Superhydrophobic Polyurethane and Silica Nanoparticles Coating with High Transparency and Fluorescence

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ABSTRACT: A superhydrophobic surface was prepared by spin-coating trimethylsiloxane functionalized SiO_2 (TMS-SiO_2) solutions onto a precoated polyurethane (PU) layer. The superhydrophobic coatings showed high stability with time, and the prepared coatings remained superhydrophobicity even after 6 months. Furthermore, the as-prepared surface showed high transparency with a transmittance above 70% in visible light region (400–800 nm). The transition of the composite surface from superhydrophobicity to hydrophilicity can be achieved by increasing the drying temperature. More interestingly, the surface showed excellent fluorescent property by the incorporation of fluorescent Europium (Eu) complex into the surface and without deteriorating the superhydrophobic and transparent properties. It was believed that the superhydrophobic surface with multifunction would broaden the applications of superhydrophobic materials. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 2959–2965, 2013

INTRODUCTION

Superhydrophobic surface with a high water contact angle (CA) above 150° and low hysteresis has attracted great interest due to their wide applications in microfluidics, windows, anti-icing coatings, functional textiles and so on.[1–3] Numerous works have been focused on the methods of preparing superhydrophobic surfaces, including layer-by-layer assembling technique,[4,5] chemical vapor deposition,[6] sol–gel method,[7–9] phase separation,[10–12] and etc.[13] However, most of these methods involve complicated process, expensive regents, especial equipment, and special substrates. Especially, superhydrophobic surface often requires a relatively higher surface roughness which is detrimental to mechanical stability and transparency of the surface. At present, these problems limit the practical applications of the superhydrophobic surfaces.

To promote the practical applications of the surperhydrophobic surfaces, some special functions such as transparent, fluorescent, and environment responsive and adhesive properties should be considered. However, only a few literatures deal with the multifunctional superhydrophobic surfaces until recently. Jiang et al.[1,14–18] prepared a series of smart surfaces that would alter the surface wettability in response to changes in environmental conditions, which had paved the way to drug delivery, biosensors, and responsive materials. Manca et al.[19] fabricated a highly transparent self-cleaning coating by spin-coating a sol-gel-based coating containing trimethylsiloxane functionalized silica nanoparticles onto a precoated silica gel layer. Yang et al.[20] prepared a superhydrophobic PU film with transparency and fluorescence based on an octadecanamide-directed assembly process. In our previous work,[21] a superhydrophobic methylsilicone resin film with luminescent property was fabricated by a simple phase separation method, which could find potential applications in water repellence of light-emitting diode and self-cleaning road sign. Although the preparations of superhydrophobic surfaces with multifunction are reported a few, the fabrication of superhydrophobic surface with multifunction such as transparent and fluorescent property is highly desirable.

Recently, inorganic materials/polymer composite superhydrophobic surfaces are reported a lot.[22–27] However, most of these coatings are prepared by blending inorganic materials with polymers, and then casting on the substrates, ignoring other properties such as transparency, fluorescence, and other properties beneficial for practical application. Very recently, great effort has been devoted to prepare transparent superhydrophobic

Additional Supporting Information may be found in the online version of this article.

surface by utilizing nanoparticles, such as layer-by-layer assembling of nanoparticles with various sizes,[28] dip-coating appropriate sizes of nanoparticles on glass or silicon substrates,[29,30] and so on.[31] In comparison with the above methods, the primary differences and advantages of this paper were: (i) the superhydrophobic surface was prepared by using PU as a binder layer, and then spin-coating TMS-SiO2 solution on the PU film, to form a transparent superhydrophobic surface with CA as high as 166.2° and a high stability with time. (ii) The wettability of the surface can be altered by changing the drying temperature, and the conversion from superhydrophobicity to hydrophilicity can be realized by increasing the temperature from 20 to 170°C. (iii) More interestingly, the superhydrophobic PU/TMS-SiO2 composite surface owned transparent and fluorescent property after introducing fluorescent Eu complex into the coating. Generally speaking, the aim of this work was to prepare a superhydrophobic surface with multifunctional properties, such as high transparency and red fluorescence, which would be expected to find applications in optoelectronic domains, self-cleaning windows, and promote the practical applications of the nonwetting surfaces.

