

Transparent and Durable SiO₂-Containing Superhydrophobic Coatings on Glass

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ABSTRACT: We fabricated novel superhydrophobic coatings based on SiO₂ nanoparticles combined with NH₂-terminated silicone (SN₂) or SN₂-modified polyurethane (SN₂-prePU) by alternately spin-coating them onto glass slides. The final fabricated surface contained SN₂/SiO₂ or SN₂-prePU/SiO₂ bilayers. The conditions of spin-coating method were also explored. SN₂-prePU with different SN₂/prePU molar ratios were synthesized to study the influence of SN₂ ratio on the water contact angles of ultimate spin-coated surfaces. The surface was found to be tunable from hydrophobic to superhydrophobic by choosing SN₂-prePU with different SN₂/prePU molar ratios or SN₂ content. Water droplets easily rolled off on these superhydrophobic surfaces. Surfaces coated with SN₂/SiO₂ bilayers showed better transparency, whereas surfaces coated with SN₂-prePU(2 : 1)/SiO₂ bilayers exhibited better durability. Droplets of varied pH were prepared to test the anti-wettability of the coatings. Results showed that the as-coated surfaces had stable superhydrophobicity to droplets with pH values ranging from 1 to 14. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41500.

KEYWORDS: durable; spin-coating; superhydrophobic coating; transparent

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INTRODUCTION

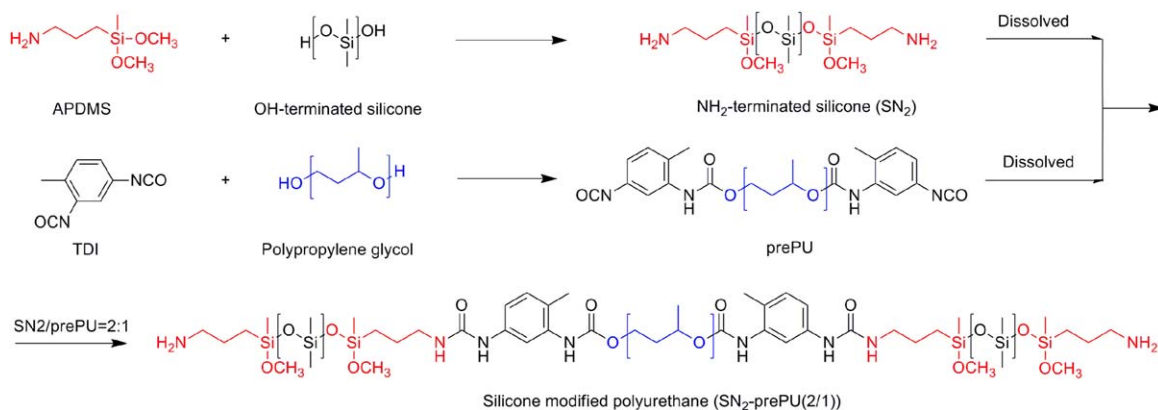
Superhydrophobic surfaces can be potentially applied in self-cleaning,^{1–3} anti-contamination,⁴ anti-corrosion,⁵ anti-fogging,⁶ anti-sticking of snow,⁷ and oil-water separation,⁸ etc. Thus, studying and fabricating superhydrophobic surfaces has emerged as one of the most popular research topics in the past 15 years.^{9,10} Superhydrophobic surfaces are those that display apparent water contact angles over 150°. Roughness and the surface free energy (or surface tension) are the two key factors that determine the hydrophobicity of surfaces.¹¹ During the past decade, intensive efforts have been exerted to develop new methods for preparing superhydrophobic surfaces that display micro- and nano-roughness. Various approaches involving physical and chemical methods have been used in constructing superhydrophobic surfaces. These approaches can be generally classified into top-down and bottom-up techniques, depending on the direction of the procedure. Top-down methods include lithographic etching,¹² template method,¹³ methods which combine lithographic etching with template,¹⁴ and plasma treatment,^{15,16} etc. Bottom-up methods usually involve chemical deposition,^{17–19} colloidal assembly,^{20,21} layer-by-layer assembly,^{22,23} hydrogen bond-based methods,²⁴ and phase separation-based methods,²⁵ etc. There are also some methods which combine

top-down and bottom-up methods, like coating polymer solutions^{26,27} or polymer-inorganic nanoparticle solutions,^{28,29} etc. Top-down approaches can fabricate excellent micro- and nano-structures with controllable sizes, shapes, morphology, and topography. However, these approaches are comparatively complex and not feasible for large-area fabrication.³⁰ On the other hand, bottom-up methods are cost effective and have potential application in the fabrication of large-area superhydrophobic surfaces. Among them, spin-coating is a facile but effective method, by which the roughness and the anti-wettability can be tuned.^{31,32}

