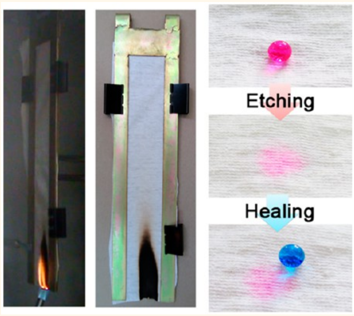
Intumescent Flame-Retardant and Self-Healing Superhydrophobic Coatings on Cotton Fabric

Shanshan Chen, Xiang Li, Yang Li, and Junqi Sun*

State Key Laboratory of Supramolecular Structure and Materials, International Joint Research Laboratory of Nano-Micro Architecture Chemistry (NMAC), College of Chemistry, Jilin University, Changchun 130012, People's Republic of China

ABSTRACT Flame-retardant and self-healing superhydrophobic coatings are fabricated on cotton fabric by a convenient solution-dipping method, which involves the sequential deposition of a trilayer of branched poly(ethylenimine) (bPEI), ammonium polyphosphate (APP), and fluorinated-decyl polyhedral oligomeric silsesquioxane (F-POSS). When directly exposed to flame, such a trilayer coating generates a porous char layer because of its intumescent effect, successfully giving the coated fabric a self-extinguishing property. Furthermore, the F-POSS embedded in cotton fabric and APP/bPEI coating produces a superhydrophobic surface with a self-healing function. The coating can repetitively and autonomically restore the superhydrophobicity when the superhydrophobicity is damaged. The resulting cotton fabric, which is flame-resistant, waterproof, and self-cleaning, can be easily cleaned by simple water rinsing. Thus, the integration of self-healing superhydrophobicity with flame retardancy provides a practical way to resolve the problem of washing durability of the flame-retardant coatings. The flame-retardant and superhydrophobic fabric can endure more than 1000 cycles of abrasion under a pressure of 44.8 kPa without losing its flame retardancy and self-healing superhydrophobicity, showing potential applications as multifunctional advanced textiles.



KEYWORDS: flame-retardant materials · intumescent · polymer films · self-healing · superhydrophobicity

Every year, fires cause serious property loss, civilian deaths, and injuries worldwide. Flame-retardant treatment on combustible materials that can delay ignition and hinder flame propagation is therefore necessary to reduce the risk of fires.[1,2] Among various flame-retardant materials, flame-retardant textiles have attracted considerable attention because they are widely used to manufacturer clothes and soft furnishings, and unmodified textiles are highly combustible.[3−6] Surface modification is an effective and convenient method of adding flame-retardant properties to combustible materials.[1,2,7,8] First, most flame retardants are concentrated at the surface of the protected textiles to achieve the highest protection. Second, flame-retardant layers do not alter the mechanical properties of the protected textiles. Third, flame-retardant layers can be purposely integrated with functional components to achieve multiple functions.

As a surface modification method, layer-by-layer (LbL) assembly has been recently proven to be highly useful and flexible in fabricating flame-retardant coatings on various substrates.[5,9−13] For instance, Grunlan and co-workers demonstrated the fabrication of intumescent flame-retardant coatings on cotton fabric by LbL assembly of polyanions, such as poly(sodium phosphate), and phytic acid with polycations, such as poly(allylamine hydrochloride) and chitosan.[5,11] These intumescent flame-retardant coatings, which are usually composed of 10 or even several tens of deposition cycles of polycation/polyanion bilayers, can give fabric a self-extinguishing property by generating a 3D porous char layer. However, the flame-retardant components are water-soluble. As a result, the LbL-assembled flame-retardant coatings cannot undergo repeated washings, which greatly hinders their application.[14] Furthermore, it is also highly desirable to fabricate LbL-assembled flame-retardant coatings in a more efficient way by largely reducing the number of film deposition cycles required.[15]

Superhydrophobic surfaces, on which water-contact angles are greater than 150°

* Address correspondence to sun_junqi@jlu.edu.cn.

Received for review January 8, 2015 and accepted March 16, 2015.