EXPERIMENTAL

Materials

Silica nanoparticles (14 nm) were supplied by Sigma-Aldrich. Polytetramethylene ether glycol (PTMG, average molecular weight 2000 $\pm$ 20, 99.9%, Mitsubishi Chemical Corporation) was dried in the vacuum oven at 80°C to remove water for 24 h before use. N, N-Dimethylformamide (DMF, 99.7%, Rionlon Bohua (Tianjin) Pharmaceutical & Chemical) was dried with Na for 24 h and freshly distilled before use. Hexamethyldisilazane (HDMS, 99.8%, Sinopharm Chemical Reagent), 2, 4-diisocyanato-1-methyl-benzen (TDI, 98.0%, Shanghai Sanyou Reagent Factory), 1, 4-Butanediol (BDO, chemically pure, Tianjin No. 1 Chemical Reagent Factory) and other reagents were used as received. Glass slides (1 $\times$ 1 cm^2) were sonicated in

absolute ethanol and acetone for 20 min respectively, and dried with a blower.

Synthesis of PU

The preparation of PU involves the two-step condensation reaction. 8.888 g (0.05 mol) TDI was mixed with 20.001 g (0.01 mol) PTMG and stirred for 3 h under N2 atmosphere at 80°C. 50.068 g DMF was subsequently added into the mixture. Then, 3.636 g (0.04 mol) BDO was added as chain extenders. The mixture was further stirred for 2 h under N2 atmosphere. After reaction, DMF was added into the PU solution until the content of PU achieved 10 wt %.

Modification of Silica Nanoparticles

The SiO2 nanoparticles modified with HDMS were prepared as follows.[19] First, 3 g of silica nanoparticles were added into 50 mL methyl-isobutyl-ketone and stirred for 30 min at 50°C. 100 mL of HDMS was added into the above solution stirring for 24 h under N2 inert atmosphere protection and the temperature maintained at 50°C. The nanoparticles were separated by centrifugation with absolute ethanol for three times and dried at 70°C under vacuum.

### Preparation of PU/TMS-SiO2 Superhydrophobic Surface

Totally, 10 wt % PU solution was spin-coated at 300 rpm for 3 s and 2500 rpm for 30 s on the glass slides, respectively. Then the samples were dried at ambient temperature for 10 min. The PU solution was spin-coated for three times. And then the TSM-SiO2 toluene solutions with the content 1–5% were spin-coated at 300 rpm for 3 s and 2500 rpm for 30 s on the previously coated PU layers, respectively. This process was repeated for two times for each sample.

