Fabricating Superhydrophobic Surfaces with Transparency/Durability by Spin-Coating Silica and Silicone or Silicone-Modified Polyurethane

功能材料与流变学实验室

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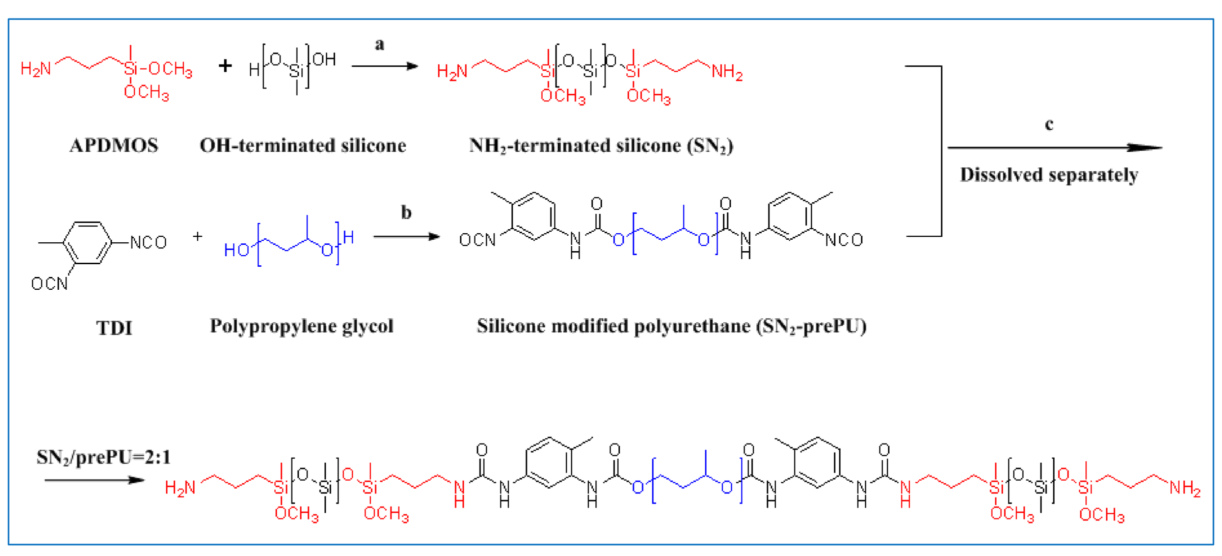
Introduction

In the latest 20 years, superhydrophobic surface with a water contact angle greater than 150° and an extreme small sliding angle have attracted enormous attention in both academic, commercial and industrial areas. Many artificial surfaces with excellent water repellency have been developed by means of hierarchical surface structure fabrication. As is known to all, a rougher surface structure can generate better anti-wettability, while it increases light scattering on the surface which makes surface opaque, hindering the potential optical application. Hence, roughness should be tuned carefully to endow the surface both superhydrophobicity and transparency. Meanwhile, tremendous methods, such as photolithography, plasma etching, templating, chemical vapor deposition, electrospinning and phase separation etc., have been employed to construct superhydrophobic surfaces. However, most techniques and methods are expensive and complicated. How to fabricate transparent superhydrophobic surface conveniently and cost-effectively is a key problem to promote the advancement and application of this research area.

In this work, silica, NH_2-terminated silicone (SN_2) and silicone-modified polyurethane with different SN_2/PU ratios (SN_2-prePU) are adopt to make up superhydrophobic surfaces. By spin-coating SN_2 (or SN_2-prePU) and SiO_2 alternately, coatings containing bilayers are obtained. Both surfaces can display contact angles larger than 150° by tuning the number of bilayers. The hydrophobic and superhydrophobic surfaces show stable water repellency under varied pH. Also, transparent superhydrophobic surface and durable superhydrophobic surface are fabricated.

