JOURNAL OF Applied Polymer SCIENCE

A Facile Dip-Coating Approach to Prepare SiO$_2$/Fluoropolymer Coating for Superhydrophobic and Superoleophobic Fabrics with Self-Cleaning Property

Jing Lin, Cheng Zheng, WenJin Ye, HuaQuan Wang, DanYan Feng, QiaoYi Li, BoWei Huan
School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou 510006, Guangdong, China
Correspondence to: J. Lin (E-mail: linjin00112043@126.com)

ABSTRACT: In this study, a facile, two-step dip-coating approach was reported for the fabrication of the superhydrophobic and super-oleophobic cotton fabrics. It was confirmed that the superhydrophobic and superoleophobic composite thin film containing modi-fied-SiO$_2$ nanoparticles and fluoropolymer had been successfully fabricated on the cotton fabrics surface, the results demonstrated that the treated cotton fabrics showed good performances, such as superhydrophobicity and superoleophobicity, low water and oil absorption ability, self-cleaning property and good laundering durability, so forth. The above approach can be applied to potentially advance superhydrophobic and superoleophobic fabrics materials for a variety of applications. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41458.

INTRODUCTION

Over the past few decades, superhydrophobic surfaces have attracted considerable interest in both academia and industry due to their various applications, such as self-cleaning, water proof, antifouling, antifogging, and anticorrosion.[1–5] It is well known that superhydrophobic/superoleophobic surfaces are usu-ally inspired by many biological materials in nature exhibiting an unusual superhydrophobicity/superoleophobicity and self-cleaning property, such as lotus leaves, rice leaves, red rose pet-als, butterfly wings, cicada wings, gecko feet, desert beetle, spi-der silks, and fish scales.[6,7] Based on the previous reported literatures, it has been found that the presence of special micro/nanostructures and low-surface-energy materials on these surfa-ces are critical for the formation of the superhydrophobicity/superoleophobicity.[8–10] To mimic the effect, enormous contribu-tions have been made to the design and fabrication of superhy-drophobic surfaces via two kinds of approaches: either creating rough structures on low-surface energy substrates or chemically modifying rough substrates with low-surface energy materials.[11]

To the best of our knowledge, many methods including dipping-drying-curing and chemical vapor deposition have been developed for the fabrication of the superhydrophobic/supero-leophobic surfaces on substrate.[12–14] For instance, Joshi et al.[15] reported a method to develop nanosilica and clay-based nano-composite coatings for superhydrophobic fabrics using dip-coating method and layer-by-layer self-assembly, nanosilica per-formed better in creating nanoroughness on cotton fabric, wherein the contact angle (CA) is >150°. Gao et al.[16] developed a cotton fabric with excellent water and oil repellency, which was coated by a series of polyhedral oligomeric silsesquioxane. Im et al.[17] created a robust superhydrophobic and superoleo-phobic surface with inverse trapezoidal microstructures on a large transparent flexible substrate, the surface also showed self-cleaning property. Motlagh et al.[18] studied durable, superhydro-phobic, superoleophobic, and corrosion resistant coating on the stainless steel surface using a scalable method, the coating was produced by introducing low-surface energy fluoropolymer/SiO$_2$ materials and fabrication of hierarchical structures. Ji et al.[19] developed a simple and low-cost fabrication method to make superhydrophobic and superoleophobic aluminum surfa-ces. Wu et al.[20] reported a facile fabrication of durable superhy-drophobic fabrics by dip coating in a nanocomposite solution of fluoro-free organosilanes. The results showed the kind of organosilane, molar ratio of organosilane in the precursor, and water concentration as well as the dip-coating parameters had great influences on the superhydrophobicity of the treated fab-rics. Zhang et al.[21] also presented a facile approach for the prep-aration of durable and robust superhydrophobic fabrics by simply dip-coating method in a nanocomposite solution com-posed of an oligomer of hexadecyltriethoxylsilane (HDTES) and HDTES-modified silica nanoparticles. Ma et al.[22] studied a
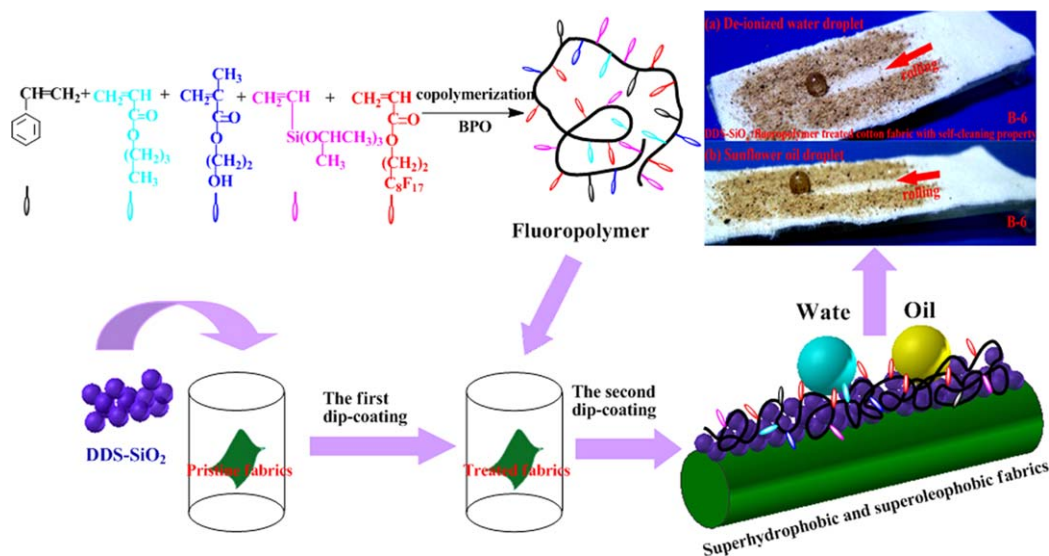
Scheme 1. The route for preparing durable superhydrophobic/superoleophobic cotton fabrics with self-cleaning property. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

versatile method to produce superhydrophobic fabrics with a CA of 175° by combining electrospinning and initiated chemical vapor deposition. All in all, superhydrophobic/superoleophobic surfaces have been obtained from single fiber, as well as woven or nonwoven fabrics, giving an extra degree of roughness to the fiber surface, along with various hydrophobic chemical coatings.[23] The main concern in superhydrophobic/superoleophobic fabrics is the retention of their properties with use. They are very weak to resist mechanical contact on their surfaces, which changes the inherent relatively large scale roughness of fabrics to lose their superhydrophobicity/superoleophobicity easily.[24,25] Therefore, more facile and effective approaches for the preparation of superhydrophobic fabrics need to be explored.