Preparation of Fluorescent Superhydrophobic Surfaces

The fluorescent Eu complex (Eu(BA)3Phen) was prepared as follows.[32] EuCl3, benzoic acid (BA), and 1, 10-phenanthroline (Phen) in the molar ration of 1 : 3 : 1 were dissolved in absolute ethanol and stirred at 70°C for 6 h. Ammonium hydroxide was added dropwise into the above mixture until the pH 6-7
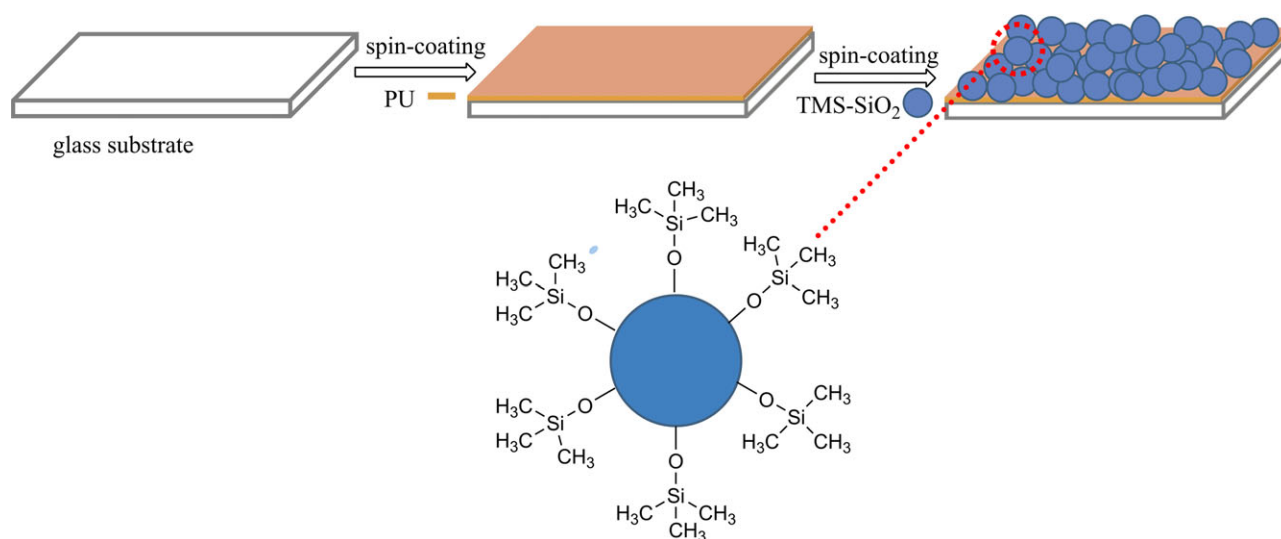
Scheme 1. The preparation process of PU/TMS-SiO2 coating. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
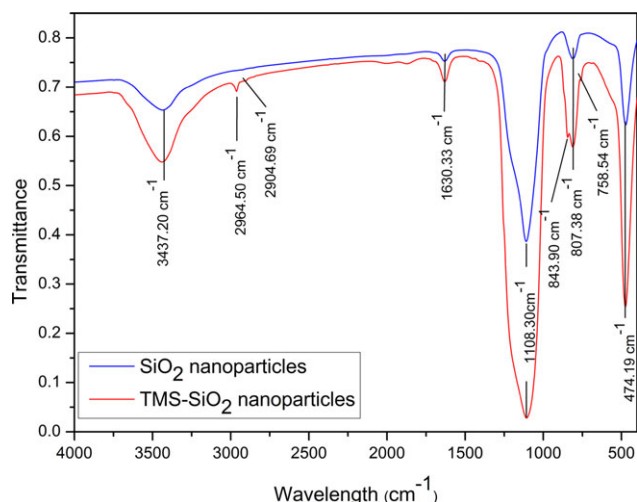
Figure 1. The FTIR spectra of SiO$_2$ nanoparticles and TMS-SiO$_2$ nanoparticles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was reached. The precipitate was separated by filtration and washed with ethanol for three times, and then dried under vacuum at 50°C for 24 h. The synthesis of Eu(BA)$_3$Phen was confirmed by Fourier Transform Infrared spectroscopy (Supporting Information Figure S2).

Totally, 0.12 g TMS-SiO$_2$ was dispersed in DMF/toluene (1 g/3 g) solution, and then 0.01 g Eu(BA)$_3$Phen was added and dispersed by ultrasonic vibration for 60 min. And then the TMS-SiO$_2$ contained solution was spin-coated at 300 rpm for 3 s and 2500 rpm for 30 s on the previously deposited homogenous PU layers for two times.

Characterization

The microstructures of the prepared surfaces were observed by JSM-6701F field emission scanning electron microscopy (FE-SEM, JEOL, Japan). The chemical composition of the prepared coating was confirmed by X-ray photoelectron spectroscopy (XPS), which was conducted on a PHI-5702 electron spectrometer (Perkin-Elmer, USA) using an AlKa line excitation source with the reference of C1s at 284.80 eV. The water contact angles (CA) were measured by DSA 100 optical contact-angle meter (Kruss company, Germany) at ambient temperature. The average CA values (with 5 μL water droplets) and sliding angles (SA, with 10 μL water droplets) were obtained by measuring the same sample at five different positions. The transparency (UV-vis spectroscopy) of the superhydrophobic surface was studied by U-3010 spectrophotometer (Hitachi, Japan). The Fourier Transform Infrared (FTIR) spectroscopy was measured by Bruker IFS 66v/s IR spectrophotometer (Bruker optics, Germany).