10.1021/acsnano.5b00121

and sliding angles are smaller than 10°, exhibit strong water repellence and possess self-cleaning, antiadhesive, and anticontamination functions.[16−21] Thus, integration of superhydrophobicity with flame retardancy can largely reduce the need for textile laundering and provide a practical way to resolve leaching flame-retardant components during textile laundering. Moreover, superhydrophobicity can render cotton fabric waterproof and reduce its surface contamination, which is useful for designing innovative and higher-value textiles for applications in harsh conditions. Fabrication of a superhydrophobic surface requires the combination of micro- and nanoscale hierarchical structures with low-surface-energy materials.[16] However, exposure to strong sunlight, chemical oxidation, or mechanical abrasion can decompose or remove rough structures and/or low-surface-energy materials, permanently destroying their superhydrophobicity.[22] Recent studies have demonstrated that endowing superhydrophobic surfaces with a self-healing capacity provides a promising way to enhance the durability of artificial superhydrophobic surfaces.[23−26] Our group has pioneered the fabrication of self-healing superhydrophobic surfaces by embedding the healing agent fluoroalkylsilane in highly rough and porous polyelectrolyte films.[23,27] Migration of the embedded fluoroalkylsilane to the film surface enables autonomic restoration of the damaged superhydrophobicity. This strategy has been extended for fabrication of self-healing superhydrophobic and superoleophobic fabric.[24,28−30] Herein, for the first time to our knowledge, we fabricated intumescent flame-retardant and self-healing superhydrophobic coatings on cotton fabric using a highly efficient and technically simple solution-dipping method. The coating consists of a bilayer of ammonium polyphosphate (APP)/branched poly(ethylenimine) (bPEI) fabricated by a dipping-LbL assembly, which is subsequently coated with fluorinated-decyl polyhedral oligomeric silsesquioxane (F-POSS). When directly exposed to flame, this trilayer coating generates a porous char layer because of its intumescent effect, successfully giving the coated fabric a self-extinguishing property. Furthermore, the F-POSS embedded in cotton fabric and the APP/bPEI coating, combined with the micro- and nanoscaled roughness of the cotton fabric surface, produce a superhydrophobic surface with a self-healing function. The flame-retardant and superhydrophobic fabric can endure more than 1000 cycles of abrasion under a pressure of 44.8 kPa without losing its flame retardancy and self-healing superhydrophobicity. Thus, this fabric shows potential application as a multifunctional advanced textile.

RESULTS AND DISCUSSION

An intumescent coating is usually composed of a carbon source, an acid source, and a blowing agent. In this work, polycation bPEI and polyanion APP were employed to fabricate intumescent flame-retardant coatings on cotton fabric, wherein APP is the acid source and bPEI is the blowing agent and carbon source.[2,6] Furthermore, bPEI also acts as a binder between the cotton fabric/APP because bPEI has the strong electrostatic/hydrogen bonding interactions. The cotton fabric was immersed in aqueous bPEI solution (4 mg/mL, pH 9.0) for 20 min to obtain a layer of bPEI. The fabric was then immersed in aqueous APP dispersion (20 mg/mL, pH 5.6) for 1 h to cover the fabric with sufficient APP. To show the deposition of APP/bPEI coating on cotton fabric, the uncoated and coated fabrics were characterized by scanning electron microscopy (SEM). The fibers of the uncoated fabric are smooth, as shown in Figure 1a,b. The weave structure of the cotton fabric was well covered after being coated with one bilayer of APP/bPEI coating (Figure 1c). The high-resolution SEM image in Figure 1d clearly shows that the conformal APP/bPEI coating fully covers the individual cotton fibers. The APP/bPEI coating is readily discerned in the slightly exfoliated area. APP particles attached to cotton fibers are also clearly shown. The as-obtained APP particles have an average size of ~15 μm. When dispersed in aqueous solution, APP particles can hydrolyze to produce small particles of various sizes ranging from several tens of nanometers to ~15 μm (Figure S1, Supporting Information). Negatively charged APP particles small in size are preferred to be assembled on top of the bPEI layer because small APP particles have a high-surface-charge density and strong electrostatic interaction with bPEI. This explains why the APP/bPEI coating has a relatively flat surface.

The low-surface-energy material F-POSS is finally deposited onto the APP/bPEI-coated cotton fabric to generate the self-healing superhydrophobicity. A novel and highly efficient method was developed to synthesize the F-POSS by the thiol-ene click reaction between vinyl-POSS and perfluorodecanethiol in the presence of 2,2-dimethoxy-2-phenylacetophenone (DMPA) as an initiator,[31] as shown in Scheme 1. The reaction is complete within 5 min under UV irradiation (Figure S2, Supporting Information). The F-POSS was deposited by immersing the APP/bPEI-coated cotton fabric in the F-POSS ethanol dispersion (10 mg/mL) for 4 min. Depositing the F-POSS on top of the APP/bPEI-coated cotton fabric does not alter the weave structure of the fabric (Figure 1e). Aside from the molecularly deposited F-POSS, the enlarged SEM image in Figure 1f clearly shows that F-POSS aggregates are also deposited on the surface of the APP/bPEI-coated cotton fibers. These aggregates are required to generate a surface with dual roughness, which is a prerequisite for the fabrication of superhydrophobic surfaces. The SEM images in Figure 1 confirm that a trilayer F-POSS/APP/bPEI coating can be successfully fabricated on the cotton fabric by using the solution-dipping method.