Herein, a facile, two-step dip-coating approach was adopted to prepare durable superhydrophobic/superoleophobic cotton fabrics with a dual-size hierarchical structure based on a complex modified SiO_2/fluoropolymer coating as shown in Scheme 1. First, fluoropolymer was synthesized by free radical solution polymerization. Single or multilayers of DDS-SiO_2 particles were then fabricated on the pristine cotton fabrics by the first dip-coating approach to build surface roughness with micro/nanostructures. To obtain the durable superhydrophobicity/superoleophobicity and good laundering durability, the fabricated fabrics were further coated with as-prepared fluoropolymer by the second dip-coating approach. Chemical structures of DDS-SiO_2 and fluoropolymer were characterized by Fourier transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC). Surface morphology and chemical composition of the treated fabrics were also characterized by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). Superhydrophobicity and superoleophobicity of the treated fabrics were investigated by surface CA analysis of deionized water and sunflower oil. The water or oil absorption capacity (AC) of the pristine and treated cotton samples was compared. Self-cleaning property and laundering durability were also evaluated for practical application.

EXPERIMENTAL

Materials

DDS-SiO_2 (commercial hydrophobic fumed silica after treated with dimethyldichlorosilane, Degussa AEROSIL® R 974, having a nominal particle size of 16 nm) was supplied from Guangzhou Heqian trade. Vinyltriisopropoxysilane (VTPS) was purchased from Ark Chemicals Industry. Perfluoroalkyl ethyl acrylate (PFEA, TEAc-8) was purchased from Top Fluorochem. Styrene (ST), butyl acrylate (BA), 2-Hydroxyethyl methacrylate (HEMA), Benzoyl peroxide (BPO) as initiator, N,N-Dimethylmethanamide (DMF), and dimethylbenzene were purchased by Aladdin Reagents. The pristine cotton fabrics were supplied by Guangzhou Liby. Sunflower oil was obtained from Long-range Share Food, China.

Preparation of Fluoropolymer

Fluoropolymer was synthesized by solution copolymerization technique using free radical initiator. In a typical synthesis, for the synthesis of poly(ST/BA/HEMA/VTPS/PFEA), 8.00 g of ST, 3.00 g of BA, 1.00 g of HEMA, 1.00 g of VTPS, 8.00 g of PFEA, 0.42 g of BPO, and 38.58 g of dimethylbenzene were mixed uniformly and added into a three-necked flake equipped with reflux condenser, mechanical stirrer, and dropping funnels, and the above mixture were added dropwise for 3 h into the flask. The polymerization was carried out at 120°C for 6 h.

DDS-SiO_2 Treated Cotton Fabrics

First, the pristine cotton fabrics (30 × 30 mm) were cleaned by ultrasonic washing in ethanol and water, respectively, followed by drying at 120°C in a vacuum oven for 1 h. The pristine cotton fabric was named as A-0. Then, a different amount of DDS-SiO_2 particles were ultrasonically dispersed in DMF for 10 min (containing 0.05, 0.1, 0.2, 0.5, 1, and 2 wt % DDS-SiO_2, respectively). Finally, the cotton fabrics were immersed in the above DDS-SiO_2 dispersions for 5 min, DDS-SiO_2 treated cotton fabrics were obtained by above dip-coating approach after being dried at 160°C in an oven for 5 min to remove the
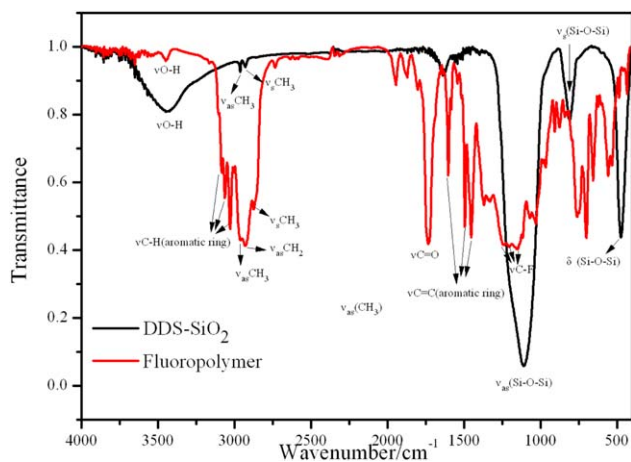
Figure 1. FTIR spectra of DDS-SiO$_2$ and fluoropolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

Figure 2. FTIR ATR spectra of pretreated cotton fabric (a) and post-treated cotton fabric (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solvent. Correspondingly, DDS-SiO$_2$ treated cotton fabrics were named as A-1, A-2, A-3, A-4, A-5, and A-6.

DDS-SiO$_2$/Fluoropolymer Treated Cotton Fabrics

The dip-coating solution containing 10 wt % fluoropolymer was prepared by adding 3.50 g of as-prepared fluoropolymer and 25.00 g of DMF. Then, DDS-SiO$_2$ treated cotton fabrics were immersed in the above solution for 5 min. Finally, the treated samples were dried at 160°C in an oven for 5 min to remove the solvent. SiO$_2$-/fluoropolymer treated cotton fabrics were named as B-1, B-2, B-3, B-4, B-5, and B-6.