Scheme and Experiment



1. SN_2 is synthesized as route a and prePU is synthesized as route b which is displayed in the left scheme graph.
2. SN_2-prePU is synthesized as route c. The structure at bottom is an example of a series of SN_2-prePU with different SN_2/prePU ratio.
3. SiO_2 is synthesized by sol-gel method.
4. The coating solution is prepared by dissolving or dispersing SN_2 (or SN_2-prePU) and SiO_2. Coating solution is spin-coated onto glass slides. Final coated surfaces contain SN_2/SiO_2 bilayers or SN_2-prePU/SiO_2 bilayers

Results

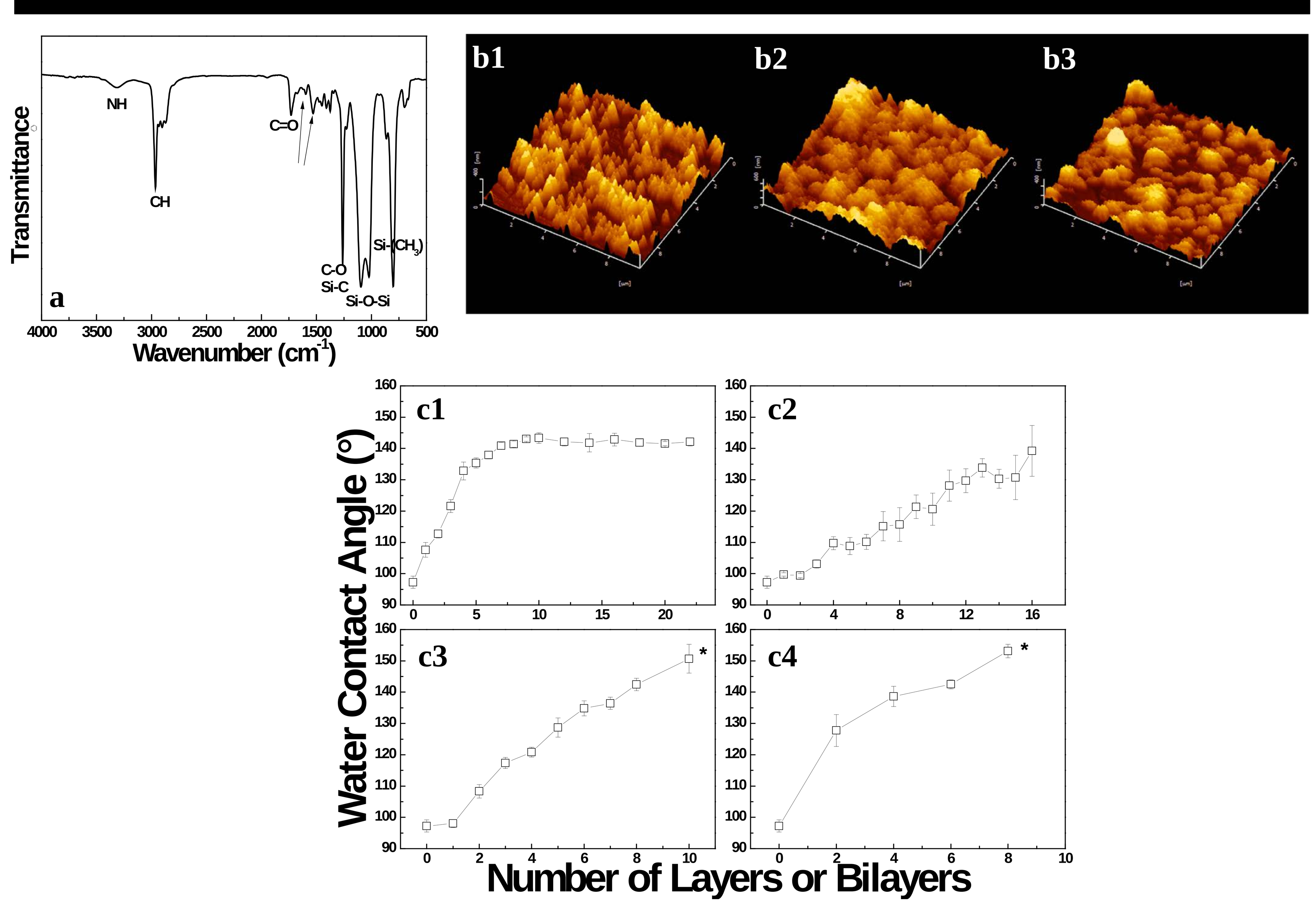


Figure 1. (a) FTIR spectrum of the synthesized SN_2-prePU(the molar ratio of SN_2 to prePU is 2/1). AFM 3D graphs of (b1) 5 SiO_2 layers, (b2) 5 SN_2/SiO_2 bilayers, and (b3) 5 SN_2-prePU/SiO_2 bilayers. Water contact angles of surfaces prepared with different conditions (c1) surfaces spin-coated with only SiO_2 layers at 2000 rpm, (c2) surfaces spin-coated with SN_2/SiO_2 bilayers at 2000 rpm; the solvent is isopropanol, (c3) surfaces spin-coated with SN_2/SiO_2 bilayers at 2000 rpm, (c4) surfaces spin-coated with SN_2/SiO_2 bilayers at 3000 rpm. If it is not specially pointed out, the solvent is ethanol. The symbol '*' in (c3) and (c4) indicates that a sessile droplet test cannot proceed on coated surfaces with more bilayers because the superhydrophobicity of the surfaces prevents the water droplet adhesion. Water droplet can slide easily on these superhydrophobic surfaces.

Table 1
Surface information of spin-coat surfaces

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

†: Surface a is coated with 5 SiO_2 layers. Surface b is coated with 5 SN_2/SiO_2 bilayers. Surface c is coated with 5 SN_2-prePU/SiO_2 bilayers. The AFM 3D graphs of these three surfaces are presented in Fig. 1.(b1), (b2) and (b3).
*: R_a, arithmetical mean deviation. **: RMS, root mean square. ***: P-V, maximum height of the profile. P-V=R_p-R_v. ****: S Ratio, is the quotient of the exact surface area to the project area. y_i is the vertical distance from the mean line to the i^{th} data point in scan region.

Table 2
Composition of SN_2 and selected SN_2-prePU and static contact angle of finally fabricated surfaces*

Sample Abbreviation	SN_2 (mol)	prePU (mol)	θ_w (°)
SN_2	1	/	larger than 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

*: The surfaces are spin-coated with 20 bilayers.