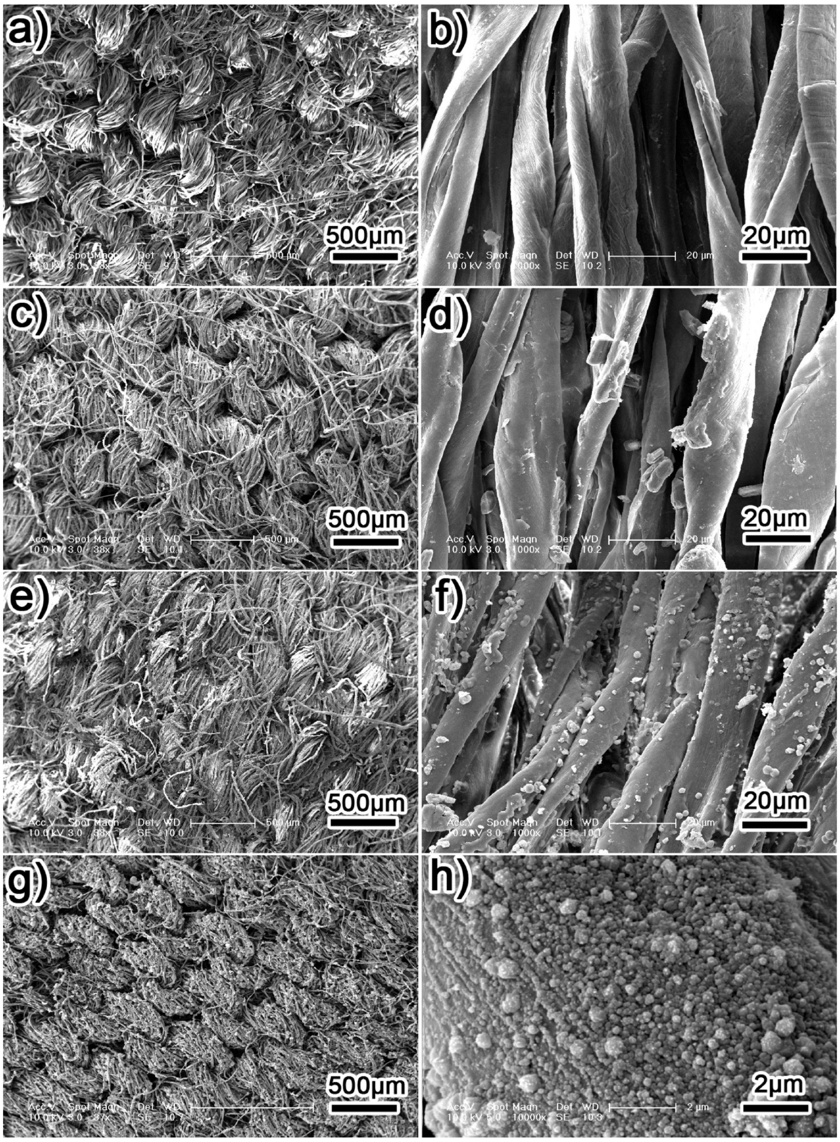
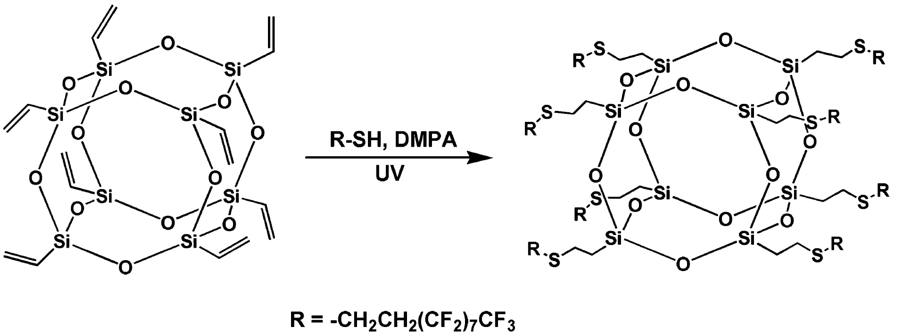


Figure 1. SEM images of uncoated and coated cotton fabric: (a,b) uncoated fabric; (c,d) APP/bPEI-coated fabric; (e,f) F-POSS/APP/bPEI-coated fabric; (g,h) F-POSS/APP/bPEI-coated fabric after vertical flame testing.



Scheme 1. Schematic of the synthesis of F-POSS.

Moreover, the successful deposition of the F-POSS/APP/bPEI coating was verified by the signals of N, P, and F in the energy-dispersive X-ray (EDX) spectrum of the F-POSS/APP/bPEI-coated cotton fabric (Figure S3, Supporting Information). The cross-sectional SEM image shows that the F-POSS/APP/bPEI coating fully covers the individual fibers. The thickness of the F-POSS/APP/bPEI coating is 246 ± 54 nm (Figure S4, Supporting Information). The weight per area of cotton fabric samples is 118.1 ± 0.4 g/m^2. Three samples were

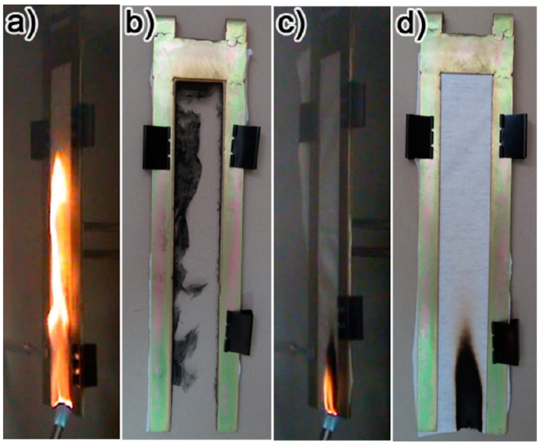


Figure 2. Vertical flame testing images of the uncoated and coated cotton fabric: (a) uncoated fabric recorded at 4 s after ignition; (b) uncoated fabric after vertical flame testing; (c) F-POSS/APP/bPEI-coated fabric recorded at 4 s after ignition; (d) F-POSS/APP/bPEI-coated fabric after vertical flame testing.

weighted to get an average mass increase after each layer deposition. The amount of deposited bPEI, APP, and F-POSS on the cotton fabric is 1.4 ± 0.1, 22.8 ± 1.4, and 15.6 ± 0.4 g/m^2, respectively.