RESULTS AND DISCUSSION

The existence of the trimethylsiloxane (TMS) group on the SiO$_2$ surface was confirmed by the FTIR spectra. Figure 1 shows the FTIR spectra of SiO$_2$ and TMS-SiO$_2$ nanoparticles. The 1108.30 cm^{-1} and 474.19 cm^{-1} peaks were ascribed to symmetric stretching modes and bending vibrations of Si—O—Si, respectively. Both the spectra showed a medium intensity band at 3437.20 cm^{-1} which belonged to the hydroxyl stretching of the Si—OH, and the weak band at 1630.33 cm^{-1} (molecular water has a deformation band near 1630 cm^{-1}) indicated that a little water remained in the samples.[33,34] In the spectrum of TMS-SiO$_2$ nanoparticles, 2964.50 and 2904.69 cm^{-1} absorption bands assigned to asymmetric and symmetric C—H stretching respectively, which confirmed the presence of TMS on SiO$_2$ particles. The very weak absorption band at 758.54 cm^{-1} was assigned to rocking vibration of Si(CH$_3$)$_3$. From above analysis, we can easily conclude that SiO$_2$ particles were modified with HDMS successfully.

In this study, PU was used as the adhesive layer (about 250 nm thick), and TMS-SiO$_2$ solutions with different contents were spin-coated on the PU layer. Figure 2(a) shows the variation of wettability of the PU/TMS-SiO$_2$ coatings with the TMS-SiO$_2$ contents ranging from 1 wt % to 5 wt %. It was found that the wettability of PU/TMS-SiO$_2$ coating was affected by the
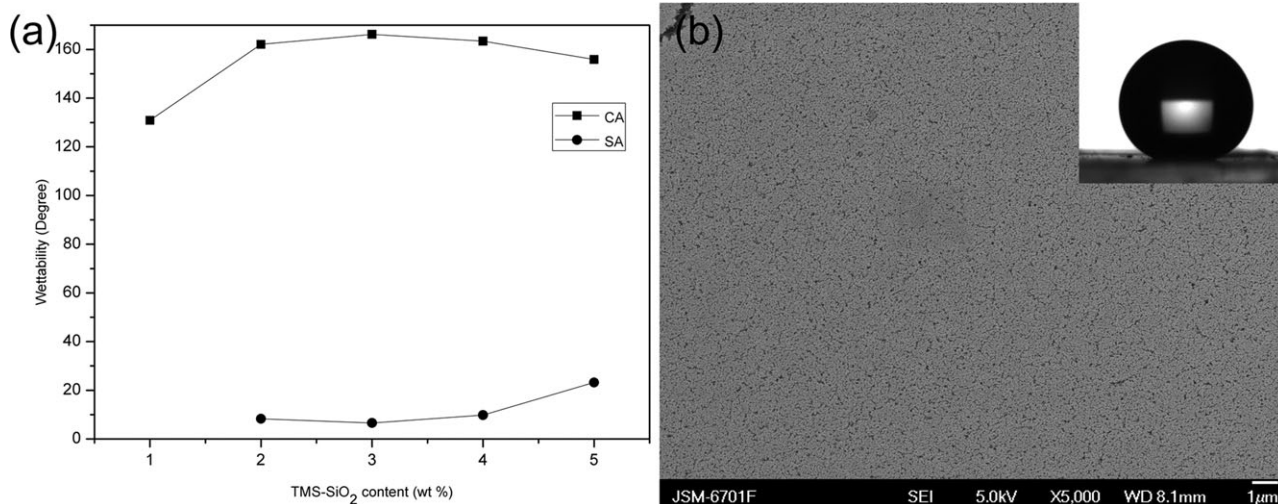
Figure 2. (a) The wetting behaviors of the PU/TMS-SiO$_2$ coatings with the TMS-SiO$_2$ contents. (b) FE-SEM image of the PU^1/TMS-SiO$_2$ surface spin-coated with 3 wt % TMS-SiO$_2$ solution. The inset showed a profile of 5 μL water drop on the PU/TMS-SiO$_2$ surface.
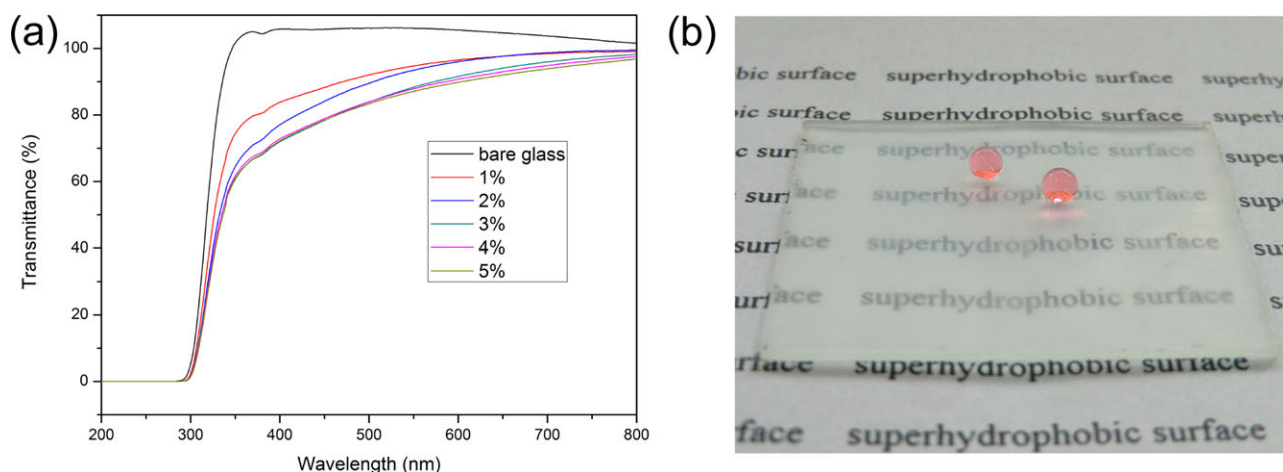
Figure 3. (a) The UV-vis spectroscopy of the bare glass substrate and PU/TMS-SiO$_2$ coating on glass with different contents (1, 2, 3, 4, and 5 wt %). (b) Image of the PU/TMS-SiO$_2$ superhydrophobic surface on glass substrate (spin-coated with 3 wt % TMS-SiO$_2$). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