For applications, several limitations need to be solved, such as transparency, durability, ability of retaining superhydrophobicity under different pH, and ability of shielding inner surfaces from corrosive liquids, etc. Various studies have attempted to fabricate transparent superhydrophobic surfaces.^{33,34} However, these surfaces either lack fine durability or need further durability tests. A good balance between transparency and durability still remains unsolved. On one hand, to obtain a transparent superhydrophobic surface, the micro- and nano-structures should be precisely tuned given that transparency and superhydrophobicity have two paradoxical requirements for the hierarchical structure. On the other hand, although the study on durability is

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Scheme 1. Preparation of SN₂ and SN₂-prePU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

quite important, only a few studies have focused on this characteristic.^{35,36} Even less have succeeded in fabricating surfaces, which show superhydrophobicity to acidic or alkaline liquids.³⁷

In this article, we will introduce a facile way to fabricate superhydrophobic surfaces by spin-coating SiO₂ nanoparticles and NH₂-terminated silicone (denoted as SN₂) or SN₂-modified polyurethane (denoted as SN₂-prePU) with nontoxic solvent. The anti-wettability, transparency, and durability of these surfaces were investigated. Aqueous solutions with pH values from 1 to 14 were prepared to inspect the anti-wettability of the as-coated surfaces under acidic and alkaline conditions.

EXPERIMENTAL

Materials

Polypropylene glycol (PPG, $M_w = 1000$ g/mol) was purchased from Gaoqiao Petrochemical Co., Ltd., Shanghai, China and was vacuum distilled to dehydrate. Hydroxyl-terminated poly(dimethyl siloxane) (OH-terminated PDMS, hydroxyl value is 4 wt %) was purchased from Quanli Chemical Co., Ltd., Wuxi, China. Amino propyl dimethoxymethyl silane (APDMS) was purchased from Debang Chemical New Materials Co., Ltd., Hubei, China. Toluene diisocyanate (TDI) was purchased from Tokyo Chemical Industry Co., Ltd., Japan. Tetraethyl orthosilicate (TEOS), ethanol and isopropanol were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Ammonia was purchased from Hangzhou Changzheng Chemical Reagent Co., Ltd., China. All reagents were used without further purification. Ultrapurified water (UP-water) was laboratory-made.

Preparation of SiO₂ Nanoparticles

SiO₂ nanoparticles were prepared through Stöber sol-gel method.^{38,39} 40 mL TEOS was diluted with 600 mL ethanol and 100 mL UP-water in a flask. The solution were stirred for 15 min. Then, 7 mL ammonia was added into the flask while under strong stirring. Stirring was continued for 24 h at 35°C. The number-average diameter of the particle was around 100 nm, which was measured by dynamic light scattering.

Preparation of SN₂ and SN₂-PrePU

Scheme 1 shows the fundamental synthetic route of SN₂ and SN₂-prePU. The top equation in Scheme 1 shows the synthesis of SN₂ (S represents silicone; N₂ represents two NH₂ functional

end groups in the molecule). APDMS (2 mol) and OH-terminated PDMS (1 mol) were added into the flask, under moderate stirring at 110–120°C. The by-product methanol was vacuum distilled. The reaction was kept for 3 to 4 h until no methanol was produced.⁴⁰

To synthesize SN₂-prePU, prePU was first synthesized with a fixed amount of PPG and TDI [The middle equation in Scheme 1]. The theoretical NCO amount was set at 5% and the final actual value of NCO amount was measured by titration to ensure that the reaction finished. Then, the quantified prePU and SN₂ were dissolved in isopropanol, respectively. The prePU solution was added dropwise into the SN₂ solution, and the mixture was stirred for another 30 min.

SN₂/prePU with various ratios were synthesized by programs displayed in Scheme 1. SN₂-prePU($x : y$) is the abbreviation of SN₂-modified polyurethane with a certain SN₂/prePU ratio (x is the molar of SN₂ and y is the molar of prePU). A sample information is listed in Table II.

