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Fabrication of cotton fabric with superhydrophobicity and flame retardancy

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ABSTRACT

A simple and facile method for fabricating the cotton fabric with superhydrophobicity and flame retardancy is described in the present work. The cotton fabric with the maximal WCA of 160° has been prepared by the covalent deposition of amino-silica nanospheres and the further graft with (heptadecafluoro-1,1,2,2-tetradecyl) trimethoxysilane. The geometric microstructure of silica spheres was measured by transmission electron microscopy (TEM). The cotton textiles before and after treatment were characterized by using scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). The wetting behavior of cotton samples was investigated by water contact angle measurement. Moreover, diverse performances of superhydrophobic cotton textiles have been evaluated as well. The results exhibited the outstanding superhydrophobicity, excellent waterproofing durability and flame retardancy of the cotton fabric after treatment, offering a good opportunity to accelerate the large-scale production of superhydrophobic textiles materials for new industrial applications.

1. Introduction

The lotus leaf and many other biological organisms exhibit the unique wetting characteristic of superhydrophobicity after millions of years of evolution (Gao & Jiang, 2004; Gao et al., 2007; Shi et al., 2007; Wang, Li, & Xu, 2012; Zheng, Gao, & Jiang, 2007). The study of lotus leaf reveals that the nature achieves this miracle by combining hierarchical structures (microscale protrusions and nanoscale pins) with low surface energy materials (epicuticular wax layer) (Guo, Liu, & Su, 2011; Yan, Gao, & Barthlott, 2011). Superhydrophobic surfaces have a water contact angle greater than 150°, attracting enormous attention in both scientific and industrial areas. So far, superhydrophobic films promise a wide range of applications in energy conversion, self-cleaning paints and windows, water/oil separation, enhanced corrosion resistance, adjusting cell/substrate adhesion in the biomedical area, functional textiles with special wettability, reducing fluid resistance for aquaculture and microfluidic devices, anti-freezing, anti-fogging (Galopin et al., 2009; Li et al., 2005; Nosonovsky & Bhushan, 2008; Ou & Rothstein, 2005; Solga, Cerman, Striffler, Spaeth, & Barthlott, 2007; Wang et al., 2006; Yao, Song, & Jiang, 2011; Zhang, Wang, Wang, Shi, & Li, 2012; Zhang, Wang, Wang, & Li, 2012), etc.

Most superhydrophobic materials have poor durability (Li, Li, & Sun, 2010). When exposed to an outdoor environment, their micron/submicron binary structures and low surface energy layers could be easily and permanently degraded by strong light, acid rain, seawater, oxidation, sand in the wind, etc. Apparently, many further developments of non-wetting surfaces were hampered by the unattainable robustness of hierarchical roughness and the instability of surface chemistry. Inspiringly, many great achievements have been got to develop mechanically robust superhydrophobic cotton surfaces, for instance, Zhu et al. (2012) fabricated a superhydrophobic fabric with both mechanical stability and easy-repairability by a facile solution-immersion process. Zhang at al. reported a superhydrophobic textile which still exhibited excellent chemical and mechanical stability after exposure, immersion and washing tests (Zhang, Wang, Wang, & Li, 2012). Zimmermann, Reifler, Fortunato, Gerhardt, and Seeger (2008) prepared a simple, one-step gas phase coating method for attaining the textile fabrics with long-term water resistance.

As we all know, the thermal stability and flame retardancy of superhydrophobic materials play the pivotal roles in practical applications, however, there is not enough attention these properties should be given. As a promising new flame retardancy approach, the layered silicate polymer nanocomposite has attracted enormous attentions around the world (Gilman, 1999; Zhu & Wilkie, 2000; Wu et al., 2012). Unfortunately, few literatures have devoted to endowing the materials with superhydrophobicity and flame retardancy simultaneously. Therefore, in the experiment described in the following, we fabricated a cotton fabric with the important functions of superhydrophobicity,

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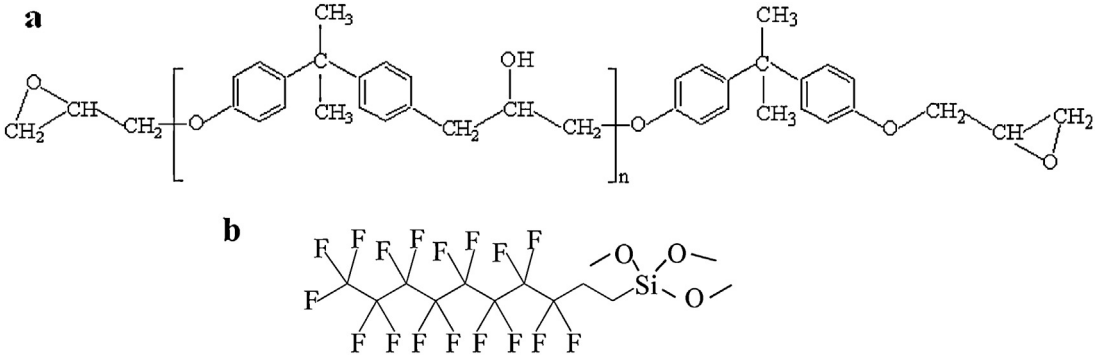

Fig. 1. Molecular structure of (a) bisphenol A epoxy resin (E-54) and (b) (heptadecafluoro-1,1,2,2-tetradecyl) trimethoxysilane.