contents of TMS-SiO$_2$ nanoparticles. With TMS-SiO$_2$ contents changing from 1 wt % to 5 wt %, the variable wettability of PU/TMS-SiO$_2$ coatings were shown in Figure 2(a). When the TMS-SiO$_2$ content was 1 wt %, the CA of the surface was 130.9° which cannot achieve superhydrophobicity. The CA was greater than 150° when the TMS-SiO$_2$ content was higher than 2 wt %. Spin-coating 3 wt % TMS-SiO$_2$ solution on the PU layer (the thickness of TMS-SiO$_2$ about 240 nm), the CA of the surface was as high as 166.2° and SA was 6.6°. With the increment of TMS-SiO$_2$ in the coating, the CA slightly decreased and SA continuously increased. A FE-SEM image of PU/TMS-SiO$_2$ surface spin-coated with 3 wt % TMS-SiO$_2$ solution was shown in Figure 2(b). As was clearly visible, the nanoparticles covered the surface homogenously and the TMS-SiO$_2$ particles aggregated together to form a rough structure which was beneficial to the superhydrophobicity of the surface. The morphologies of the coatings were not obviously changed with the TMS-SiO$_2$ contents (Supporting Information Figure S3).

The as prepared PU/TMS-SiO$_2$ coatings showed very high stability when the surfaces were kept at temperatures between 18 and 35°C (room temperature) in ambient atmosphere for a long time. Almost no change of CA values of the PU/TMS-SiO$_2$ coatings (3 wt % TMS-SiO$_2$) was detected after 4 days storage and the CA could remain to 154.7° for a relatively long storage period (six months), implying the prepared superhydrophobic surface was extremely stable. In addition, the adhesion between TMS-SiO$_2$ and PU was also discussed in our work. The CA was used to measure the adhesion performance of TMS-SiO$_2$ and PU. The samples used in this experiment were sonicated in water for 3 min and dried under N$_2$. TMS-SiO$_2$ coating which was prepared by spin-coating on glass substrate showed superhydrophobicity with a CA about 163.1°. After ultrasonic in water for 3 min, the surface showed a CA about 51.4°, suggesting the poor adhesion between the TMS-SiO$_2$ and glass substrate. However, the CA of PU/TMS-SiO$_2$ coating decreased slightly from 166.2° to 163.6° after ultrasonic, indicating the strong adhesion between TMS-SiO$_2$, PU, and glass.