Figure 1 shows the FTIR spectrum of the synthesized SN₂-prePU(2 : 1) as a typical example of a series of SN₂-prePU with different ratios. The peak at 3311 cm⁻¹ can be attributed to the N–H stretching vibration. The peaks at 2962 and 2898 cm⁻¹

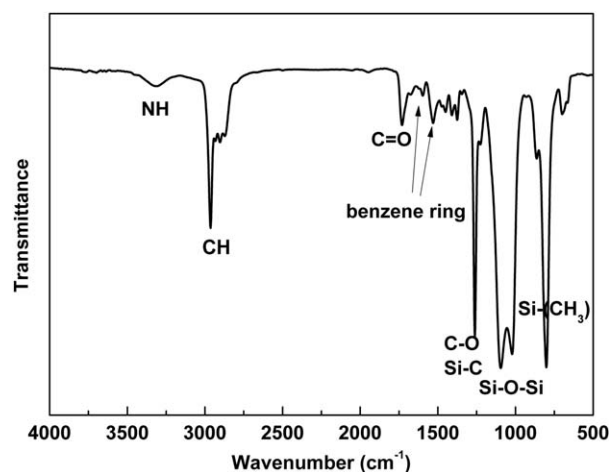


Figure 1. FTIR spectrum of the synthesized SN₂-prePU(2 : 1).

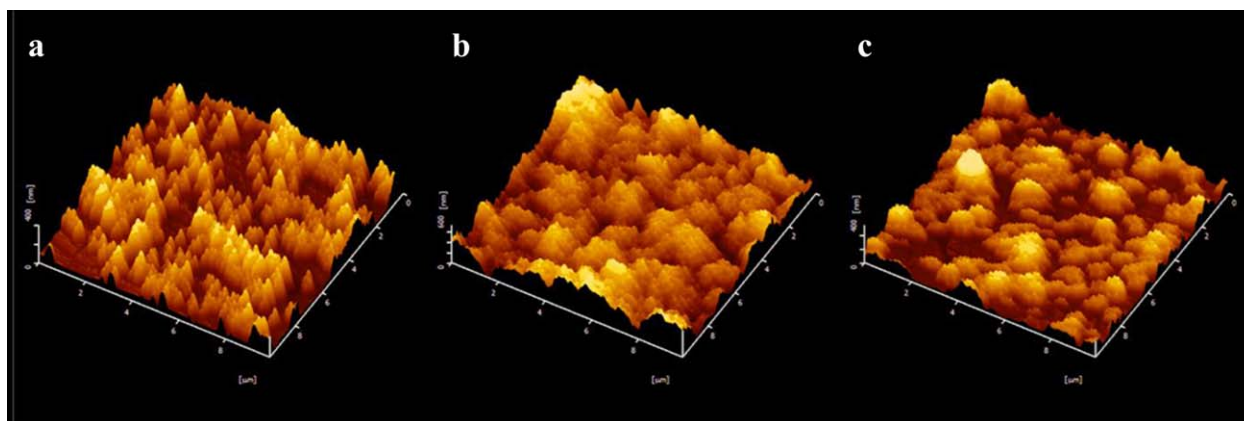


Figure 2. AFM 3D graphs of (a) surface *a*, 5 spin-coated SiO₂ layers, (b) surface *b*, 5 spin-coated SN₂/SiO₂ bilayers, and (c) surface *c*, 5 of spin-coated SN₂-prePU(2 : 1)/SiO₂ bilayers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

represent the C—H stretching vibration of CH₃, whereas the peaks at 2946 and 2863 cm⁻¹ correspond to the C—H stretching vibration of CH₂. The peak at 1730 cm⁻¹ can be attributed to the C=O stretching vibration of the urea and urethane groups. The peaks at 1694 and 1527 cm⁻¹ are the characteristic peak for benzene ring of TDI. The peak at 1261 cm⁻¹ corresponds to the stretching vibration of C—O and Si—C. The peaks at 1095 and 1022 cm⁻¹ are attributed to Si—O—Si stretching vibration. All characteristic peaks can be found on the FTIR spectra of other SN₂-prePU. The only difference of these FTIR spectra is the peak intensity of these characteristic peaks, which is due to the different SN₂/prePU ratios of SN₂-prePU. The calculated molecular weight of SN₂/prePU(2 : 1) is 3897 g/mol. The molecular weight measured by gel permeation chromatography is 3804 g/mol. These results indicate that SN₂/prePU(2 : 1) is synthesized as designed.

Spin-Coat Superhydrophobic Surfaces

The SN₂ solution (or SN₂-prePU solution) and SiO₂ dispersion were diluted in nontoxic solvents, such as ethanol or isopropanol. The concentration of SN₂ or SN₂-prePU solution was 0.25 wt %, whereas the concentration of SiO₂ was 1.0 wt %. For the surface fabricated by SN₂/SiO₂ bilayers, the SN₂ solution was first spin-coated onto a glass slide at 3000 rpm. Second, the SiO₂ dispersion was spin-coated onto the afore-coated glass. These procedures were repeated for desired times and then the surface has several SN₂/SiO₂ bilayers. At last, the SN₂ solution was spin-coated on the topside. For the surface coated with SN₂-prePU/SiO₂ bilayers, only the organic component SN₂ was replaced by SN₂-prePU, and the other procedures were the same.