stable waterproofing and flame retardancy by the covalent deposition of amino-functionalized silica nanospheres on epoxy-functionalized cotton textile to generate surface roughness, followed by the hydrophobization with (heptadecafluoro-1,1,2,2-tetradecyl) trimethoxysilane. Compared with the method of others, which needs a complicated and unmanageable synthesis route of poly(POSS-co-methyl methacrylate-co-4-vinylbenzyl fluoroether carboxylate) and the further treatment of cotton fabric (Gao, He, & Qing, 2011), this fabricating procedure is considerably simple and facile. The static water contact angle of our superhydrophobic sample could achieve 160° for a 5 μL droplet. The geometric microstructure and wetting behavior have been conducted by utilizing scanning electron microscopy and optical contact angle meter, respectively. Characterizations by X-ray photoelectron spectrometer, Fourier transform infrared spectroscopy and transmission electron microscopy were also investigated. In addition, we have explored the diverse performances of superhydrophobic cotton fabric to identify whether this superhydrophobic cotton could be applied in practical purposes.

2. Experimental

2.1. Materials

Cotton fabric (100% cotton) was obtained locally, and has been ultrasonically washed before usage by distilled water, acetone and ethanol, respectively. TEOS (98.0%), ethanol (99.7%) and ammonia (28.0%) were purchased from Tianjin Kaitong Chemical Reagent Co., Ltd. Bisphenol A epoxy resin (E-54) as shown in Fig. 1a was provided by Wuxi Resin Plant. 3-Aminopropyl(diethoxy)methylsilane

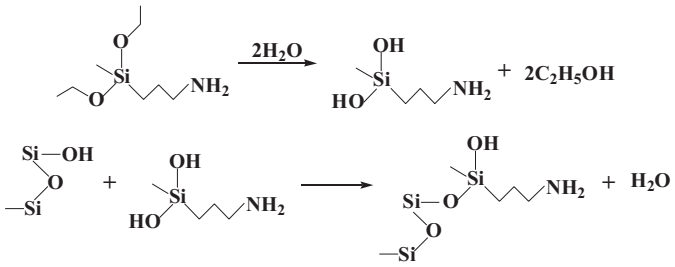

Fig. 2. Amino-functionalization of silica nanosphere.

was obtained from Aladdin Chemistry Co., Ltd. (Heptadecafluoro-1,1,2,2-tetradecyl) trimethoxysilane as presented in Fig. 1b was provided by Sicong New Material Development Co., Ltd. All the reagents in the experiment were used as received without further purification.

2.2. Preparation of modified silica solution

The silica nanoparticles were prepared by the method of Stöber, Fink, and Botn (1968) and Costa, Valadares, and Galembeck (2007). Typically, 4 ml TEOS was added to 50 ml ethanol with 4, 3, 2 or 1 mL NH_4OH as the catalyst, and then the mixture was kept within an ultrasonic water bath (53 kHz to 100 W, 37 °C). Two hours later the silica nanospheres were collected and purified by repeated centrifugation for three times in absolute ethanol, and then dried in a vacuum oven at 60 °C for 6 h.

The specific procedure to modify silica particles was as follows: 0.1 g silica spheres were uniformly dispersed to 15 ml ethanol in the

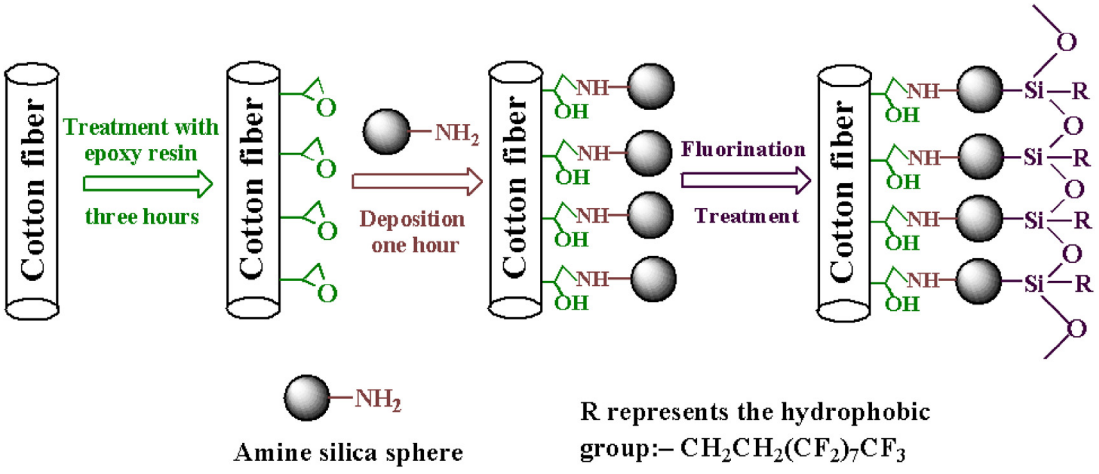

Fig. 3. Schematic illustration of the fabricating procedure of superhydrophobic fabric.