Characterization

Structures of the DDS-SiO$_2$ and fluoropolymer were characterized by FTIR, recorded in KBr discs on a Bruker Vector 33 FTIR spectrometer (Bruker Instruments, Germany) over the range 4000–400 cm^{-1}. The cotton fabrics with pretreatment and post-treatment (A-0 and B-6, respectively) were further investigated by FTIR attenuated total reflectance (ATR) spectroscopy (FTIR ATR, Nicolet 6700) over the range 4000–700 cm^{-1}. Molecular weight distributions of samples were measured by GPC (PL-GPC 50, Polymer Laboratories Varian). Tetrahydrofuran was used as the eluent at a flow rate of 1 mL/min. The calibration curve was obtained with polystyrene standards. The surface morphologies and elements of pristine and treated cotton fabrics were observed by SEM/EDX (SEM, LEO 1530 VP, Oberkochem, Germany; EDX, Oxford INCA 350, UK). CA analysis of water (surface tension: 72.0 mNm^{-1}) and oil on cotton fabrics were performed with an optical CA meter (OCA40 Micro, Dataphysics, Germany). A daily-used liquid, sunflower oil (surface tension: 28.5 mNm^{-1}) served as an indicator to examine the oil-repellency stability. The CA was determined by averaging measurements taken from at least five different positions on each cotton fabric sample. The water and oil AC of the pristine and treated cotton samples were measured with a sheet of 30 × 30 mm. Each fabric sample was dipped into deionized water and sunflower oil, and kept in it for 1 h to allow water and oil absorption. Then, the fabrics were taken out of it. The excess water or oil on the surfaces of wet samples was
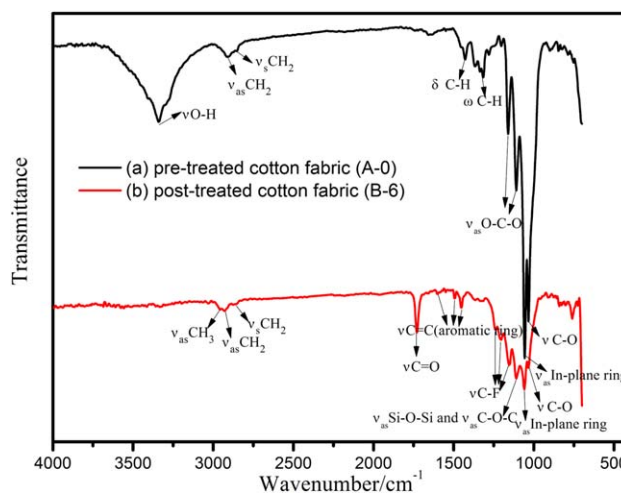
wiped out with filter paper and the samples were weighed. AC was calculated as: AC $= (W_s - W_d)/W_d \times 100\%$, where W_s is the swelled weight and W_d is the vacuum dried weight. The self-cleaning property of the treated cotton fabric was investigated by choosing daily sand soil as contaminants. Superhydrophobic and superoleophobic durability was evaluated by a accelerated laundering tests according to AATCC test method 61-1996. One 45 min standard wash using rotate wash fastness tester SLH-FZ001A is equivalent to five typical hand or home laundering. The regression of a water droplet CA on fabrics was measured after 5, 10, 15, 20, 25, and 30 repeated wash cycles.

RESULTS AND DISCUSSION

Chemical Structure Characterization

The molecular structures of DDS-SiO$_2$ and fluoropolymer were characterized by FTIR as shown in Figure 1. As for DDS-SiO$_2$, the broad band at around 3443 cm^{-1} was attributed to v O—H,[26,27] which could be coming from residual hydroxyl groups on the surface of silica. The bands at around 2962 and
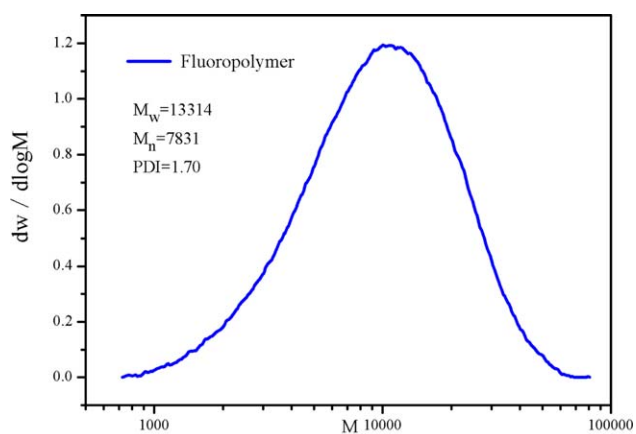