Characterization

Contact angles were measured by an optical contact angle measuring device (Harke-SPCA, Peking Harke Experimental Instrument Factory, China). The transmittance of the surfaces was characterized using UV-vis spectrophotometer (CARY 100 Bio, Varian Inc., USA). The transmittance data (*T*%) plotted in Figure 5(b) is calculated using the formula, $T\% = \frac{T_c}{T_{\text{glass}}} \times 100\%$, where *T_c* is the transmittance of coated surfaces and *T_{glass}* is the transmittance of the untreated glass slide. The morphology was observed using the

atomic force microscope (AFM, in DFM mode, SPI3800N, SII Nano Technology Inc., Japan). The arithmetical mean deviation of the surface, $R_a = \frac{1}{n} \sum_{i=1}^n |y_i|$ (*y_i* is the vertical distance from the mean line to the *i*th data point in the scan region), the root mean square of surface, $RMS = \sqrt{\frac{1}{n} \sum_{i=1}^n y_i^2}$, the maximum height of the surface profile, P-V = *R_p* - *R_v* (in which *R_p* = max *y_i*, *R_v* = min *y_i*), and the quotient of the exact surface area to the project area, *S* Ratio, can be measured using AFM.

RESULTS AND DISCUSSION

Static Water Contact Angle

Spin-coating could lead to close-packed colloidal crystals because of shear-induced ordering.^{41,42} It is also positive to have the close-pack of SiO₂ nanoparticles, since aggregation enlarges the surface roughness, which further generates the superhydrophobicity of the surface according to Wenzel model or Cassie-Baxter model.^{43,44} However, the interaction between rigid SiO₂ and SiO₂ nanoparticles is not large enough to guarantee a stable surface structure. As a result, the supernormal anti-wettability wrecks in a short time. Thus, SN₂ and SN₂-prePU are introduced. And the morphology of the surfaces spin-coated with different compositions were studied. The surface coated with 5 SiO₂ layers is denoted as surface *a*; the surface coated with 5 SN₂/SiO₂ bilayers is denoted as surface *b*; and the surface coated with 5 SN₂-prePU(2 : 1)/SiO₂ bilayers is denoted as surface *c*. The surface morphology is investigated using AFM and Figure 2 shows 3D topographic graphs of these surfaces. The surface information are listed in Table I. The light and rough area in Figure 2(a–c) indicates the surfaces that were covered with SiO₂.

Table I. Surface Information of Surface *a*, Surface *b*, and Surface *c*

Surface	<i>R_a</i> (nm)	RMS (nm)	P-V (nm)	<i>S</i> ratio	θ_w (°)
<i>a</i>	72.3	83.8	400.9	1.198	45.3 ± 5.2
<i>b</i>	100.5	125.9	723.7	1.272	128.8 ± 3.1
<i>c</i>	68.1	83.3	547.1	1.230	124.5 ± 3.9

Note: surface *a*, 5 spin-coated SiO₂ layers; surface *b*, 5 spin-coated SN₂/SiO₂ bilayers; surface *c*, 5 spin-coated SN₂-prePU(2 : 1)/SiO₂ bilayers.