Because the roughness required to achieve superhydrophobicity was detrimental to transparency of the surface, transparency and surface roughness were competitive properties for superhydrophobic surface. In order to fabricate transparent surface, the roughness of surface was preferably smaller than 100 nm.[30] Therefore, 14 nm SiO$_2$ particles were used to reduce the roughness of the coatings in this experiment. Figure 3(a) shows the UV-vis spectroscopy of the bare glass substrate and PU/TMS-SiO$_2$ coatings on glass with different TMS-SiO$_2$ contents. It could be observed that all the PU/TMS-SiO$_2$ coatings possessed a good transmittance of above 70% in the visible light region (400–800 nm). With increase of the TMS-SiO$_2$ content, the transmittance of the surface was decreased slightly. As shown in Figure 3(b), the characters on the paper were clearly seen through PU/SiO$_2$ coating with 3% TMS-SiO$_2$ content.

The effect of temperature on the wettability of PU/TMS-SiO$_2$ coating was investigated. Figure 4(a) shows the variation of CA on the PU/TMS-SiO$_2$ coatings (3 wt % TMS-SiO$_2$) with the drying temperature. The CA of the PU/TMS-SiO$_2$ surface decreased from 166.2° to 82.8° when the drying temperature increased from 20 to 170°C. The transition