The F-POSS/APP/bPEI-coated cotton fabric was subjected to vertical flame testing to evaluate its flame-retardant properties. The uncoated fabric served as a control. These fabrics were exposed to a direct flame for 12 s before removing the flame. Upon exposure to direct flame, the uncoated fabric ignited immediately and the flame quickly spread. The flame on the uncoated fabric was vigorous and bright at 4 s after ignition, as shown in Figure 2a. The uncoated fabric was completely burned within 14 s (Figure 2b and Supporting Information movie 1). In contrast, the flame on the F-POSS/APP/bPEI-coated fabric was suppressed at 4 s after ignition (Figure 2c). The coated fabric self-extinguished after the flame source was removed. After burning, only 10 cm of the fabric became charred and turned black, whereas most of the top of the fabric remained intact (Figure 2d and Supporting Information movie 2). Therefore, the F-POSS/APP/bPEI coating gave the cotton fabric the flame-retardant property by producing a protective char layer. The charred fabric was observed by SEM to study the flame-retarding mechanism. The SEM image in Figure 1g shows that the F-POSS/APP/bPEI-coated fabric in the burned area maintained the fabric structure and integrity well. Additionally, the surface of the burned fiber was covered with a dense char layer of bubbles and became very rough (Figure 1h). EDX spectra indicate that the relative content of P in the char layer was significantly higher than that in the F-POSS/APP/bPEI coating before the combustion test. The disappearance of fluorine in the charred layer shows that the fluorine in the F-POSS was consumed and vaporized during combustion (Figure S3, Supporting Information). The porous char layer was produced because of the intumescent effect, which leads to swelling and expansion of the F-POSS/APP/bPEI coating during burning.[5,10] For the F-POSS/APP/bPEI-coated fabric, the cellulose in cotton works as the carbon source, APP as the acid source, and bPEI as the blowing agent and carbon source. When exposed to fire, APP catalyzed the dehydration of the carbon source of cellulose and bPEI and led to char formation. The decomposition of the blowing agent releases inert gases that foam the forming char to generate a swollen and porous char layer. This char layer acts as a barrier to heat, fuel, and oxygen transfer, thereby effectively protecting the underlying cotton fabric from fire spread.[5,6] Therefore, the intumescent effect of the APP/bPEI coating during combustion gives the coated fabric excellent flame-retardant ability. We believe the silsesquioxanes in the F-POSS can work as inorganic fillers to reinforce the intumescent char layer.

Depositing low-surface-energy F-POSS on top of the APP/bPEI-coated cotton fabric creates a superhydrophobic surface. After being coated with the F-POSS, the flame-retardant fabric has a water-contact angle of ~160° and a sliding angle of ~4° (Figure 3a). Water droplets readily roll off this type of fabric surface. Therefore, the F-POSS/APP/bPEI-coated fabric is waterproof and self-cleaning because water cannot wet the fabric and the rolling water droplets can remove dust from the fabric. The bending rigidity values of the uncoated and F-POSS/APP/bPEI-coated fabric are 4.3×10^{-2} and 9.2×10^{-2} cN·cm^2/cm, respectively. In comparison, the bending rigidity values of the commercial fire-retardant fabric and daily used fabrics for jeans and shirts (bought from local market) are measured to be 314.2×10^{-2}, 81.3×10^{-2}, and 11.8×10^{-2} cN·cm^2/cm, respectively. The gas permeability values of the fabric decrease from 971.4 to 467.9 mm/s after being coated with F-POSS/APP/bPEI coating. The permeability values of commercial fire-retardant fabric and jean fabric are measured to be 1.2 and 35.3 mm/s. These results indicate that the F-POSS/APP/bPEI-coated fabric still has satisfactory flexibility and gas permeability for practical use. This is because, on the one hand, the F-POSS/APP/bPEI coating only has a thickness of 246 ± 54 nm, and on the other hand, the coating wraps the individual fibers but does not completely block the interstices between them (Figure 1e,f). The self-healing superhydrophobicity of the coated fabric was then examined by etching it with O_2 plasma. This process decomposes the F-POSS on the surface of the coated fabric, as sunlight can do when the superhydrophobic cotton fabric is for outdoors use. As shown in Figure 3a, the superhydrophobic cotton fabric became superhydrophilic after O_2 plasma etching, confirming that the surface F-POSS was etched away and that hydrophilic bPEI and APP polyelectrolytes were exposed. After the O_2-plasma-etched cotton