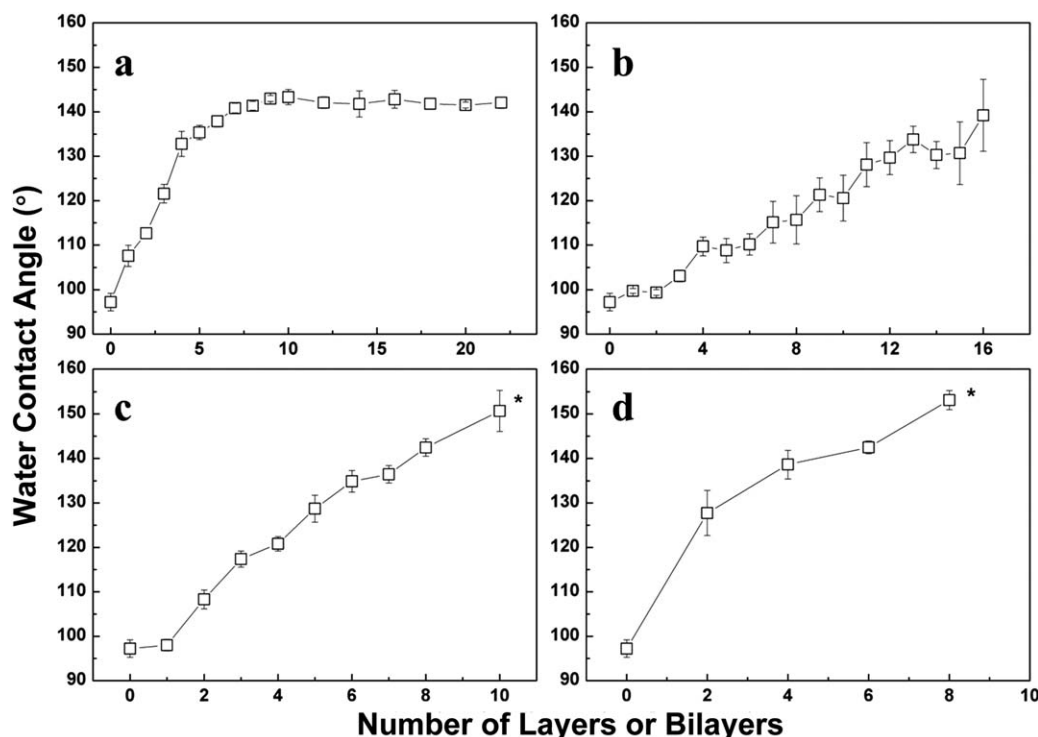


Figure 3. (a) θ_w of surfaces spin-coated with only SiO₂ layers at 2000 rpm. (b) θ_w of surfaces spin-coated with SN₂/SiO₂ bilayers at 2000 rpm, while the solvent is isopropanol. (c) θ_w of surfaces spin-coated with SN₂/SiO₂ bilayers at 2000 rpm. (d) θ_w of surfaces spin-coated with SN₂/SiO₂ bilayers at 3000 rpm. If it is not specially pointed out, the solvent is ethanol.

The SiO₂ coverage of surface *b* is much higher than those from surfaces *a* and *c*. Meanwhile, the R_a , RMS, P-V, and S Ratio of surface *b* are also larger than those from the other two, implying a rougher surface structure. These results indicate that SN₂ can help SiO₂ with the formation of a rougher surface structure to some extent. Thus, surface *b* exhibits the largest water contact angle (θ_w). Surface *a* has a similar R_a and RMS to those of surface *c*. However, the θ_w of surface *c* is much larger than that of surface *a*, which demonstrates that the organic component (SN₂ in SN₂-prePU) endows the surface with low surface energy and improves the anti-wettability of the spin-coated surface.

The conditions of the spin-coating method like rotational speed and solvent influence the morphology and will finally affect the hydrophobicity of the surfaces. Thus, the θ_w of the surfaces spin-coated with SiO₂ alone or SN₂/SiO₂ under different conditions were measured and displayed in Figure 3(a–d). It should be specifically pointed out that the glass slides were all coated with one layer of SN₂ first to enable all the surfaces at the same original spin-coating condition. Hence, the surface spin-coated with once SN₂ layer is denoted as the surface spin-coated with 0 bilayer or SiO₂ mono layer and the corresponding θ_w is $97.2 \pm 2.0^\circ$. For surfaces spin-coated with only SiO₂, the horizontal ordinate represents the layers of SiO₂. For other spin-coated surfaces, the horizontal ordinate represents the bilayers. The increase in layers or bilayers results in the increase in θ_w for all surfaces, which is believed that the increasing layers or bilayers enlarges the roughness of the surface structure as well as the hydrophobicity. However, in Figure 3(a), as the spin-coated time

exceeds 10, the θ_w of the surfaces coated with SiO₂ layers displays around 140° , showing no further increment. However, the θ_w of the surfaces coated with SN₂/SiO₂ bilayers increase monotonously with the number of spin-coated bilayers [Figure 3(b–d)].

The solvent also plays an important role in constructing rough surfaces. The surfaces obtained using ethanol as the solvent showed larger θ_w than those obtained using isopropanol as can be seen by comparing Figure 3(b) with Figure 3(c). Because of the weaker polarity of isopropanol than ethanol, it is more compatible with both organic and inorganic components.⁴⁵ Also, isopropanol volatilizes slower than ethanol during spin-coating, which offers the components much more time to disperse homogeneously on the surface. Consequently, isopropanol facilitates the formation of a smoother surface structure, which generates lower θ_w . In addition, a higher rotational speed favors the dispersion of SiO₂ particles.⁴¹ Thus, the surfaces spin-coated at 3000 rpm [Figure 3(d)] exhibit larger θ_w than the surface spin-coated at 2000 rpm [Figure 3(c)] under the same spin-coated times. The symbol “*” in Figure 3(c,d) indicates that a sessile droplet test cannot proceed on coated surfaces with more bilayers because the superhydrophobicity of the surfaces prevents water droplet adhesion. Water droplets can roll off easily on these superhydrophobic surfaces when they are slightly tilted (Supporting Information Video S1). When water is injected onto them, water droplets bounce off the surfaces at once (Supporting Information Video S2, some areas of the glass are not coated with the superhydrophobic coatings to illustrate the difference more clearly).