Figure 3. GPC curves of fluoropolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
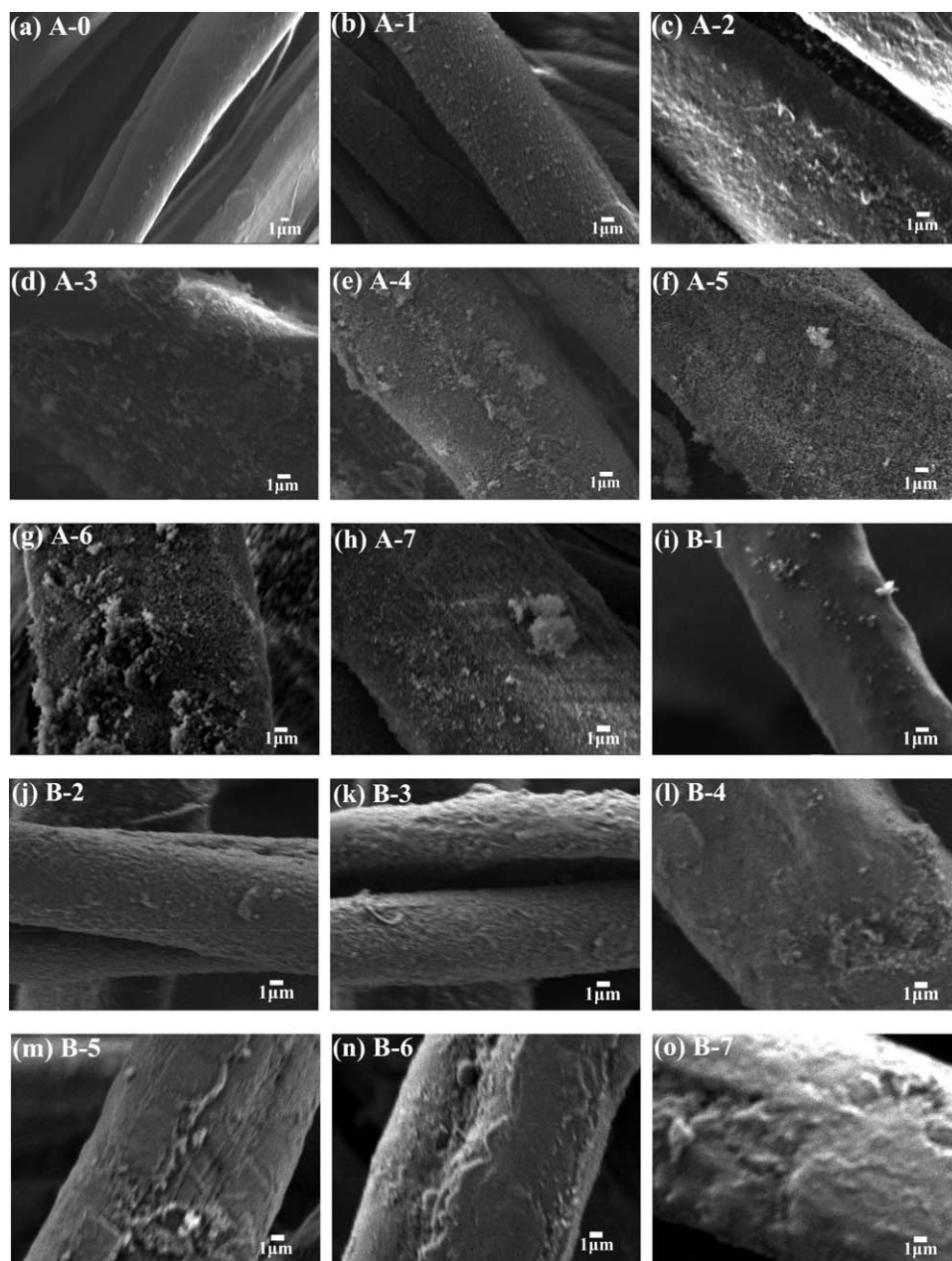
Figure 4. SEM images of pristine cotton fabric (A-0) (a); DDS-SiO$_2$ treated cotton fabrics (A-1, A-2, A-3, A-4, A-5, A-6, A-7) (b–h); The corresponding DDS-SiO$_2$ /fluoropolymer (10 wt %) treated cotton fabrics (B-1, B-2, B-3, B-4, B-5, B-6, B-7) (i–o).

2872 cm^{-1} were ascribed to v_{as} CH$_3$ and v_s CH$_3$, respectively,[28,29] which was coming from the introduced dimethyldichlorosilane for modifying silica. The bands around at 1107, 806, and 474 cm^{-1} were assigned to v_{as} Si—O—Si, v_s Si—O—Si, and δ Si—O—Si, respectively.[30–32] As for fluoropolymer, the broad band at around 3443 cm^{-1} was attributed to v O—H coming from the hydroxyl groups of HEMA monomers. The band at around 3083, 3062, and 3028 cm^{-1} were related to v C—H of aromatic ring.[33] Peaks at around 2962, 2927, and 2873 cm^{-1} were assigned to v_{as} CH$_3$, v_{as} CH$_2$, and v_s CH$_3$, respectively. Bands at around 1734 cm^{-1} was associated with v C=O.[34,35] Bands at around 1602, 1495, and 1454 cm^{-1} were

attributed to typical benzene ring skeletal vibrations. The bands around 1240, 1204, and 1150 cm^{-1} were assigned to v C—F.[36] In addition, the cotton fabrics with pretreatment and posttreatment were further charactered by FTIR ATR spectra as shown in Figure 2. The spectra of the pretreated cotton fabric sample (A-0) were mainly characterized by bands at 3340 cm^{-1} (O—H stretching), 2918 cm^{-1} (asymmetric —CH$_2$ stretching), 2852 cm^{-1} (symmetric —CH$_2$ stretching), 1428 cm^{-1} [C—H wagging (in-plane bending)], 1316 cm^{-1} (C—H wagging), 1160 and 1109 cm^{-1} (asymmetric C—O—C stretching), 1057 cm^{-1} (asymmetric in-plane ring stretching), and 1032 cm^{-1} (C—O stretching). These are characteristics bands of cellulose.[37] After
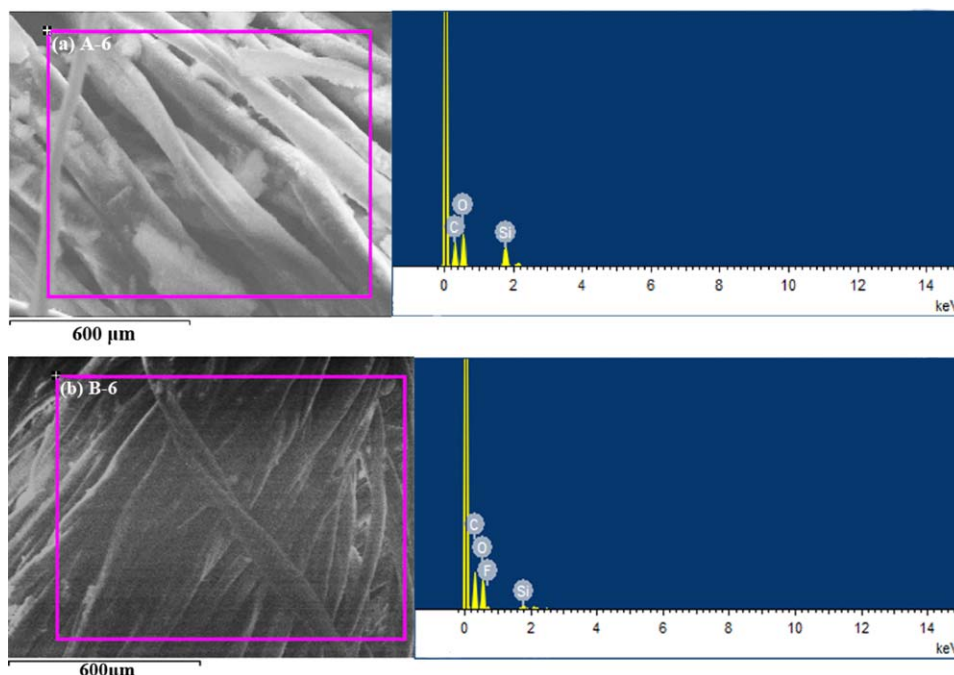
Figure 5. EDX spectra of A-6 (a) and B-6 (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