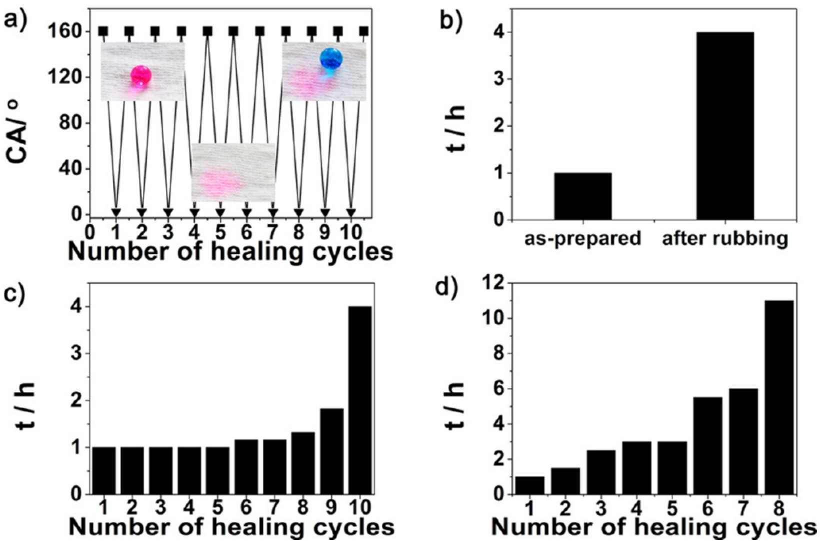


Figure 3. (a) Water-contact angle changes of the F-POSS/APP/bPEI-coated fabric upon repeated O_2 plasma etching (▼) and self-healing (■). Inset: Shapes of water droplets (5 μL) of the as-prepared (top left), O_2-plasma-etched (bottom), and healed (top right) cotton fabric. (b) Time required for the as-prepared and rubbed F-POSS/APP/bPEI-coated fabric to restore its original superhydrophobicity under a 35% RH environment at the first etching–healing cycle. (c,d) Time required to restore superhydrophobicity *versus* the number of etching–healing cycles for as-prepared (c) and rubbed (d) cotton fabric under a 100% RH environment.

fabric was left in a slightly humid environment with a relative humidity (RH) of ∼35% for ∼1 h (Figure 3b), the fabric regained its original superhydrophobicity. Therefore, the F-POSS/APP/bPEI-coated cotton fabric not only can retard the flame but also can autonomically heal the damaged superhydrophobicity. Figure 3a shows that the damaging/healing process can be repeated at least 10 times without obviously decreasing the original superhydrophobicity of the coated fabric. The self-healing of the superhydrophobic cotton fabric is dependent on the damaging/healing cycles, with the healing process gradually becoming slower with the repetition of damage/healing cycles (Figure 3c). The full restoration of the superhydrophobicity takes ∼4 h under a 100% RH environment at the tenth damaging/healing cycle. These results suggest that the durability of the self-healing ability of the superhydrophobic fabric enables its long-term application. The self-healing ability originates from the embedded healing agent F-POSS in the APP/bPEI-coated cotton fabric. During the deposition, the F-POSS not only deposited on the fabric surface but also diffused into the APP/bPEI coating and the underlying cotton fabric. Once the top layer of the F-POSS on the coated fabric surface decomposes, the surface of the APP/bPEI-coated fabric becomes hydrophilic, which drives the embedded perfluorodecanyl chains of the F-POSS to migrate to the coating surface to lower its surface energy. In this way, the damaged superhydrophobicity of the cotton fabric is repaired.[23,27] Previously reported self-healing superhydrophobic fabric, in which the hydrophobic healing agent is directly embedded in the fabric, requires heat treatment or takes a long time under room temperature to heal damage.[24] By comparison, the superhydrophobic fabric reported here easily and rapidly heals damage because the hydrophilic APP/bPEI coating expels the embedded hydrophobic perfluorodecanyl chains of the F-POSS to speed up its migration to the coating surface.

The durability of the flame-retardant and self-healing superhydrophobic cotton fabric was examined by repeatedly rubbing the coatings with a cylindrical copper under an applied pressure of 44.8 kPa. After 1000 cycles of rubbing, the SEM images in Figure 4a,b clearly show that some of the fibers in the coated cotton fabric are broken. The water-contact angle and slide angle on the rubbed cotton fabric decreased to ∼153 and ∼6°, respectively, which was still superhydrophobic. The rubbed fabric was etched with O_2 plasma to examine the influence of rubbing on the self-healing superhydrophobicity of the cotton fabric. The surface of the rubbed and O_2-plasma-etched cotton fabric can also restore its superhydrophobic property after being transferred to an ambient environment with 35% RH for ∼4 h, which is four times longer than that used to repair the nonrubbed cotton fabric (Figure 3b). The damaging/healing process of the rubbed cotton fabric can be repeated more than eight times in a 100% RH environment (Figure 3d). Furthermore, the healing process becomes slower with increasing damaging/healing cycles. This result demonstrates that the rubbed cotton fabric still retains its self-healing superhydrophobicity. The flame-retardant ability of the F-POSS/APP/bPEI-coated fabric after 1000 cycles of rubbing was also investigated. The rubbed area, with a length of 20 cm from the bottom, is marked with a rectangle in Figure 4c. As indicated in