Table II. Composition Information of SN₂ and Selected SN₂-prePU and θ_w of the Surfaces Spin-Coated with 20 SN₂/SiO₂ Bilayers or 20 SN₂-prePU/SiO₂ Bilayers.

Sample abbreviation	SN ₂ (mol)	prePU (mol)	θ_w (°)
SN ₂	1	/	>160
SN ₂ -prePU(1 : 1.4)	1	1.4	133.2 ± 1.6
SN ₂ -prePU(1.4 : 1)	1.4	1	140.1 ± 0.3
SN ₂ -prePU(1.6 : 1)	1.6	1	154.9 ± 1.1
SN ₂ -prePU(1.8 : 1)	1.8	1	153.4 ± 2.6
SN ₂ -prePU(2 : 1)	2	1	159.2 ± 1.4

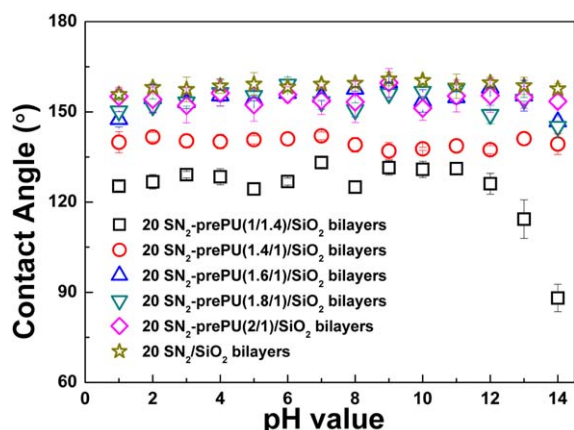


Figure 4. Contact angles for droplets of different pH on spin-coated surfaces. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Using the optimized conditions (solvent: ethanol; rotational speed: 3000 rpm), both SN₂/SiO₂ bilayers and SN₂-prePU/SiO₂ bilayers are spin-coated onto the glass slides. For com-

parison, the number of spin-coated bilayers for these surfaces is set to be 20. Table II shows the water contact angles of surfaces spin-coated with different organic components, that is, SN₂ or SN₂-prePU with different compositions. The θ_w was observed to increase with increasing of SN₂ molar ratio in the SN₂-prePU. When the molar ratio of SN₂/prePU is higher than 1.6 : 1, the coated surfaces become superhydrophobic ($\theta_w > 150^\circ$). The R_a and RMS surface spin-coated with 20 SN₂/SiO₂ bilayers are 498.0 and 594.0 nm, respectively, whereas the R_a and RMS of the surface spin-coated with 20 SN₂-prePU(2 : 1)/SiO₂ bilayers are 121.3 and 154.6 nm, respectively. The data in Table I further supports the idea that SN₂ helps in the formation of a rougher structure than SN₂-prePU while the number of bilayers are equal. Therefore, SN₂ not only decreases the surface energy of the coated surface but also favors a much rougher structure. The decrease in surface energy and the increase in surface roughness will be beneficial for the fabrication of superhydrophobic surfaces. Hence, the surface coated with more SN₂ displays better anti-wettability, and thus, showing greater θ_w .

Contact Angle to Droplets of Varied pH

Stable superhydrophobicity under varied pH conditions can expand the possible application of the superhydrophobic surfaces and can also shield the coated substrates from corrosive liquids, lengthening their service time. Figure 4 shows that except for the surface coated with 20 SN₂-prePU(1 : 1.4)/SiO₂ bilayers, all the spin-coated surfaces show stable contact angles to droplets of different pH, which indicates the stable anti-wettability. Specifically, the surfaces coated with 20 SN₂-prePU(1.6 : 1)/SiO₂ bilayers, 20 SN₂-prePU(1.8 : 1)/SiO₂ bilayers, 20 SN₂-prePU(2 : 1)/SiO₂ bilayers, and 20 SN₂/SiO₂ bilayers show contact angles larger than 150° to the droplets of pH ranging from 1 to 14. In other words, the superhydrophobic surfaces we fabricated were able to exhibit stable antiwettability under either acidic or alkaline conditions.

