil	Spray coating	20–450 °C	4–10	N.A.	N.A.	N.A.	[39]
Silica and PDMS	Two-layer spray coating	N.A.	2–12	N.A.	2 h	N.A.	[40]
Silica and PTMS	Spray coating	−18–200 °C	N.A.	UV 10 h	N.A.	Resistant	[41]
Silica and PDMS	Dip-coating	20–95 °C	N.A.	Environmental conditions for 7 months	10 min	N.A.	[42]
Silica and coupling agents	Low-temperature spray coating	−18–250 °C	1–13	Sunlight up to 3 weeks	7 h	Resistant	This manuscript

Note: "N.A." Not reported.

Hardly any change of the hydrophobic performance was observed for the coating after violent ultrasonication for the extended time spanning from 1 to 7 h, as shown in Figure 7(d). The CA remained greater than 150° after the longest ultrasonication for 7 h, showing a remarkable improvement compared to conventional sol–gel coatings.<sup>39</sup> The fortified micro-nano-structure by silane KH-560 coupling agent was found as a major mechanism for the progress. For the coating without the addition of KH-560, the hydrophobicity was significantly diminished after a 10-second sonication (Fig. 9(a)). In this case, the structure was seriously damaged as shown in Figures 9(b) and (d). However, no structural change occurred in the coating with addition of KH-560 (Figs. 9(c and e)), which indicates that the surface structure was robust enough to sustain the significant shear forces raised by shockwaves during sonication.

The coating was then treated in a more direct and violent way. The coated glass slide was scratched repeatedly with a sharp blade. Figure 7(e) showed that liquid droplets rolled off effortlessly on the slightly tilted and coated glass slide after the destructive attempt, same as the brand-new coated glass. The durable toughness of the coating originated from the fact that the hardness of silica is higher than the steel blade, as well as abundant coupling interaction in the matrix of the coating as discussed above. Therefore, although blade scratching may have removed part of the coating and left a few scratches, the massive structure of the coating was not destroyed by the blade, and hence the performance was kept as before. Table I compares similar hydrophobic and environmental durable coatings as reported in recent literatures. It suggests that our novel coating strategy represents one among the best performances. Various critical conditions were considered in this study, and the coating has shown satisfying performance at the same time, which shed light on multi-purpose, versatile superhydrophobic and practically durable surface coatings.

## CONCLUSIONS

In summary, we have demonstrated a novel and facile strategy for preparation of superhydrophobic coatings with superior chemical stability and mechanical durability. Chemically modified silica nanoparticle suspension was prepared by a low-temperature sol–gel process and fortified with silane coupling agents that were spray-coated on substrates, forming a protective layer. The high CA of 159° and low RA of ~3° enabled surface superhydrophobic and “self-cleaning.” Dirt was automatically removed with the rolling of water droplets. Moreover, the as-shown superhydrophobic coatings possess satisfied stability at harsh practical conditions. For example, temperature changed from −18 to 250 °C, pH 1–13 after several weeks of sunlight exposure. Meanwhile, the coating was proven mechanically durable, which can endure the long-term attack from violent ultrasonic shockwaves or repeated scratching with a sharp steel blade. Moreover, more efforts are still needed to further ameliorate its optical performance. Altogether, it is believed that the proposed silica-based, superhydrophobic and durable coating, prepared by a facile and energy-saving strategy, is applicable in various harsh conditions, promoting its extensive applications in both household and industrial conditions.

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## REFERENCES

1. B. Wilhelm and C. Neinhuis, Purity of the sacred lotus, or escape from contamination in biological surfaces. *Planta* 202, 1 (1997).
2. M. Abraham, The lotus effect: Superhydrophobicity and metastability. *Langmuir* 20, 3517 (2004).
3. L. X. Shi, X. Liu, W. S. Wang, L. Jiang, and S. T. Wang, A self-pumping dressing for draining excessive biofluid around wounds. *Adv. Mater.* e1804187 (2018).