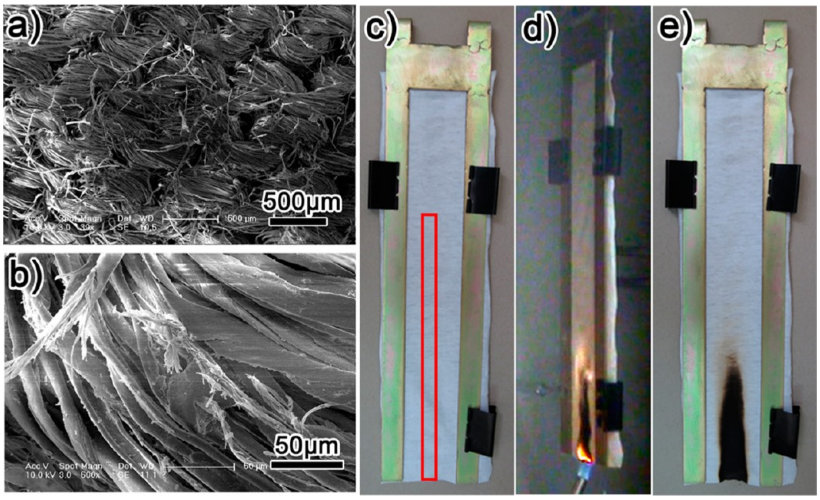


Figure 4. (a,b) SEM images of the F-POSS/APP/bPEI-coated cotton fabric after 1000 cycles of abrasion. (c−e) Vertical flame testing images of the F-POSS/APP/bPEI-coated cotton fabric after 1000 cycles of abrasion: (c) abrasion area on the F-POSS/APP/bPEI-coated cotton fabric is marked with a rectangle; (d) fabric recorded at 4 s after ignition; (e) fabric after vertical flame testing.

Figure 4d, the flame spread for 13 cm from the bottom of the fabric at 4 s after ignition. However, the fabric self-extinguished immediately after the removal of the flame. The top section of the rubbed cotton fabric was unburned (Supporting Information movie 3). Therefore, the flame-retardant and self-healing superhydrophobic F-POSS/APP/bPEI coatings on the cotton fabric show excellent durability against repeated rubbing. This result suggests that the flame-retardant APP/bPEI coating and the hydrophobic F-POSS might penetrate deeply into the fibers of the cotton fabric, which enables the preservation of the flame-retardant and self-healing superhydrophobic functions of the fabric even under heavy scratching.

CONCLUSION

In conclusion, we have demonstrated the first fabrication of flame-retardant and self-healing superhydrophobic cotton fabric by using a convenient solution-dipping method that involves the sequential deposition of a trilayer of bPEI, APP, and F-POSS. The resulting multifunctional cotton fabric is flame-resistant, waterproof, and self-cleaning. One bilayer of bPEI/APP coating is sufficient to provide an efficient char layer on cotton fabric to extinguish flame because of the intumescent effect. The humidity-driven migration of embedded F-POSS in bPEI/APP-coated fabric enables multiple healing of the damaged superhydropobicity of the fabric, which significantly prolongs the lifespan of superhydrophobicity. The as-prepared flame-retardant and self-healing superhydrophobic cotton fabric exhibits satisfactory durability against repeated abrasion for practical application. The self-healing superhydrophobic cotton fabric can be readily cleaned with simple water rinsing, which provides a practical way to resolve the problem of washing durability of flame-retardant coatings. The present fabrication method of durable, intumescent flame-retardant, and self-healing superhydrophobic cotton fabric is technically simple and cost-effective. We believe that this method can also be applied to other fabrics to enrich the fabrication of innovative textiles and extend their applications.

METHODS

Materials. bPEI ($M_w \approx 25\,000$), 1H,1H,2H,2H-perfluorodecanethiol, and DMPA were purchased from Sigma−Aldrich. Vinyl-POSS was purchased from Shenyang Amwest Technology Company. APP ($n > 1000$) was purchased from Shenzhen Ruihong Chemicals Co., Ltd. Cotton fabric was supplied by Qinling Mountains Cloth Company. All chemicals were used without further purification.

Synthesis of F-POSS[31]. Perfluorodecanethiol (0.32 mL) and initiator DMPA (6 mg) were added to a solution of vinyl-POSS (0.1 g) in dichloromethane (1.5 mL) at room temperature. After UV irradiation for 5 min, white precipitates were produced. These precipitates were collected and washed repeatedly with dichloromethane. Finally, the precipitates were dried in an oven at 60 °C. Detailed Fourier transform infrared spectroscopy (FTIR) spectra of F-POSS are shown in the Supporting Information.

Coating Fabrication. Cotton fabric was first immersed in an aqueous solution of bPEI (4 mg/mL, pH 9.0) for 20 min to deposit a layer of bPEI. After being washed with deionized water, the bPEI-coated fabric was squeezed to remove the adsorbed water. The bPEI-coated fabric was then immersed in aqueous APP dispersion (20 mg/mL) for 1 h followed by water washing. After the APP/bPEI-coated fabric was dried in an oven at 60 °C to completely remove the adsorbed water, the flame-retardant fabric was obtained. To give the flame-retardant fabric the self-healing superhydrophobicity, the APP/bPEI-coated fabric was finally immersed in ethanol dispersion of F-POSS (10 mg/mL) for 5 min to adsorb sufficient F-POSS onto the resultant fabric. The F-POSS/APP/bPEI-coated fabric was finally dried in an oven at 60 °C.