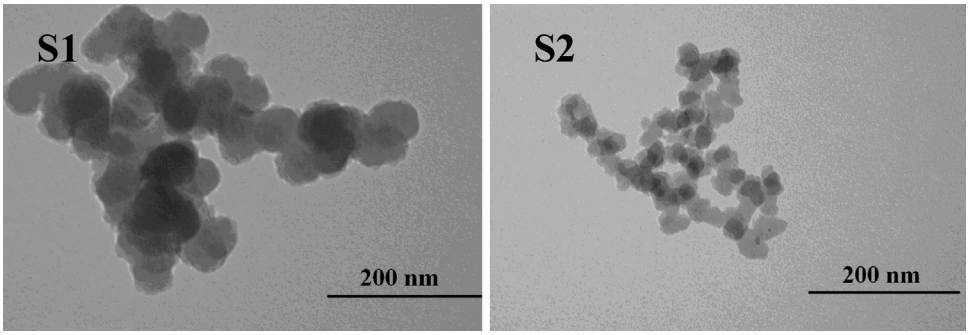

Fig. 4. TEM images of silica nanospheres prepared with optimal ammonia content as the catalyst (**S1**: 3 mL, **S2**: 2 mL).

presence of 3-aminopropyl(diethoxy)methylsilane (0.1 ml) via 1 h of magnetic stirring at ambient temperature. Finally, modified silica solution was obtained for the next step. Fig. 2 shows the grafting of 3-aminopropyl(diethoxy)methylsilane molecule onto the silica nanosphere surface.

2.3. Fabrication of superhydrophobic cotton fabric

As detailed in Fig. 3, the cotton sample was first introduced in a solution of epoxy resin (1%, m/v, in anhydrous acetone) at ambient temperature for 3 h, carefully rinsed with acetone, and then dried with nitrogen. Subsequently, the epoxidized cotton was immersed in the modified silica solution for 1 h, and then rinsed with ethanol. Ultimately, the cotton with a layer of silica nanospheres was fluorinated in the solution of (heptadecafluoro-1,1,2,2-tetradecyl) trimethoxysilane (1%, v/v, in anhydrous methanol) at ambient temperature for 1 h, followed by rinsing with methanol and drying with nitrogen.

2.4. Characterization

The geometric microstructures of cotton samples and silica nanoparticles were characterized by using scanning electron microscopy (SEM, FEI QUANTA200) and transmission electron microscopy (TEM, JEOL JEM2100), respectively. The elemental composition of silica samples and superhydrophobic films was determined by Fourier transform infrared spectroscopy (FT-IR, Magna-IR 560, Nicolet) and X-ray photoelectron spectrometer (XPS, PHI Thermo Fisher Scientific Company Quantera), respectively. The measurement of water contact angle (WCA) was carried out by utilizing an optical contact angle meter (Powreach, JC2000C) with 5 μL de-ionized water droplet at ambient temperature, and the final WCA was determined by averaging the measurements taken from at least five different positions on each cotton samples. Thermogravimetric analysis (TGA) was performed with an NETZSCH TG209F3 (Thermogravimetric analyzer, CTA instruments) equipped with a crucible. The sample was heated in air from 25 °C to 750 °C at a rate of 10 °C/min.

3. Results and discussion

3.1. Synthesis of silica nanospheres

The silica nanospheres were synthesized by a typical sol–gel process containing the hydrolysis of TEOS and the condensation of hydrolyzed silica species (Stöber et al., 1968; Wang et al., 2011). To our best knowledge, the size distribution of silica spheres is the critical factor to the Lotus effect. Therefore, the reaction time, the preparation method and the NH_4OH content to prepare silica nanoparticles were strictly controlled in this study. Fig. 4 presents the TEM images of silica nanospheres prepared with optimal ammonia content as the catalyst (**S1**: 3 mL, **S2**: 2 mL). From the images, we can find that the diameter ranges of **S1** and **S2** are 50–70 nm and 10–30 nm, respectively. Apparently, the observation shows that the diameter of as-prepared silica spheres diminishes along with the decrease of ammonia content, which is corresponding to the well-known research of Stöber et al. (1968). In addition, the as-obtained silica nanospheres were hydrophilic, and possess a poor monodispersity as shown in Fig. 4, which is attributed to the insufficient atomic coordination and abundant hydroxyl groups on silica surface.