4. B. Wang, Y. B. Zhang, L. Shi, J. Li, and Z. G. Guo, Advances in the theory of superhydrophobic surfaces. *J. Mater. Chem.* 22, 20112 (2012).
5. Y. B. Zhang, Y. Chen, L. Shi, J. Li, and Z. G. Guo, Recent progress of double-structural and functional materials with special wettability. *J. Mater. Chem.* 22, 799 (2012).
6. E. J. Falde, S. T. Yohe, Y. L. Colson, and M. W. Grinstaff, Superhydrophobic materials for biomedical applications. *Biomaterials* 104, 87 (2016).
7. Y. Koc, A. J. de Mello, G. McHale, M. I. Newton, P. Roach, and N. J. Shirtcliffe, Nano-scale superhydrophobicity: Suppression of protein adsorption and promotion of flow-induced detachment. *Lab Chip* 8, 582 (2008).
8. J. L. Wang, J. A. Kaplan, Y. L. Colson, and M. W. Grinstaff, Stretch-induced drug delivery from superhydrophobic polymer composites: Use of crack propagation failure modes for controlling release rates. *Angew. Chem. Int. Edit.* 55, 2796 (2016).
9. X. M. Li, D. Reinhoudt, and M. C. Calama, What do we need for a superhydrophobic surface? A review on the recent progress in the preparation of superhydrophobic surfaces. *Chem. Soc. Rev.* 36, 1350 (2007).
10. A. Nakajima, K. Hashimoto, and T. Watanabe, Transparent superhydrophobic thin films with self-cleaning progress. *Langmuir* 16, 7044 (2000).
11. L. C. Gao and T. J. McCarthy, The "lotus effect" explained: Two reasons why two length scales of topography are important. *Langmuir* 22, 2966 (2006).
12. X. Deng, L. Mammen, Y. F. Zhao, P. Lellig, K. Müllen, C. Li, H. J. Butt, and D. Vollmer, Transparent, thermally stable and mechanically robust superhydrophobic surfaces made from porous silica capsules. *Adv. Mater.* 23, 2962 (2011).
13. T. T. Ren, M. Q. Yang, K. K. Wang, Y. Zhang, and J. H. He, CuO nanoparticles-containing highly transparent and superhydrophobic coatings with extremely low bacterial adhesion and excellent bactericidal property. *ACS Appl. Mater. Inter.* 10, 25717 (2018).
14. L. Y. Li, J. F. Zhu, S. D. Zhi, E. Y. Liu, G. Wang, Z. X. Zeng, W. J. Zhao, and Q. J. Xue, Study of adhesion and friction drag on a rough hydrophobic surface: Sandblasted aluminum. *Phys. Fluids* 30, 071903 (2018).
15. K. Manabe, S. Nishizawa, K. H. Kyung, and S. Shiratori, Optical phenomena and antifrosting property on biomimetics slippery fluid-infused antireflection films via layer-by-layer comparison with superhydrophobic and antireflective films. *ACS Appl. Mater. Inter.* 6, 13985 (2014).
16. Al. Leon and R. C. Advincula, Reversible superhydrophilicity and superhydrophobicity on a lotus-leaf pattern. *ACS Appl. Mater. Inter.* 6, 22666 (2014).
17. Y. Y. Yan, N. Gao, and W. Barthlott, Mimicking natural superhydrophobic surfaces and grasping the wetting process: A review on recent progress in preparing superhydrophobic surfaces. *Adv. Colloid Interface Sci.* 169, 80 (2011).
18. A. V. Rao, S. D. Bhagat, H. Hirashima, and G. M. Pajonk, Synthesis of flexible silica aerogels using methyltrimethoxysilane (MEMS) precursor. *J. Colloid Interface Sci.* 300, 279 (2006).
19. P. Cai, N. N. Bai, L. Xua, C. Tan, and Q. Li, Fabrication of superhydrophobic wood surface with enhanced environmental adaptability through a solution-immersion process. *Surf. Coat. Technol.* 277, 262 (2015).
20. B. Balu, J. S. Kim, V. Breedveld, and D. W. Hess, Tunability of the adhesion of water drops on a superhydrophobic paper surface via selective plasma etching. *J. Adhes. Sci. Technol.* 23, 361 (2009).
21. C. Aulin, S. H. Yun, L. Wågberg, and T. Lindstrom, Design of highly oleophobic cellulose surfaces from structured silicon templates. *ACS Appl. Mater. Inter.* 1, 2443 (2009).
22. S. van Pelt, A. Frijns, R. Mandampambil, and J. den Toonder, Local wettability tuning with laser ablation redeposits on PDMS. *Appl. Surf. Sci.* 303, 456 (2014).