Coating Characterization. FTIR spectra were obtained using a Bruker IFS 66 V spectrophotometer. The digital images of films were captured by a Sony Cyber-shot DSC-H10 camera. The SEM images were obtained under an XL30 ESEM FEG scanning electron microscope. Energy-dispersive X-ray spectra were obtained on an EDAX Genesis 2000 X-ray microanalysis system attached to an XL30 ESEM FEG SEM. Water-contact angle measurements were performed with a Drop Shape Analysis System DSA10-MK2 (Kruess, Germany) at ambient temperature with a 5 μL water droplet as the indicator. The bending rigidity of the fabrics were tested on a Kawabata Evaluation System (Kyoto University, Japan). The gas permeability of the fabrics was examined on a fabric air permeability tester (YG461E, Wuhan Guoliang Instrument Co., Ltd., China) under a 100 Pa pressure drop.

Flammability and Antiabrasion of Fabric. A vertical flame test was performed on uncoated and coated cotton fabric with a size of 8 cm × 30 cm using an automatic vertical flammability cabinet (CZF-3, Jiangning Nanjing Analytical Instrument Co., Ltd.). The fire from a gas burner was applied on the tested fabric for 12 s and then removed. The abrasion test was performed using a commercial abrasion tester (YB571-III, Wenzhou Darong Textile Instrument Co., Ltd.). A cylindrical copper with a diameter of 16 mm repeatedly scratched the fabric with a speed of 30 cm/s under an applied pressure of 44.8 KPa (Figure S5, Supporting Information).

Conflict of Interest: The authors declare no competing financial interest.

Acknowledgment. This work was supported by the National Basic Research Program (2013CB834503) and the National Natural Science Foundation of China (NSFC Grants 21225419 and 21221063).

Supporting Information Available: Video of flame-retardant test and detailed characterization data from optical microscopy, SEM, FTIR, and EDX. This material is available free of charge *via* the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