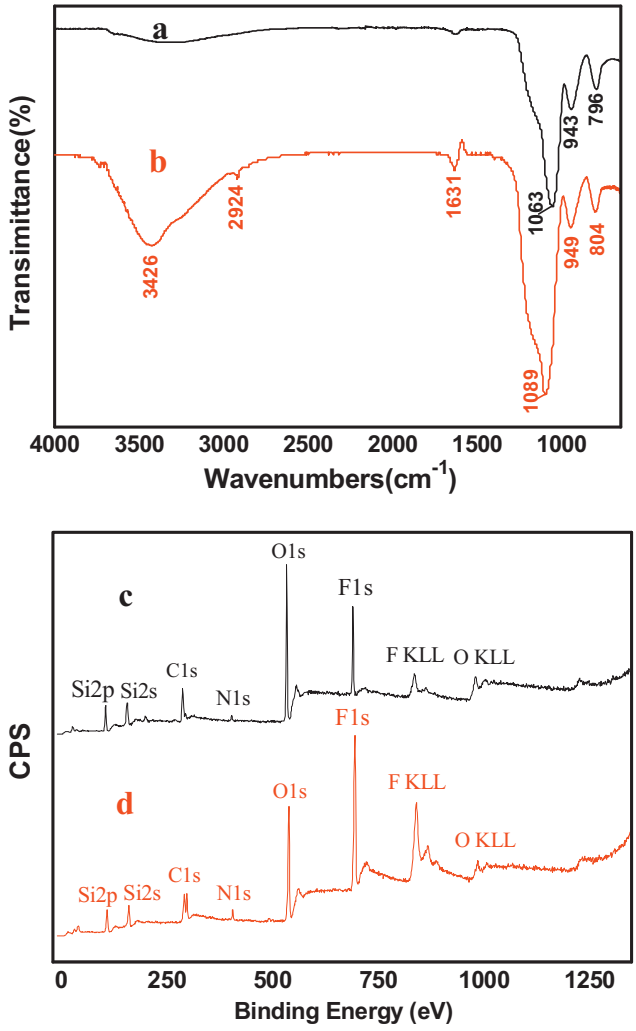

Fig. 5. FI-IR spectra of (a) pure and (b) amino-functional silica; XPS spectra of superhydrophobic films on cotton samples with (c) **S1** and (d) **S2**.

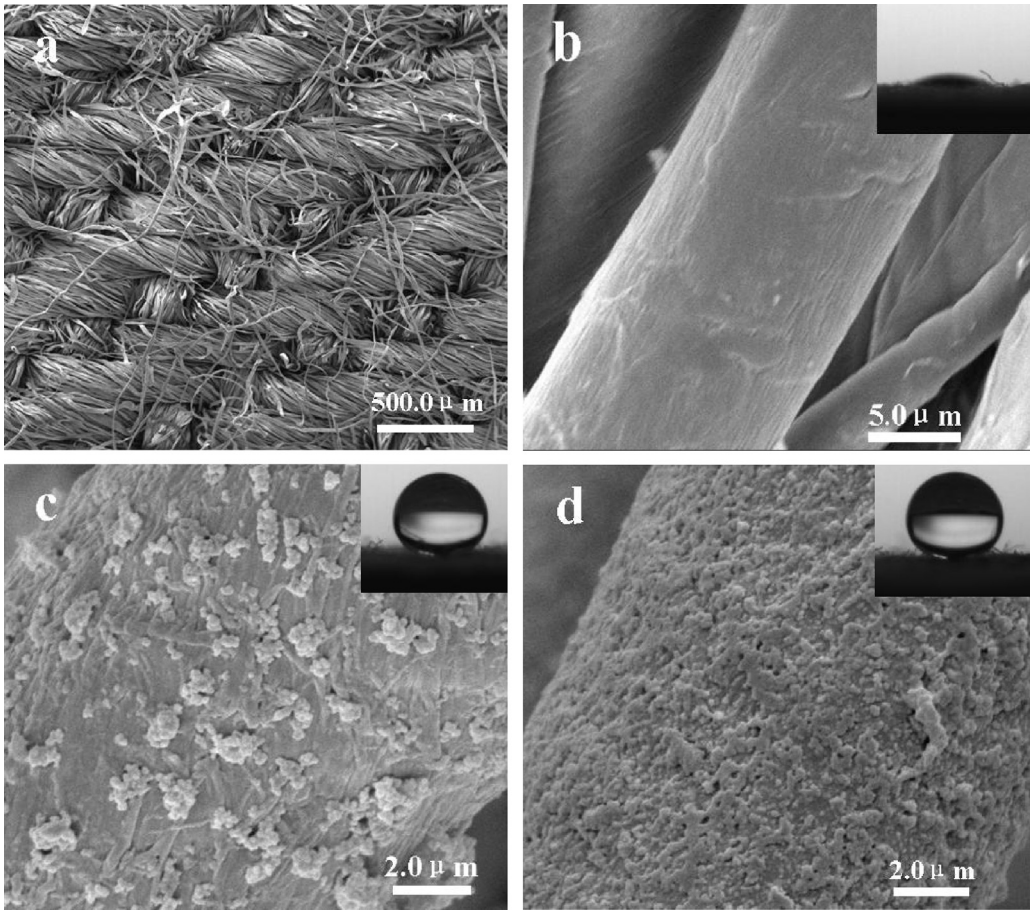

Fig. 6. SEM images of pristine cotton fabric (a and b) and treated cotton samples with (c) **S1** and (d) **S2**. The insets of (b), (c) and (d) are the pictures of water droplets on the cotton surface before and after treatment.

3.2. Chemical composition analysis

As described in Fig. 2, the as-prepared silica nanospheres were grafted with amino groups (3-aminopropyl(diethoxy)methylsilane) by a self-assembly process. In order to verify the grafting process, FT-IR analysis of pure and amine silica nanospheres has been provided. From Fig. 5a and b, we can observe the Si—O—Si asymmetric and symmetric stretching vibrations at 790–810 cm^{-1} and 1060–1090 cm^{-1}, indicating that the main structure of silica was not changed after the silanization reaction (Hsieh, Chen, Wu, & Min, 2010; Vinogradova, Estrada, & Moreno, 2006). Differently, the FT-IR spectrum of amine silica showed the new signals at 2924 cm^{-1} and 3426 cm^{-1}, which stem from the C—H stretching absorption and O—H stretching absorption (Jradi, Laour, Daneault, & Chabot, 2011), respectively. Moreover, the shoulder at 1631 cm^{-1} (N—H bending) further testifies that the amino-functionalization of silica nanospheres has been done.