from superhydrophobicity to hydrophilicity was achieved by increasing the drying temperature. Figure 4(b–d) shows the microstructures of the PU/TMS-SiO$_2$ coatings drying at different temperatures. Drying at 20°C [Figure 4(b)], the surface was rough, and the micro and nanoscale structure which was composed by the aggregation of TMS-SiO$_2$ nanoparticles made the surface superhydrophobic. When the drying temperature increased [Figure 4(c,d)], the PU layer aggregated on the surface, and the TMS-SiO$_2$ particles were embedded into the PU layer. The effect of the temperature on the wettability of the composite coating may due to the movement of PU chain above the melting temperature (about 31.5°C, seen in Supporting Information Figure S4). When the temperature was far above the melting temperature of PU, the chains of PU can move easily and the PU may penetrate into the space between the silica nanoparticles, resulting in the aggregation of PU on the surface. The aggregation of hydrophilic PU on the surface would damage
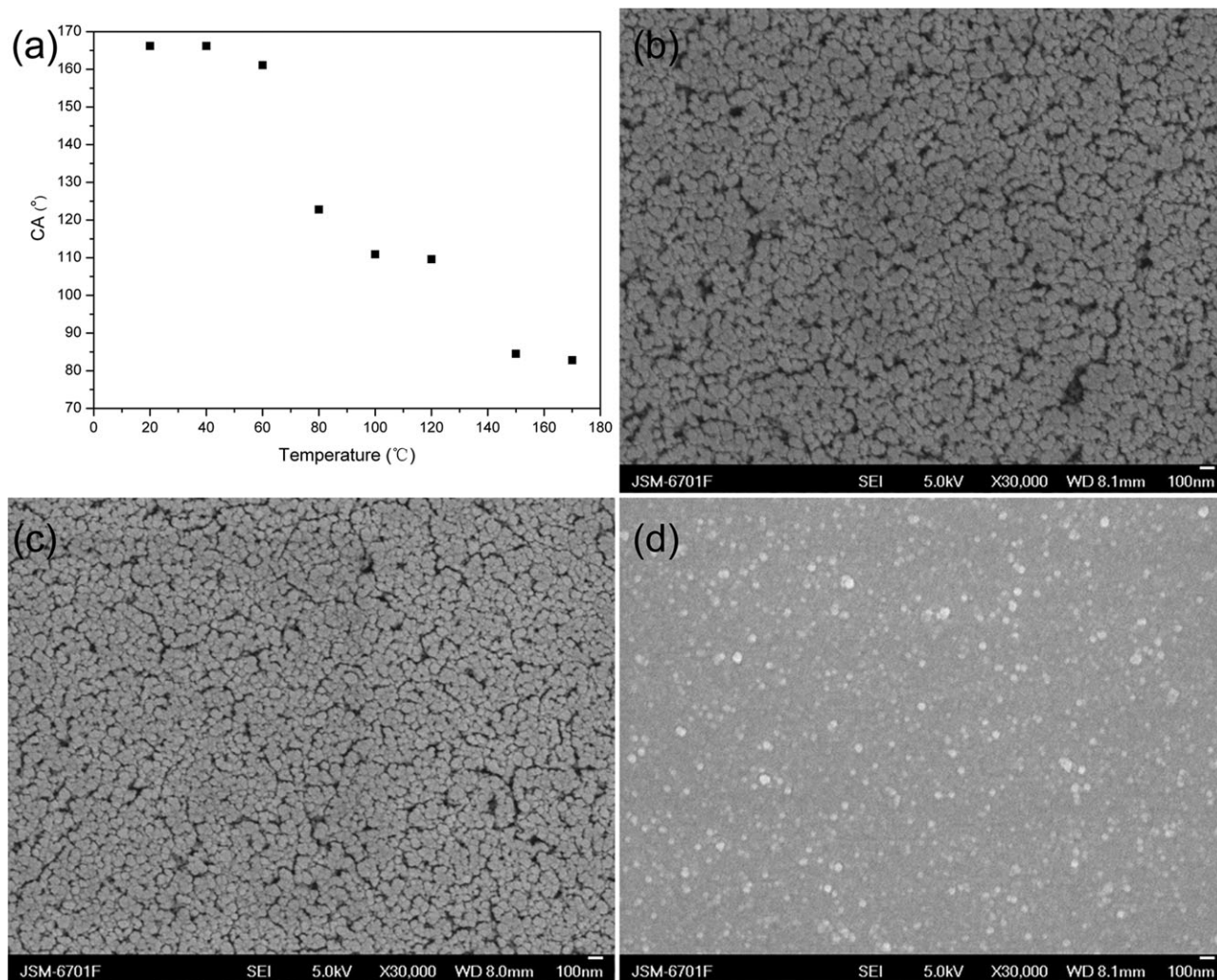
Figure 4. (a) The variation of CA on the PU/TMS-SiO$_2$ coatings (3 wt % TMS-SiO$_2$) with the drying temperature. (b–d) FE-SEM images of PU/TMS-SiO$_2$ coatings (3 wt %) drying at 20, 80, and 150°C.