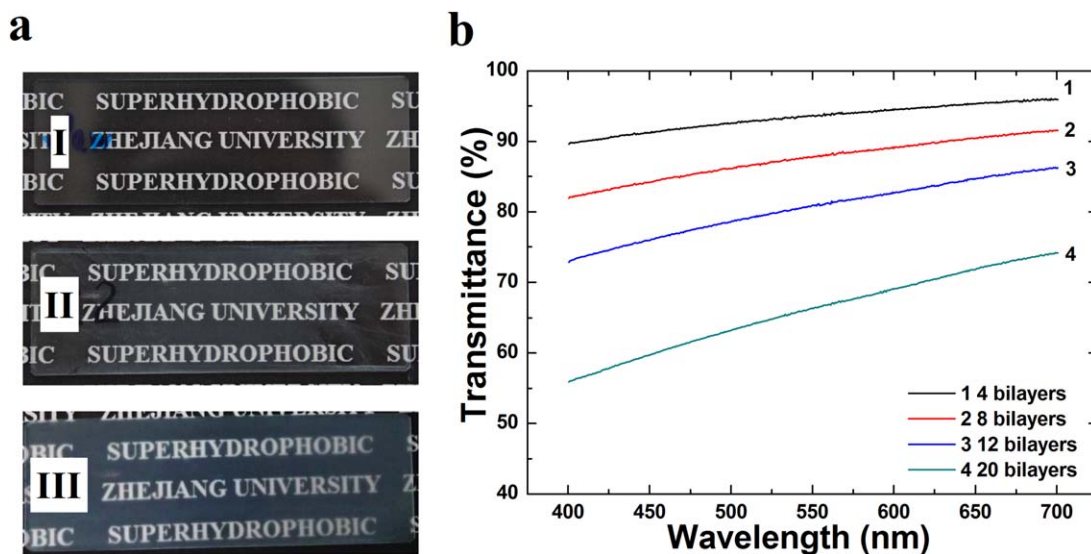


Figure 5. (a) Photographs for (I) untreated glass slide, (II) the glass slide coated with 20 SN₂/SiO₂ bilayers and (III) the glass slide coated with 20 SN₂-prePU(2 : 1)/SiO₂ bilayers. (b) Transmittance of surfaces spin-coated with different SN₂/SiO₂ bilayers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

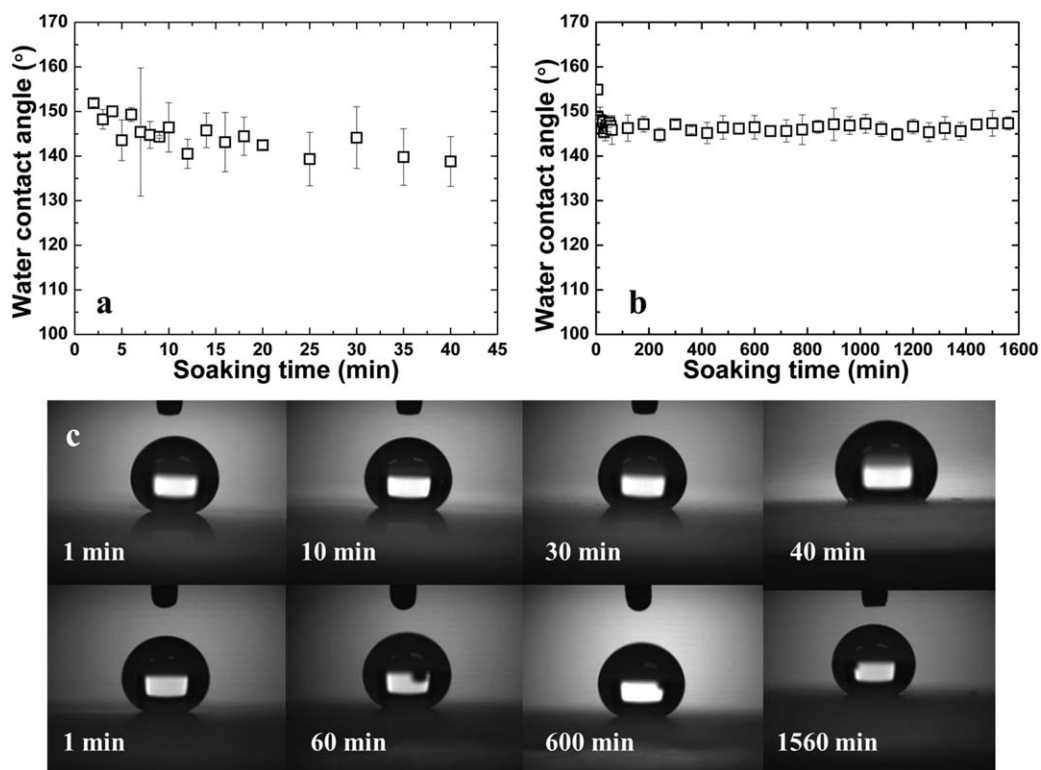


Figure 6. θ_w of the surfaces spin-coated with (a) 20 SN₂/SiO₂ bilayers and (b) 20 SN₂-prePU(2 : 1)/SiO₂ bilayers for different soaking time. (c) Photographs of water droplets on the spin-coated surfaces at different soaking time points. The upper four photographs are for the superhydrophobic surface coated with 20 SN₂/SiO₂ bilayers and the lower four photographs are for the superhydrophobic surface coated with 20 SN₂-prePU(2 : 1)/SiO₂ bilayers.