Here, we employed X-ray photoelectron spectroscopy (XPS) to characterize the chemical composition of the superhydrophobic silica film on cotton surface. As shown in Fig. 5c and d, seven peaks of Si2p, Si2s, C1s, N1s, O1s, F1s and FKLL could be clearly observed in both spectra of the superhydrophobic film fabricated by different sizes of silica nanospheres. Except for the XPS peaks of Si2p, Si2s and O1s corresponding to the pure silica, the peak of N1s demonstrates again that the 3-aminopropyl(diethoxy)methylsilane molecule has adhered to the silica surface by chemical bonding just as displayed in Fig. 3. Moreover, the rest three peaks (O1s, F1s and FKLL) in Fig. 5c and d present that the fluorination of silica layer on cotton fabric via (heptadecafluoro-1,1,2,2-tetradecyl) trimethoxysilane was done.

3.3. Studies on surface morphology and wettability

As shown in Fig. 6, the geometric microstructures and wetting behavior of the cotton fabric before and after decoration have been conducted by utilizing scanning electron microscopy (SEM) and optical contact angle meter, respectively. From Fig. 6a, we can clearly observe the regular weave structure of pristine cotton textile with bits of protruding fibers. In its magnified SEM image, there are many longitudinal corrugations appearing on the fiber (with the diameter of about 15 μm) surface. Moreover, Fig. 6b shows that the pristine cotton fabric can be immediately wetted by the water droplet, the outstanding hydrophilicity of which is caused by the abundant hydroxyl groups and numerous holes in its woven structure. When the fabric was treated with **S1** in the presence of epoxy resin and coupling agent, many nanospheres adhered to the fiber surface randomly, significantly roughening the cotton surface (Fig. 6c). Importantly, its wettability has transformed into superhydrophobicity with the WCA of 155° after further fluorination of (heptadecafluoro-1,1,2,2-tetradecyl) trimethoxysilane. However, after the covalent deposition of **S2**, the corrugation structure of cotton fiber completely disappeared, and numerous silica nanospheres compactly covered on its surface. After fluorination treatment, the wetting behavior of this cotton surface obtained a great improvement with the WCA of 160°.

Apparently, the cotton sample with **S2** possessed a superior hydrophobicity, and its surface morphology exhibits a larger roughness as well (Fig. 6c and d), which is absolute in compliance with Cassie–Baxter theory (Feng & Jiang, 2006). In consequence, we could explain the superhydrophobicity of cotton surfaces

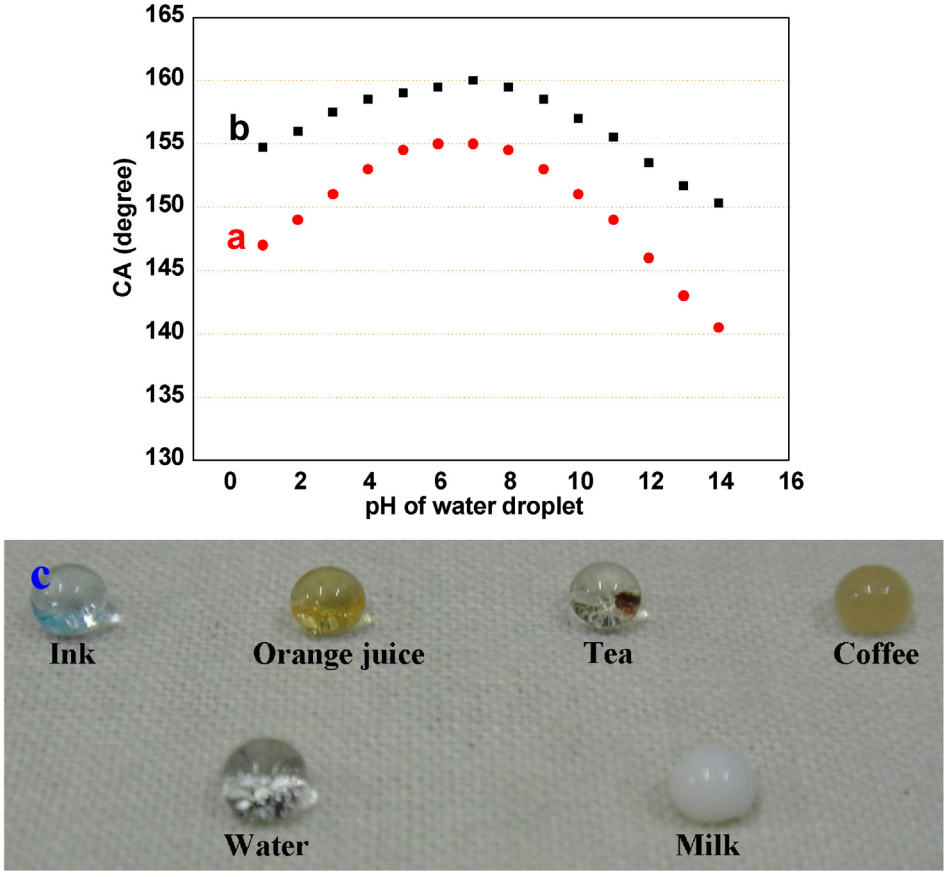

Fig. 7. Relationship between pH of water droplet and CA on the treated cotton fabric with (a) **S1** and (b) **S2**; (c) photograph of common household liquids on the superhydrophobic cotton fabric with **S2**.

fabricated in this experiment by the combination of two aspects: firstly, the roughness of nanostructure created by the covalent deposition of bisphenol A epoxy resin and silica spheres decorated via 3-aminopropyl(diethoxy)methylsilane; and secondly, the hydrophobic layer grafted on the surface of silica film during the silanization by (heptadecafluoro-1,1,2,2-tetradecyl) trimethoxysilane molecules.