treated by DDS-SiO$_2$/fluoropolymer, some new bands appeared due to the post-treated cotton fabric (B-6) coated DDS-SiO$_2$/fluoropolymer. Peak at 2962 cm^{-1} was assigned to v_{as} CH$_3$ from DDS-SiO$_2$ and fluoropolymer. Band at 1730 cm^{-1} was characteristic of v C=O coming from fluoropolymer. Bands at 1602, 1495, and 1454 cm^{-1} were attributed to typical benzene ring skeletal vibrations from fluoropolymer. Bands at 1240, 1204, and 1150 cm^{-1} were assigned to v C—F from fluoropolymer. Band at 1110 cm^{-1} was attributed to v_{as} Si—O—Si from DDS-SiO$_2$ and v_{as} C—O—C from cotton cellulose. Band at 1057 cm^{-1} was assigned to asymmetric in-plane ring stretching from cotton cellulose. Band at 1032 cm^{-1} was associated with C—O stretching.

GPC has been established as a powerful technique to determine the relative molecular weight of polymer samples as well as the distribution of molecular weights. The synthesis of fluoropolymer was also confirmed by GPC analysis as shown in Figure 3. Average molecular weight (Mw), number-average molecular weight (Mn), and polydispersity index were 13,314, 7831, and 1.700, respectively.

Table I. Chemical Composition of the Treated Cotton Surface by EDX Analysis

Elements	C	O	Si	F
A-6				
wt %	25.53	71.45	3.02	0
at %	31.73	66.67	1.61	0
B-6				
wt %	25.53	68.34	0.28	5.85

Surface Morphology and Chemical Composition of the Treated Fabrics

Surface morphology of the DDS-SiO$_2$ and DDS-SiO$_2$/fluoropolymer treated cotton fabrics were investigated by SEM (Figure 4). For pristine cotton fabrics [Figure 4(a)], a smooth surface of cotton fibers with the diameter of about 10–20 μm was clearly observed. For a comparison, after treated by DDS-SiO$_2$ or DDS-SiO$_2$/fluoropolymer, comparative rough surfaces of cotton fibers were observed from Figure 4(b) to Figure 4(o). For DDS-SiO$_2$ treated cotton fabric, it was found that, with increasing of DDS-SiO$_2$ content in the dispersions which the cotton fabrics were immersed in, more DDS-SiO$_2$ nanoparticles were assembled to form single or multilayers and densely deposited on the surface of the fabrics, which significantly roughened the surface of the fabrics. Combination of nanoroughness of DDS-SiO$_2$ and the inherent microroughness of fabrics created a micro/nanobinary surface roughness on the cotton fabrics surface, which would greatly change the hydrophobicity/oleophobicity of the surface of the fabrics. To avoid DDS-SiO$_2$ being exfoliated from the surface of the fabrics, the as-prepared DDS-SiO$_2$ treated cotton fabrics were further treated by fluoropolymer solution, it was observed that the DDS-SiO$_2$/fluoropolymer treated cotton fabrics were coated with a fluoropolymer layer. Obviously, the deposition of the polymer layer was favorable to promote the adhesion permanent of DDS-SiO$_2$ nanoparticles on the fibers surface to prevent it from falling off. In addition, after carrying out the accelerated laundering tests for 30 repeated wash cycles, A-7 and B-7 correspond to A-6 and B-6 after laundering tests, it was apparent that DDS-SiO$_2$ particles on the A-7 noticeably decreased, for a comparison, the decrease of DDS-SiO$_2$ particles on the B-7 was in-remarkable, indicated that fluoropolymer covered on the DDS-SiO$_2$ particles could prevent it being exfoliated from the surface of the fabrics. EDX
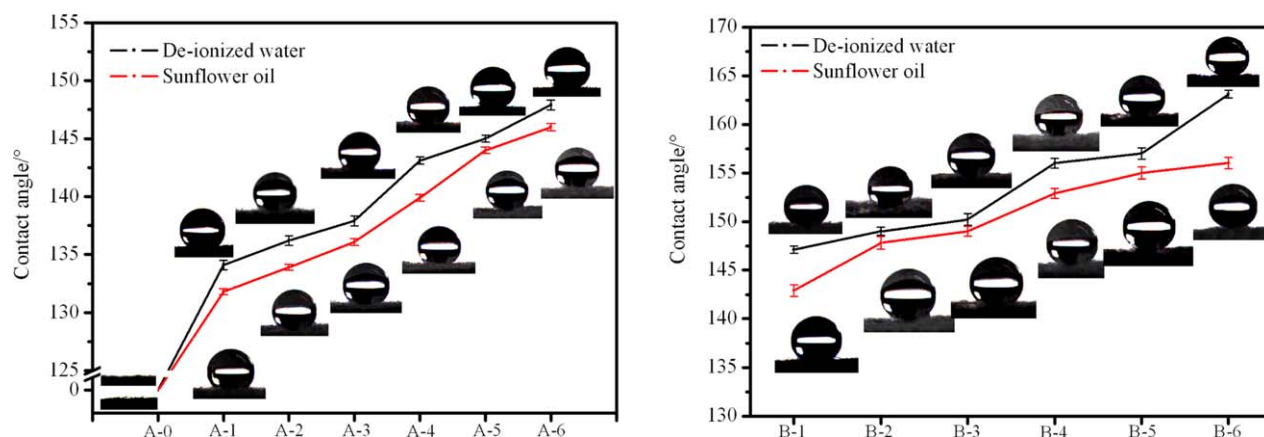
Figure 6. CA of DDS-SiO$_2$ treated cotton fabrics (a) and DDS-SiO$_2$/fluoropolymer treated cotton fabrics (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