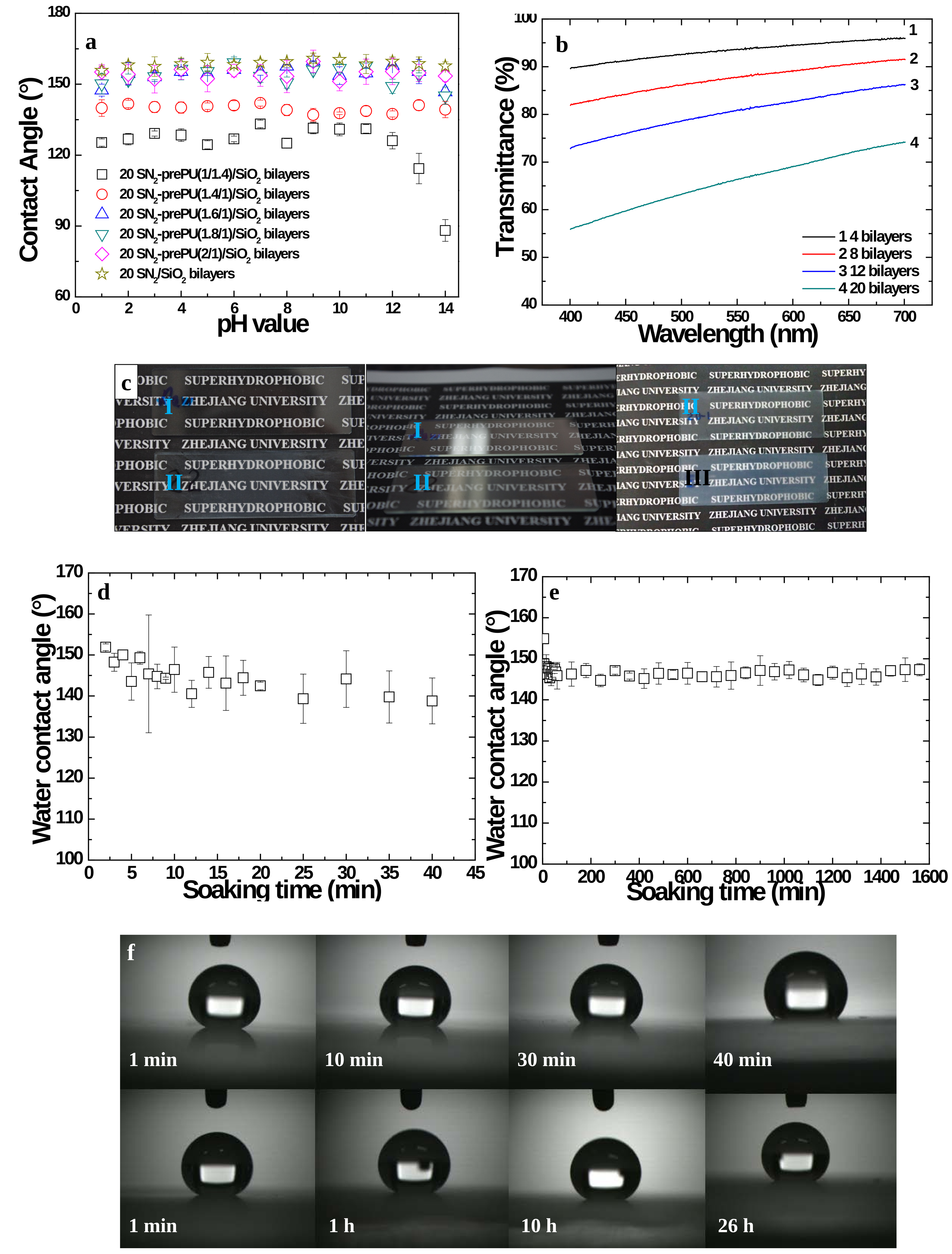


Figure 2. (a) Contact angles for droplets of different pH values on spin-coated surfaces. (b) Transmittance curves of surfaces spin-coated with different SN_2/SiO_2 bilayers. Transmittance=(T_c/T_{glass})×100%, where T_c is the transmittance of coated surfaces and T_{glass} is the transmittance of the glass slide. (c) Photographs for (I) the untreated glass slide and (II) the glass with 20 SN_2/SiO_2 bilayers, and photographs for (II) and (III) 20 SN_2-prePU(2/1)/SiO_2 bilayers. Water contact angles of the surfaces coated with (d) 20 SN_2/SiO_2 bilayers and (e) 20 SN_2-prePU(2/1)/SiO_2 bilayers for different soaking time. (f) 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 SN_2/SiO_2 bilayers and the lower four photographs are for the superhydrophobic surface coated with 20 SN_2-prePU(2/1)/SiO_2 bilayers.

Conclusion

In summary, transparent superhydrophobic surfaces are fabricated by spin-coating SN_2 and SiO_2, while superhydrophobic surfaces with better durability are fabricated by spin-coating SN_2-prePU(2/1) and SiO_2. These spin-coated surfaces show stable water contact angles to droplets of varied pH. While in the procedure of spin-coating, SN_2 and SN_2-prePU favor the aggregation of SiO_2 nanoparticles which facilitates the formation of rougher surface structure. Meanwhile, due to its Si-O-Si main chain, SN_2 provides hydrophobicity. PU enhances the adhesion between coatings and glass slide, and within bilayers, which improves the durability of the coatings.

Reference

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