3.4. Durability and flammability

Durability and flammability of superhydrophobic materials are the extremely important respects that need to be investigated for industrial applications. Consequently, we had evaluated the diverse performances of superhydrophobic cotton fabrics to identify whether these cotton samples could be applied to the practical purposes. Fig. 7a and b shows the relationship between pH of water droplet and CA on the treated cotton samples. It can be clearly observed that the water-repellent fabric with **S2** always meets the standard of superhydrophobicity in the pH range from 1 to 14, while the CA values of the cotton sample with **S1** preserve larger than 150° only in the pH range from 3 to 10. This observation indicates that the treated fabric with **S2** possesses not only a better hydrophobicity but also a more extraordinary stability under corrosive liquids such as acidic and basic solutions. Therefore, the research target in our following investigations is the superhydrophobic fabric with **S2**.

As shown in Fig. 7c, when the common household liquid drops onto this cotton sample, it always displays to be a sphere. The WCA of superhydrophobic sample had no obvious change even after the exposure for several months in ambient condition. More importantly, we find that this cotton surface could preserve the superhydrophobic property after undergoing the immersion for 24 h in organic reagents such as ethanol, toluene and n-hexane solutions, and the ultrasonic washing in tap-water with detergent. In order to testify the significant improvement and novelty of this study, we also investigated the washing resistance of the cotton sample which was fabricated without functionalizing the cotton and silica. Fig. 8a and b describes the relationship curves of the two samples after ultrasonic washing (53 kHz to 100 W, each sample was kept in 50 ml tap-water with 1 g neutral detergent at 30 °C). Apparently, the superhydrophobic layer on cotton sample without functionalization got a complete destruction (with WCA from 155° to 0°) within 180 s of ultrasonic washing, while the wetting behavior of our cotton sample displayed a slight decline, still possessing an extraordinary superhydrophobicity after test for 300 s. It reveals that the presences of epoxy resin and coupling agent for preparing superhydrophobic cotton fabric not only enlarged the WCA, but also enormously enhanced the adhesion between silica spheres and cotton surface by chemical bonding. To all appearance, the superhydrophobicity and durability of the waterproof fabric fabricated by this method have got a significant improvement.

Limiting oxygen index (LOI) is one of the most common parameters to evaluate the flammability of materials, which is defined as the minimum concentration of oxygen in an oxygen–nitrogen mixture (Gao et al., 2011). As we all know, the higher LOI value, the better flame retardancy, and the cotton fabric is a type of easily flammable material which has a low LOI value (18–19%) as well. In this experiment, the LOI value of cotton fabric we used was 18.3% only, but dramatically increased to be 20.9% after the treatment with epoxy resin/amino-functional **S2**/perfluorocarbon silane, displaying the significant improvement of flame retardancy. Moreover, we have also evaluated the

Table 1
Effects of chemical additives on the thermal properties of cotton samples.

Samples	$T_{-5\,wt\%}$ (°C)	T_{max} (°C)	V_{max} (%/min)	$Residue_{max}$ (%)	Main degradation region (°C)	$Residue_{750°C}$ (%)
Pristine cotton	290.8	350.9	−23.5	50.3	290–380	13.4
+Silica	303.5	353.6	−23.3	50.4	290–380	18.0
+Fluorination	105.3	352.3	−22.7	43.9	290–380	11.5
+Epoxidation	237.6	356.2	−16.7	46.6	230–390	6.9
+Amino-function	245.0	357.5	−13.3	54.4	260–420	19.5
Superhydrophobic cotton	262.2	353.4	−11.0	63.9	260–450	15.6

The data were obtained from TGA and DTG.