analysis of the large area on the DDS-SiO$_2$ treated fabric (A-6) and DDS-SiO$_2$/fluoropolymer treated cotton fabrics (B-6) was carried out to determine the elements content on the surface of the cotton fabrics. The results are shown in Figure 5 and Table I. It was found that C, O, and Si were present in A-6 indicating the presence of DDS-SiO$_2$, C, O, Si, and F were present in B-6 indicating the presence of DDS-SiO$_2$/fluoropolymer. C and O came from DDS-SiO$_2$ and cellulose of the cotton fabric. For A-6, the atomic ratio of C : O : Si was 31.73 : 66.67 : 1.61. For B-6, the atomic ratio of C : O : Si : F was 31.65 : 63.61 : 0.15 : 4.59, it was indicated the introduction of fluoropolymer make the surface with rich in fluorine elements which could lower the surface free energy of cotton fabrics, which was consistent with the literature reported by Hare that the surface-free energy decreased in the order —CH$_2$>—CH$_3$>—Si—O>—CF$_2$>—CF$_2$H>—CF$_3$.[38] All in all, a dual-size hierarchical structure and low-surface-energy elements such as silicon and fluorine existed on the treated cotton fabrics surface.

Superhydrophobicity and Superoleophobicity of the Treated Fabrics

As already mentioned, with increasing of DDS-SiO$_2$ content in the dispersions which the cotton fabrics were immersed in, from A-1 to A-6, surfaces of DDS-SiO$_2$ treated fabrics became
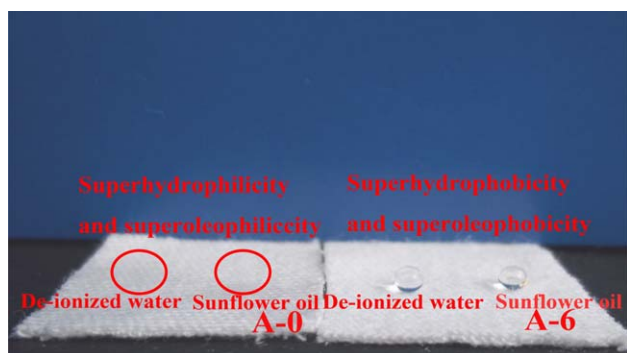

Figure 7. Photograph of A-0 with superhydrophilic and superhydrophobic property and A-6 with superhydrophobicity and superoleophobicity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

rougher, hydrophobicity, and oleophobicity of the treated cotton fabrics were assessed by CA measurements of deionized water and sunflower oil. Figure 6 showed the CA images of cotton fabrics before and after treatment. It was observed that, when the droplets were put onto the surface of pristine cotton fabrics, the deionized water/oil droplets immediately wetted and fully absorbed by pristine cotton fabrics (CA of both deionized water and oil: 0°), the outstanding hydrophilicity and oleophilicity were attributed to the existing the numerous holes in its woven structure, so that the liquid droplets were easy to enter into the larger scale holes. However, after treatment of the cotton fabrics by DDS-SiO$_2$ or DDS-SiO$_2$/fluoropolymer, CA of both water and oil greatly increased, indicating that both water and oil repellency of the treated cotton fabrics were significantly improved. As observed in Figure 6(a), CA of water and oil on DDS-SiO$_2$ treated cotton fabrics increased from 0° (A-0) to 147.9° (A-6) and from 0° (A-0) to 146.0° (A-6), respectively, which attributes to (1) double-scale roughness created by modified SiO$_2$ nanoparticles and the macroscopic weave structure of textile fabrics, and (2) low-surface free energy originated from DDS-SiO$_2$. Furthermore, CA of water and oil on DDS-SiO$_2$/fluoropolymer treated cotton fabric increased from 147.1° (B-1) to 163.1° (B-6) and from 142.9° (B-1) to 156.0° (B-6), respectively, indicating that the fabricated surface (B-6) exhibited both superhydrophobicity and superoleophobicity, which originated from low-surface energy fluorine-containing materials and surface roughness. Figure 7 showed photograph of water and oil droplets on pristine cotton surface (A-0) and DDS-SiO$_2$/fluoropolymer treated fabrics (B-6). It was found that the pristine cotton fabric could be immediately wetted by the water and oil droplets, CA of them is 0°, indicating that the pristine cotton fabric has a good hydrophilicity and oleophilicity. For a comparison, both water and oil droplets on the B-6 maintained a nearly circular shape with a CA >150° because of its outstanding superhydrophobicity and superoleophobicity.