1. Weil, E. D.; Levchik, S. V. *Flame Retardants for Plastics and Textiles: Practical Applications*; Carl Hanser Verlag GmbH & Co. KG: Cincinnati, OH, 2009.
2. Lu, S. Y.; Hamerton, I. Recent Developments in the Chemistry of Halogen-Free Flame Retardant Polymers. *Prog. Polym. Sci.* **2002**, *27*, 1661–1712.
3. Prival, M. J.; McCoy, E. C.; Gutter, B.; Rosendranz, H. S. Tris(2,3-dibromopropyl) Phosphate: Mutagenicity of a Widely Used Flame Retardant. *Science* **1977**, *195*, 76–78.
4. Devaux, E.; Rochery, M.; Bourbigot, S. Polyurethane/Clay and Polyurethane/POSS Nanocomposites as Flame Retarded Coating for Polyester and Cotton Fabrics. *Fire Mater.* **2002**, *26*, 149–154.
5. Li, Y.-C.; Mannen, S.; Morgan, A. B.; Chang, S.; Yang, Y.-H.; Condon, B.; Grunlan, J. C. Intumescent All-Polymer Multilayer Nanocoating Capable of Extinguishing Flame on Fabric. *Adv. Mater.* **2011**, *23*, 3926–3931.
6. Alongi, J.; Carosio, F.; Malucelli, G. Current Emerging Techniques To Impart Flame Retardancy to Fabrics: An Overview. *Polym. Degrad. Stab.* **2014**, *106*, 138–149.
7. Liang, S. Y.; Neisius, N. M.; Gaan, S. Recent Developments in Flame Retardant Polymeric Coatings. *Prog. Org. Coat.* **2013**, *76*, 1642–1665.
8. Kim, M.-J.; Jean, I.-Y.; Seo, J.-M.; Dai, L.; Baek, J.-B. Graphene Phosphonic Acid as an Efficient Flame Retardant. *ACS Nano* **2014**, *8*, 2820–2825.
9. Li, Y.-C.; Schulz, J.; Mannen, S.; Delhom, C.; Condon, B.; Chang, S.; Zammarano, M.; Grunlan, J. C. Flame Retardant Behavior of Polyelectrolyte−Clay Thin Film Assemblies on Cotton Fabric. *ACS Nano* **2010**, *4*, 3325–3337.
10. Laachachi, A.; Ball, V.; Apaydin, K.; Toniazzo, V.; Ruch, D. Diffusion of Polyphosphates into (Poly(allylamine) montmorillonite) Multilayer Films: Flame Retardant-Intumescent Films with Improved Oxygen Barrier. *Langmuir* **2011**, *27*, 13879–13887.
11. Laufer, G.; Kirkland, C.; Morgan, A. B.; Grunlan, J. C. Intumescent Multilayer Nanocoating, Made with Renewable Polyelectrolytes, for Flame-Retardant Cotton. *Biomacromolecules* **2012**, *13*, 2843–2848.
12. Laufer, G.; Kirkland, C.; Cain, A. A.; Grunlan, J. C. Clay−Chitosan Nanobrick Walls: Completely Renewable Gas Barrier and Flame-Retardant Nanocoatings. *ACS Appl. Mater. Interfaces* **2012**, *4*, 1643–1649.
13. Wang, L. L.; Zhang, T.; Yan, H. Q.; Peng, M.; Fang, Z. P. Modification of Ramie Fabric with a Metal-Ion-Doped Flame-Retardant Coating. *J. Appl. Polym. Sci.* **2013**, *129*, 2986–2997.
14. Alongi, J.; Di Blasio, A.; Carosio, F.; Malucelli, G. UV-Cured Hybrid Organic−Inorganic Layer by Layer Assemblies: Effect on the Flame Retardancy of Polycarbonate Films. *Polym. Degrad. Stab.* **2014**, *107*, 74–81.
15. Cain, A. A.; Murray, S.; Holder, K. M.; Nolen, C. R.; Grunlan, J. C. Intumescent Nanocoating Extinguishes Flame on Fabric Using Aqueous Polyelectrolyte Complex Deposited in Single Step. *Macromol. Mater. Eng.* **2014**, *299*, 1180–1187.
16. Xia, F.; Jiang, L. Bio-inspired, Smart, Multiscale Interfacial Materials. *Adv. Mater.* **2008**, *20*, 2842–2858.
17. Zhang, X.; Shi, F.; Niu, J.; Jiang, Y.; Wang, Z. Superhydrophobic Surfaces: From Structural Control to Functional Application. *J. Mater. Chem.* **2008**, *18*, 621–633.
18. Verho, T.; Bower, C.; Andrew, P.; Franssila, S.; Ikkala, O.; Ras, R. H. A. Mechanically Durable Superhydrophobic Surfaces. *Adv. Mater.* **2011**, *23*, 673–678.
19. Deng, X.; Mammen, L.; Butt, H. J.; Vollmer, D. Candle Soot as a Template for a Transparent Robust Superamphiphobic Coating. *Science* **2012**, *335*, 67–70.
20. Mishchenko, L.; Hatton, B.; Bahadur, V.; Taylor, J. A.; Krupenkin, T.; Aizenberg, J. Design of Ice-Free Nanostructured Surfaces Based on Repulsion of Impacting Water Droplets. *ACS Nano* **2010**, *4*, 7699–7707.
21. Jung, Y. C.; Bhushan, B. Mechanically Durable Carbon Nanotube-Composite Hierarchical Structures with Superhydrophobicity, Self-Cleaning, and Low-Drag. *ACS Nano* **2009**, *3*, 4155–4163.
22. Spaeth, M.; Barthlott, W. Lotus-Effect (R): Biomimetic Super-hydrophobic Surfaces and Their Application. In *Smart Textiles*; Vincenzini, P., Paradiso, R., Eds.; Trans Tech Publications: Zurich, Switzerland, 2009; Vol. 60, pp 38−46.
23. Li, Y.; Li, L.; Sun, J. Bioinspired Self-Healing Superhydrophobic Coatings. *Angew. Chem., Int. Ed.* **2010**, *49*, 6129–6133.
24. Wang, H.; Xue, Y.; Ding, J.; Feng, L.; Wang, X.; Lin, T. Durable, Self-Healing Superhydrophobic and Superoleophobic Surfaces from Fluorinated-Decyl Polyhedral Oligomeric Silsesquioxane and Hydrolyzed Fluorinated Alkyl Silane. *Angew. Chem., Int. Ed.* **2011**, *50*, 11433–11436.
25. Wang, X. L.; Liu, X. J.; Zhou, F.; Liu, W. M. Self-Healing Superamphiphobicity. *Chem. Commun.* **2011**, *47*, 2324–2326.
26. Ionov, L.; Synytska, A. Self-Healing Superhydrophobic Materials. *Phys. Chem. Chem. Phys.* **2012**, *14*, 10497–10502.
27. Li, Y.; Chen, S.; Wu, M.; Sun, J. All Spraying Processes for the Fabrication of Robust, Self-Healing, Superhydrophobic Coatings. *Adv. Mater.* **2014**, *26*, 3344–3348.
28. Liu, Y.; Liu, Z.; Liu, Y.; Hu, H.; Li, Y.; Yan, P.; Yu, B.; Zhou, F. One-Step Modification of Fabrics with Bioinspired Polydopamine@Octadecylamine Nanocapsules for Robust and Healable Self-Cleaning Performance. *Small* **2015**, *11*, 426–431.
29. Zhou, H.; Wang, H.; Niu, H.; Gestos, A.; Lin, T. Robust, Self-Healing Superamphiphobic Fabrics Prepared by Two-Step Coating of Fluoro-Containing Polymer, Fluoroalkyl Silane, and Modified Silica Nanoparticles. *Adv. Funct. Mater.* **2013**, *23*, 1664–1670.
30. Wang, H. D.; Zhou, H.; Gestos, A.; Fang, J.; Lin, T. Robust, Superamphiphobic Fabric with Multiple Self-Healing Ability against Both Physical and Chemical Damages. *ACS Appl. Mater. Interfaces* **2013**, *5*, 10221–10226.
31. Hoyle, C. E.; Bowman, C. N. Thiol-Ene Click Chemistry. *Angew. Chem., Int. Ed.* **2010**, *49*, 1540–1573.