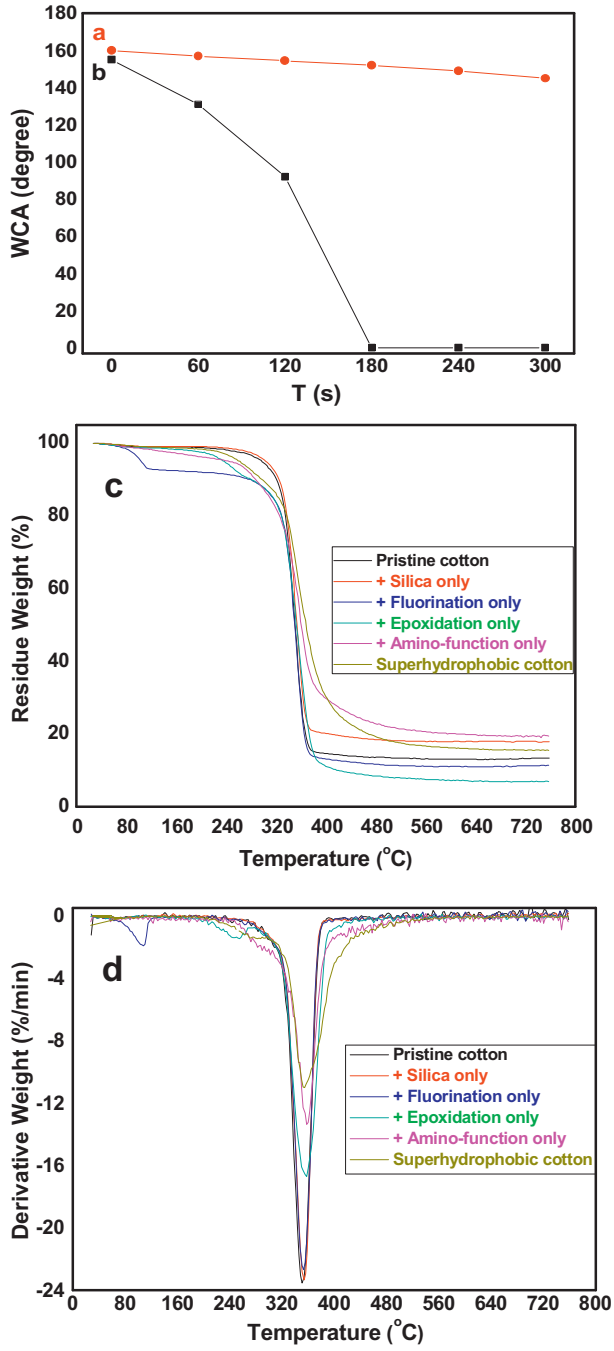

Fig. 8. Relationship between washing time and WCA of the treated cotton samples (a) with and (b) without epoxy resin and coupling agent. TGA (c) and DTG (d) curves of cotton samples in air. The silica we used in this section was **S2**.

thermal degradation behavior of the cotton samples before and after decoration with the chemicals for fabricating superhydrophobic fabric (Fig. 8c, d and Table 1). The TGA curves present that the temperature regions of main thermal degradation are in of 290–380 °C for pristine cotton and the cotton with silica or after fluorination, 230–390 °C for the cotton after epoxidation, 260–420 °C for the cotton after amino-function, and 260–450 °C for superhydrophobic cotton, showing an obvious increase of the temperature region for thermal degradation. Correspondingly, the velocity maximums of weight loss (and temperature) for these samples are −23.5%/min (350.9 °C), −23.3%/min (353.6 °C), −22.7%/min (352.3 °C), −16.7%/min (356.2 °C), −13.3%/min (357.5 °C) and −11.0%/min (353.4 °C), indicating an dramatic decrease of the velocity maximum of weight loss. The $residue_{750°C}$ for cotton fabric obtained an increase from 13.4% to 15.6% after superhydrophobic treatment, however, the animo-functional cotton sample possesses a larger $residue_{750°C}$ of 19.5%.

These observations demonstrate that the nanocomposite film on cotton fabric, including silica, perfluorocarbon silane, epoxy resin and coupling agent, indeed worked as a barrier to heat or mass transport during the thermal degradation and burning process (Wu et al., 2012). Apparently, the coupling agent (3-aminopropyl(diethoxy)methylsilane) has been testified to be the most effective proportion for the flame retardancy and thermal stability of superhydrophobic sample. As a conclusion, the results all above confirmed the excellent durability and flame retardancy of superhydrophobic cotton fabric which were fabricated by the covalent deposition of amino-silica nanospheres and the further graft with (heptadecafluoro-1,1,2,2-tetradecyl)trimethoxysilane, offering a good opportunity to accelerate the large-scale production of superhydrophobic textiles materials for new industrial applications.

4. Conclusion

As a summary of this study, we have reported a simple and facile method for fabricating the cotton textiles with the important functions of superhydrophobicity, waterproofing durability and flame retardancy. The wetting behavior of cotton sample after covalent deposition and further decoration has been transformed from superhydrophicity to superhydrophobicity with the maximum WCA of 160°. Importantly, the hydrophobic property of the cotton fabric which was prepared with **S2** is superior in the conditions of immersion in corrosive liquids and organic reagents, exposure to ambient air, and ultrasonic washing in tap-water with detergent. Moreover, the investigation results also demonstrate the excellent waterproofing durability, outstanding superhydrophobicity and flame retardancy of the as-obtained cotton fabric, which offers an opportunity to facilitate the development of superhydrophobic textiles materials for new practical purposes.

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References

Costa, C. A. R., Valadares, L. F., & Galembeck, F. (2007). Stöber silica particle size effect on the hardness and brittleness of silica monoliths. *Colloids and Surfaces A – Physicochemical and Engineering Aspects*, *302*, 371–376.

Feng, X. J., & Jiang, L. (2006). Design and creation of superwetting/antiwetting surfaces. *Advanced Materials*, *18*, 3063–3078.

Galopin, E., Piret, G., Szunerits, S., Lequette, Y., Faille, C., & Boukherroub, R. (2009). Selective adhesion of *Bacillus cereus* spores on heterogeneously wetted silicon nanowires. *Langmuir*, *26*, 3479–3484.

Gao, X., & Jiang, L. (2004). Biophysics: Water-repellent legs of water striders. *Nature*, *432*, 36.

Gao, Y., He, C. L., & Qing, F. L. (2011). Polyhedral oligomeric silsesquioxane-based fluoroether-containing terpolymers: Synthesis, characterization and their water and oil repellency evaluation for cotton fabric. *Journal of Polymer Science Part A: Polymer Chemistry*, *49*, 5152–5161.

Gao, X. F., Yan, X., Yao, X., Xu, L., Zhang, K., Zhang, J. H., et al. (2007). The dry-style antifogging properties of mosquito compound eyes and artificial analogues prepared by soft lithography. *Advanced Materials*, *19*, 2213–2217.