Transparency of Spin-Coated Surfaces

Figure 5(a) shows the contrast of transparency between the untreated glass slide (I), the glass slide spin-coated with 20 SN₂/SiO₂ bilayers (II), and the glass slide spin-coated with 20 SN₂-prePU(2 : 1)/SiO₂ bilayers (III). The surface coated with 20 SN₂/SiO₂ bilayers (II) exhibited good transparency. Compared with the surface coated with 20 SN₂/SiO₂ bilayers (II), the surface coated with 20 SN₂-prePU(2 : 1)/SiO₂ bilayers (III) shows slight opacity, which could be attributed to the micro-phase separation between SN₂ and PU blocks. Figure 5(b) shows the transmittance of the as-fabricated surfaces with different SN₂/SiO₂ bilayers. The transmittance decreases with the increase in the number of bilayers. The transmittance of the surfaces spin-coated with 8 and 12 SN₂/SiO₂ bilayers still remains at a high level. The surface coated with eight bilayers exhibits not only superhydrophobicity [Figure 3(d)], but also good transparency (transmittance > 80% in wavelength ranging from 400 to 700 nm).

Durability of the Spin-Coated Surfaces

Durability is important in the long-time application of superhydrophobic surfaces. The glass slides spin-coated with 20 SN₂/SiO₂ bilayers and 20 SN₂-prePU(2 : 1)/SiO₂ bilayers were soaked into water and were taken out from the water for 1 min. Afterwards, the θ_w was measured, and the coated glass slides were soaked in water for another 1 min. Figure 6(a,b) show the θ_w of the superhydrophobic surfaces coated with 20 SN₂/SiO₂ bilayers and 20 SN₂-prePU(2 : 1)/SiO₂ bilayers, respectively, after different soaking times. For the surface coated with 20

SN₂/SiO₂ bilayers, the θ_w of some parts falls immediately to lower than 150° just after being soaked for 2 min. The coatings are further damaged by water after being soaked for another 4 min, displaying a further decrement of θ_w , which can be down to approximate 130° on some areas of the coating and a much larger standard deviation. After being soaked for 40 min, most areas of the coated surface show irreversible damage. The huge θ_w decrement can be distinctly observed from the droplet shapes at different time points in the upper four photographs in Figure 6(c). Due to the low adhesive strength of SN₂ onto glass slides, the surface coated with 20 SN₂/SiO₂ bilayers can only retain its superhydrophobicity for several minutes when it is soaked into water.

The surface coated with SN₂-prePU(2 : 1)/SiO₂ bilayers, however, can retain its superhydrophobicity (stable θ_w around 150°) when it has been soaked into water for 26 h, despite the occurrence of a little decrement at the very beginning of the test. The droplet retains its spherical shape after being soaked for different times [lower four photographs in Figure 6(c)]. The existence of PU components enhances the adhesive strength within SN₂-prePU(2 : 1)/SiO₂ bilayers and between the coatings and the glass slide, avoiding the damage of the coatings. As a result, the durability of the coating increases.

CONCLUSIONS

Superhydrophobic coatings made with cheap and easy-synthesized materials (SN₂ or SN₂-prePU as the organic

component and SiO₂ nanoparticles as the inorganic component) were fabricated by a convenient spin-coating method. Increasing the number of SN₂/SiO₂ bilayers or SN₂-prePU/SiO₂ bilayers and increasing the SN₂ molar ratio in the organic component SN₂-prePU of the coatings are beneficial for the hydrophobicity of the as-obtained surfaces. The largest water contact angle can be larger than 160°, and the water droplets can easily rolled off the superhydrophobic surfaces. The surface coated with SN₂/SiO₂ shows good transparency, whereas the surface coated with SN₂-prePU(2 : 1)/SiO₂ exhibits excellent durability. Both superhydrophobic surfaces coated with SN₂/SiO₂ bilayers and SN₂-prePU/SiO₂ bilayers exhibit stable super antiwettability to droplets of varied pH values ranging from 1 to 14.

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