Water/Oil Repellence, Absorption Capability, and Self-Cleaning Property

To assess the water-repellence of the treated fabrics, AC of treated cotton fabrics were measured after undergoing the immersion for 1 h in water and sunflower oil, interestingly, as
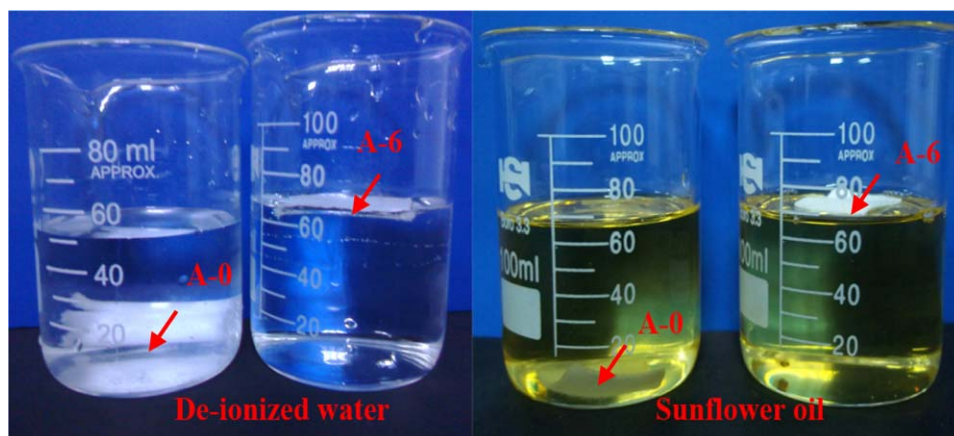
Figure 8. Photographs of A-0 and A-6 immersed in deionized water and sunflower oil. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

shown in Figure 8, the pristine cotton (A-0) was immediately drenched and sunk to the bottom of beaker when it was placed in water and oil. However, the superhydrophobic and superoleophobic cotton fabrics could hardly immerse into them and always floated on them. Figure 9 showed water/oil absorption ability of the pristine and treated cotton fabrics. It is well known that cotton is a porous material with good absorption abilities. Water and oil absorption ability of the pristine cotton fabrics were 192 and 196 wt %, respectively. In comparison, the treated cotton fabrics showed a significantly lower absorption capability for water and oil. From A-1 to A-6 or from B-1 to B-6, both water and oil absorption capability presented a declining trend. The results were consistent with the previous CA. The larger the CA, the smaller water and oil absorption capability. B-6 had a lowest water and oil absorption capability with 0.8 and 2.3 wt %, respectively, indicated that B-6 had a good water/oil repellence. In addition, the self-cleaning property of the treated cotton fabric covered a large amount of sand soil was investigated as shown in Figure 10. It could be seen that a water

or oil droplet was rolling over the treated cotton fabric (B-6), partial sand soil was removed along the path of the rolled droplet, indicating that DDS-SiO$_2$/fluoropolymer treated cotton fabric (B-6) had self-cleaning property just like the lotus leaf.

Laundering Durability

For practical applications, the durability of the treated cotton fabric needs to be investigated. The accelerated laundering tests were to evaluate the washing fastness to laundering of DDS-SiO$_2$ and DDS-SiO$_2$/fluoropolymer coated cotton fabrics by measuring the regression of a water droplet CA after 5, 10, 15, 20, 25, and 30 repeated wash cycles. From Figure 11, the results showed that the CA of water and oil on DDS-SiO$_2$ treated cotton fabrics decreased greatly from 124 to 69° and from 122 to 65°, respectively, indicated that deposited DDS-SiO$_2$ was easy to detach from the cotton fabrics surface. For a comparison, the CA of water and oil on DDS-SiO$_2$/fluoropolymer treated cotton fabrics did not change much with an increasing number of laundering cycles from 162 to 153° and from 154 to 150°, respectively. B-6 still kept good superhydrophobicity and superoleophobicity with a CA >150°, which may be due to fluoropolymer film covering the DDS-SiO$_2$ and the Si—O—C bond formed between fluoropolymer film and the fabric.
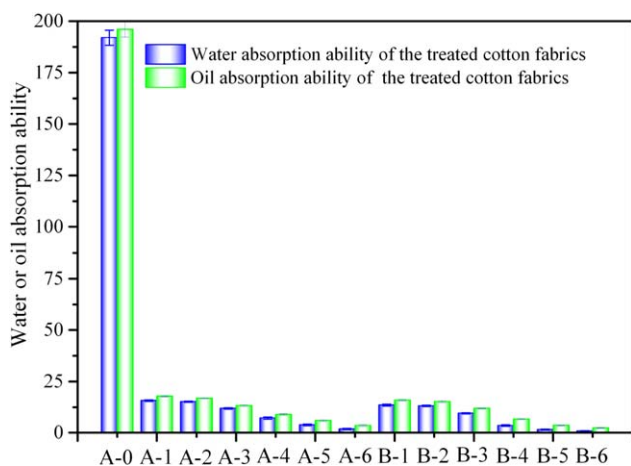