23. H. E. Jeong, S. H. Lee, J. K. Kim, and K. Y. Suh, Nanoengineered multiscale hierarchical structures with tailored wetting properties. *Langmuir* 22, 1640 (2006).
24. K. Liu, Y. Tian, and L. Jiang, Bio-inspired superhydrophobic and smart materials: Design, fabrication, and application. *Prog. Mater. Sci.* 58, 503 (2013).
25. L. B. Zhang, Y. Li, J. Q. Sun, and J. C. Shen, Lay-by-layer fabrication of broad-band superhydrophobic antireflective coatings in near-infrared region. *J. Colloid Interface Sci.* 319, 302 (2008).
26. T. Wang, X. G. Hu, and S. J. Dong, A general route to transform normal hydrophilic cloths into superhydrophobic surfaces. *Chem. Commun.* 18, 1849 (2007).
27. T. L. Sun, L. Feng, X. F. Gao, and L. Jiang, Bioinspired surfaces with special wettability. *Acc. Chem. Res.* 38, 644 (2005).
28. Y. Rahmawan, L. Xu, and S. Yang, Self-assembly of nanostructures towards transparent, superhydrophobic surfaces. *J. Mater. Chem. A* 1, 2955 (2013).
29. C. Pereira, C. Alves, A. Monteiro, C. Magen, A. M. Pereira, A. Ibarra, M. R. Ibarra, P. B. Tavares, J. P. Araujo, G. Blanco, J. M. Pintado, A. P. Carvalho, J. Pires, M. F. R. Pereira, and C. Freire, Designing novel hybrid materials by one-pot co-condensation: From hydrophobic mesoporous silica nanoparticles to superamphiphobic cotton textiles. *ACS Appl. Mater. Inter.* 3, 2289 (2011).
30. X. Zhang, F. Shi, J. Niu, Y. G. Jiang, and Z. Q. Wang, Superhydrophobic surfaces: From structural control to functional application. *J. Mater. Chem.* 18, 621 (2008).
31. X. Deng, L. Mammen, H. J. Butt, and D. Vollmer, Candle soot as a template for a transparent robust superamphiphobic coating. *Science* 335, 67 (2012).
32. X. Y. Ling, I. Y. Phang, G. J. Vancso, J. Huskens, and D. N. Reinhoudt, Stable and transparent superhydrophobic nanoparticle films. *Langmuir* 25, 3260 (2009).
33. S. Sarkar, A. Chunder, W. F. Fei, L. N. An, and L. Zhai, Superhydrophobic mats of polymer-derived ceramic fibers. *J. Am. Ceram. Soc.* 91, 2751 (2008).
34. Z. K. He, M. Ma, X. R. Lan, F. Chen, K. Wang, H. Deng, Q. Zhang, and Q. Fu, Fabrication of a transparent superamphiphobic coating with improved stability. *Soft Matter* 7, 6435 (2011).
35. X. Deng, L. Mammen, Y. F. Zhao, P. Lellig, K. Müllen, C. Li, H. J. Butt, and D. Vollmer, Transparent, thermally stable and mechanically robust superhydrophobic surfaces made from porous silica capsules. *Adv. Mater.* 23, 2962 (2011).
36. X. J. Liu, Y. Wang, Z. Chen, K. Y. Ben, and Z. S. Guan, A self-modification approach toward transparent superhydrophobic glass for rainproofing and superhydrophobic fiberglass mesh for oil/water separation. *Appl. Surf. Sci.* 360, 789 (2016).
37. M. Manca, A. Cannavale, L. D. Marco, A. S. Arico, R. Cingolani, and G. Gigli, Durable superhydrophobic and antireflective surface by trimethylsilanized silica nanoparticles-based sol-gel processing. *Langmuir* 25, 6357 (2009).
38. W. H. Huang and C. S. Lin, Robust superhydrophobic transparent coatings fabricated by a low-temperature sol-gel process. *Appl. Surf. Sci.* 305, 702 (2014).
39. K. Seo, M. Kim, S. Seok, and D. H. Kim, Transparent superhydrophobic surface by silicone oil combustion. *Colloids Surf. A* 492, 110 (2016).
40. Z. Z. Zhang, B. Ge, X. H. Men, and Y. Li, Mechanically durable, superhydrophobic coatings prepared by dual-layer method for anti-corrosion and self-cleaning. *Colloids Surf. A* 490, 182 (2016).
41. Y. Li, X. H. Men, X. T. Zhu, B. Ge, F. J. Chu, and Z. Z. Zhang, One-step spraying to fabricate nonfluorinated superhydrophobic coatings with high transparency. *J. Mater. Sci.* 51, 2411 (2016).
42. Z. K. He, M. Ma, X. R. Lan, F. Chen, K. Wang, H. Deng, Q. Zhang, and Q. Fu, Fabrication of a transparent superamphiphobic coating with improved stability. *Soft Matter* 7, 6435 (2011).