Gilman, J. W. (1999). Flammability and thermal stability studies of polymer layered-silicate (clay) nanocomposites. *Applied Clay Science*, *15*, 31–49.

Guo, Z. G., Liu, W. M., & Su, B. L. (2011). Superhydrophobic surfaces: From natural to biomimetic to functional. *Journal of Colloid and Interface Science*, *353*, 335–355.

Hsieh, C. T., Chen, W. Y., Wu, F. L., & Min, W. (2010). Superhydrophobicity of a three-tier roughened texture of microscale carbon fabrics decorated with silica spheres and carbon nanotubes. *Diamond and Related Materials*, *19*, 26–30.

Jradi, K., Laour, D., Daneault, C., & Chabot, B. (2011). Control of the chemical and physical behaviour of silicon surfaces for enhancing the transition from hydrophilic to superhydrophobic surfaces. *Colloids and Surfaces A – Physicochemical and Engineering Aspects*, *374*, 33–41.

Li, Y., Cai, W. P., Duan, G. T., Cao, B. Q., Sun, F. Q., & Lu, F. (2005). Superhydrophobicity of 2D ZnO ordered pore arrays formed by solution-dipping template method. *Journal of Colloid and Interface Science*, *287*, 634–639.

Li, Y., Li, L., & Sun, J. Q. (2010). Bioinspired self-healing superhydrophobic coatings. *Angewandte Chemie International Edition*, *49*, 6129–6133.

Nosonovsky, M., & Bhushan, B. (2008). Superhydrophobic surfaces for energy conservation and conversion. *Journal of Adhesion Science and Technology*, *22*, 2105–2115.

Ou, J., & Rothstein, J. P. (2005). Drag reduction and m-PIV measurements of the flow past ultrahydrophobic surfaces. *Physics of Fluids*, *17*, 103606.

Shi, F., Niu, J., Liu, J. L., Liu, F., Wang, Z. Q., Feng, X. Q., et al. (2007). Towards understanding why a superhydrophobic coating is needed by water striders. *Advanced Materials*, *19*, 2257–2261.

Stöber, W., Fink, A., & Botn, E. (1968). Controlled growth of monodisperse silica spheres in the micron size range. *Journal of Colloid and Interface Science*, *26*, 62–69.

Solga, A., Cerman, Z. B., Striffler, F., Spaeth, M., & Barthlott, W. (2007). Biological surfaces and their technical potential. *Bioinspiration & Biomimetics*, *2*, S126.

Vinogradova, E., Estrada, M., & Moreno, A. (2006). Colloidal aggregation phenomena: Spatial structuring of TEOS-derived silica aerogels. *Journal of Colloid and Interface Science*, *298*, 209–212.

Wang, S. L., Liu, C. Y., Liu, G. C., Zhang, M., Li, J., & Wang, C. Y. (2011). Fabrication of superhydrophobic wood surface by a sol–gel process. *Applied Surface Science*, *258*, 806–810.

Wang, Y., Sims, C. E., Marc, P., Bachman, M., Li, G. P., & Allbritton, N. L. (2006). Micropatterning of living cells on a heterogeneously wetted surface. *Langmuir*, *22*, 8257–8262.

Wang, Y. F., Li, B. X., & Xu, C. Y. (2012). Fabrication of superhydrophobic surface of hierarchical ZnO thin films by using stearic acid. *Superlattices and Microstructures*, *51*, 128–134.

Wu, G. M., Schartel, B., Bahr, H., Kleemeier, M., Yu, D., & Hartwig, A. (2012). Experimental and quantitative assessment of flame retardancy by the shielding effect in layered silicate epoxy nanocomposites. *Combustion and Flame*, *159*, 3616–3623.

Yan, Y. Y., Gao, N., & Barthlott, W. (2011). Mimicking natural superhydrophobic surfaces and grasping the wetting process: A review on recent progress in preparing superhydrophobic surfaces. *Advances in Colloid and Interface Science*, *169*, 80–105.

Yao, X., Song, Y. L., & Jiang, L. (2011). Applications of the bio-inspired special wettable surfaces. *Advanced Materials*, *23*, 719–734.

Zimmermann, J., Reifler, F. A., Fortunato, G., Gerhardt, L. C., & Seeger, S. (2008). A simple, one-step approach to durable and robust superhydrophobic textiles. *Advanced Functional Materials*, *18*, 3662–3669.

Zhang, M., Wang, C. Y., Wang, S. L., Shi, Y. L., & Li, J. (2012). Fabrication of coral-like superhydrophobic coating on filter paper for water–oil separation. *Applied Surface Science*, *261*, 764–769.

Zhang, M., Wang, S. L., Wang, C. Y., & Li, J. (2012). A facile method to fabricate superhydrophobic cotton fabrics. *Applied Surface Science*, *261*, 561–566.

Zheng, Y. M., Gao, X. F., & Jiang, L. (2007). Directional adhesion of superhydrophobic butterfly wings. *Soft Matter*, *3*, 178–182.

Zhu, J., & Wilkie, C. A. (2000). Thermal and fire studies on polystyrene–clay nanocomposites. *Polymer International*, *49*, 1158–1163.

Zhu, X. T., Zhang, Z. Z., Yang, J., Xu, X. G., Men, X. H., & Zhou, X. Y. (2012). Facile fabrication of a superhydrophobic fabric with mechanical stability and easy-repairability. *Journal of Colloid and Interface Science*, *380*, 182–186.