superhydrophobicity of the PU/TMS-SiO$_2$ film. Moreover, the TMS-SiO$_2$ particles embedded into PU film would reduce the roughness of the coating. For these two factors, the CA decreased with increasing drying temperature.

XPS was employed to investigate the chemical composition of the superhydrophobic surface. As shown in Figure 5, the atomic ratio of C/O/Si was 12.53%/62.88%/24.59%, when the drying temperature was 20°C. As the drying temperature increased to 80°C, the atomic ratio of C/O/Si was 26.49%/52.51%/21.00%. After drying at 150°C for 5 h, the ratio of C/O/Si was changed to 49.61%/35.53%/14.86%. The element of Si came from TMS-SiO$_2$, and both PU and TMS-SiO$_2$ contained C and O element. With the increase of drying temperature, the ratio of Si decreased from 24.59% to 14.86%, indicating that the content of TMS-SiO$_2$ on the surface was decreased. The increase ratio of C accounted for the aggregation of PU on the surface. These results were further demonstrated that transition of the PU/TMS-SiO$_2$ from superhydrophobic to hydrophilic by drying temperature was mainly caused by the combined effect of the change of microstructure and composition on the surface.
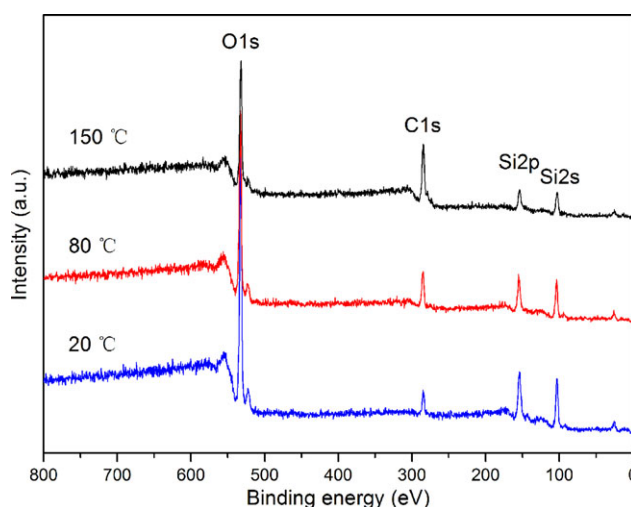
Figure 5. XPS spectra of PU/TMS-SiO$_2$ coating (3 wt % TMS-SiO$_2$) drying at different temperatures: 20, 80, and 150°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
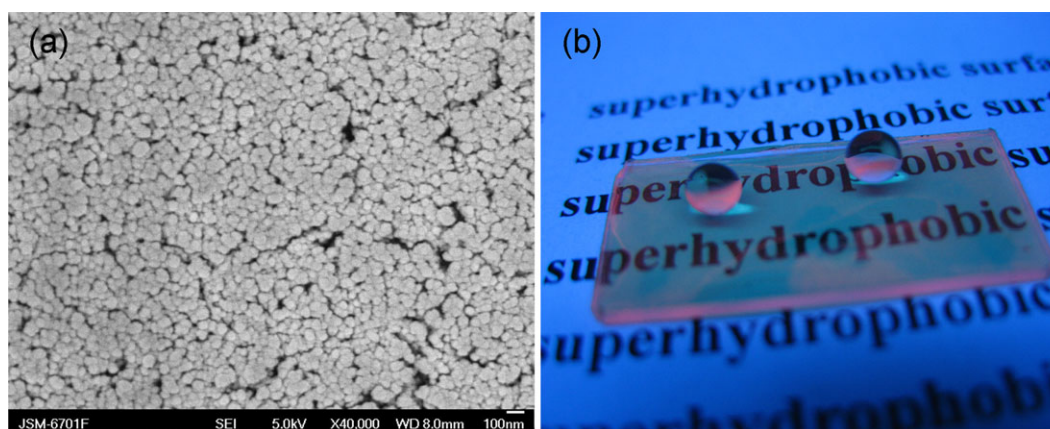
Figure 6. (a) FE-SEM images of the PU/TMS-SiO$_2$ coating after adding the Eu(BA)$_3$Phen. (b) The photograph of PU/TMS-SiO$_2$ coating with red fluorescence and high transparence (taken under UV lamp). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Eu(BA)$_3$Phen was added into the TMS-SiO$_2$ solution (3 wt %), and then spin-coated onto the PU layer. Figure 6(a) shows that the microstructure was almost the same with the PU/SiO$_2$ coating. The film exhibited micro and nano structure which made the surface superhydrophobic. The as-prepared surface showed superhydrophobicity with CA about 154.2° and fluorescent property. By introducing fluorescent Eu complex, the superhydrophobic surface with red fluorescence and high transparency can be easily obtained, as shown in Figure 6(b). The fluorescence emission spectra of PU/TMS-SiO$_2$ surface and PU/TMS-SiO$_2$ surface with Eu(BA)$_3$Phen was shown in Supporting Information Figure S5.

CONCLUSIONS

In summary, a highly transparent superhydrophobic surface was prepared by spin-coating TMS-SiO$_2$ solution onto a precoated PU layer. The CA of the PU/TMS-SiO$_2$ coating with 3 wt % TMS-SiO$_2$ was as high as 166.2° and SA was 6.6°. The coating showed superhydrophobic property even after six months storage indicating a high stability of the as prepared coating. The surface can be easily converted from superhydrophobic to hydrophilic by drying at elevated temperatures which may cause by the movement of PU chains above the melting temperature. After introducing the fluorescent Eu complex into the composite film, the transparent superhydrophobic surface showed red fluorescence. This superhydrophobic coating may find potential applications in water proof light-emitting devices, solar cell panels, window treatments and so on.

ACKNOWLEDGMENTS

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