Figure 9. Water/oil absorption ability of DDS-SiO$_2$ and DDS-SiO$_2$/fluoropolymer treated cotton fabrics after undergoing the immersion in water and sunflower oil. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 10. Image showing self-cleaning property of DDS-SiO$_2$/fluoropolymer treated cotton fabric. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
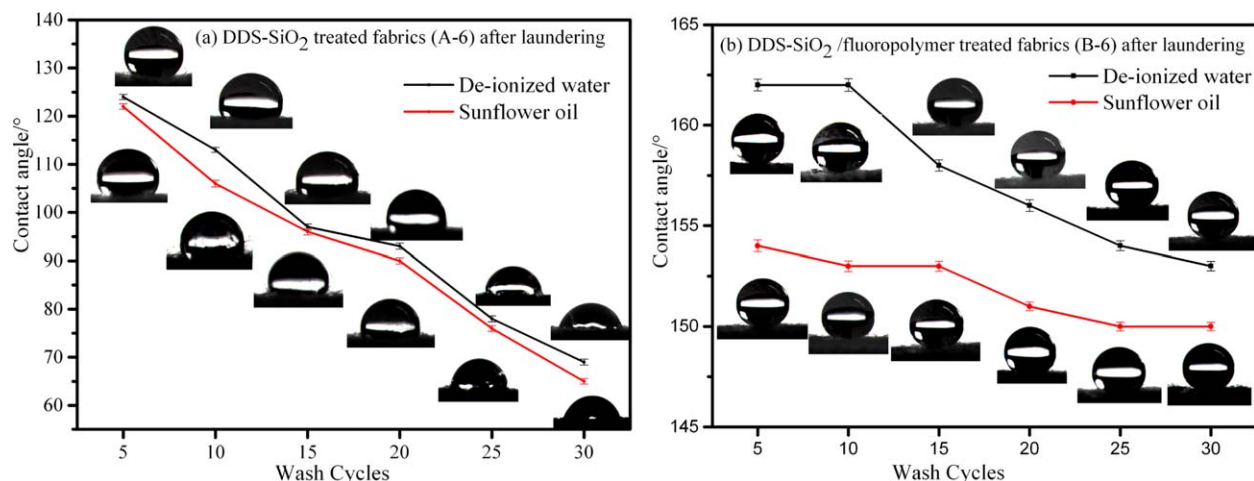
Figure 11. CA of DDS-SiO$_2$ treated cotton fabrics (a) and DDS-SiO$_2$/fluoropolymer treated cotton fabrics (b) after laundering. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

CONCLUSIONS

In this study, a facile, two-step dip-coating approach was developed for the fabrication of the superhydrophobic/superoleophobic cotton fabrics with the important functions of the superhydrophobicity, superoleophobicity, low water/oil absorption ability, and self-cleaning property and good laundering durability, which offers an opportunity to accelerate the large-scale production of superhydrophobic/superoleophobic fabrics for new industrial applications. As compared with pristine cotton fabric (A-0), the treated cotton fabrics showed good superhydrophobicity and superoleophobicity, and the superhydrophobic and superoleophobic degree were dependent on the contents of DDS-SiO$_2$ particles and fluoropolymer, which attributes to (1) double-scale roughness created by modified SiO$_2$ nanoparticles and the macroscopic weave structure of fabrics, and (2) low-surface free energy originated from DDS-SiO$_2$ and fluoropolymer. CA of deionized water and sunflower oil on B-6 reached 162° and 154°, respectively. B-6 had a lowest water and oil absorption capability with 0.8 and 2.3 wt %, respectively, B-6 also exhibited good self-cleaning property and still kept good superhydrophobicity and superoleophobicity with a CA >150° after laundering durability testing.

REFERENCES

1. Wang, B.; Zhang, Y. B.; Shi, L.; Li, J.; Guo, Z. G. *J. Mater. Chem.* **2012**, *22*, 20112.

2. Lee, J. S.; Ryu, J. K.; Park, C. B. *Soft Matter.* **2009**, *5*, 2717.

3. Liu, K.; Yao, X.; Jiang, L. *Chem. Soc. Rev.* **2010**, *39*, 3240.

4. Ahmad, A. L.; Mohammed, H. N.; Ooi, B. S.; Leo, C. P. *J. Polym. Res.* **2013**, *20*, 289.

5. Luo, Z. Z.; Wang, Y. J.; Yang, Q.; Luo, Y. M.; Tan, S. *J. Polym. Res.* **2014**, *21*, 447.

6. Sun, M. X.; Watson, G. S.; Zheng, Y. M.; Watson, J. A.; Liang, A. P. *J. Exp. Biol.* **2009**, *212*, 3148.

7. Liu, K.; Du, J.; Wu, J.; Jiang, L. *Nanoscale* **2012**, *4*, 768.

8. Zhang, Y. L.; Xia, H.; Kim, E. K.; Sun, H. B. *Soft Matter* **2012**, *8*, 11217.

9. An, Q. F.; Xu, W.; Hao, L. F.; Fu, Y. S.; Huang, L. X. *J. Appl. Polym. Sci.* **2013**, *128*, 3050.

10. Jiang, C.; Zhang, Y. M.; Wang, Q. H.; Wang, T. M. *J. Appl. Polym. Sci.* **2013**, *129*, 2959.

11. Seyedmehdi, S. A.; Zhang, H.; Zhu, J. *J. Appl. Polym. Sci.* **2013**, *128*, 4136.

12. Li, G.; Zheng, H. T.; Wang, Y. X.; Wang, H.; Dong, Q. B.; Bai, R. K. *Polymer* **2010**, *51*, 1940.

13. Li, S. H.; Zhang, S. B.; Wang, X. H. *Langmuir* **2008**, *24*, 5585.

14. Zimmermann, J.; Reifler, F. A.; Fortunato, G.; Gerhardt, L. C.; Seeger, S. *Adv. Funct. Mater.* **2008**, *18*, 3662.

15. Joshi, M.; Bhattacharyya, A.; Agarwal, N.; Parmar, S. *Bull. Mater. Sci.* **2012**, *35*, 933.

16. Gao, Y.; He, C. L.; Qing, F. L. *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 5152.

17. Im, M.; Im, H.; Lee, J. H.; Yoon, J. B.; Choi, Y. K. *Soft Matter* **2010**, *6*, 1401.

18. Motlagh, V. N.; Birjandi, F. C.; Sargolzaei, J.; Shahtahmassebi, N. *Appl. Surf. Sci.* **2013**, *283*, 636.

19. Ji, S.; Ramadhianti, P. A.; Nguyen, T. B.; Kim, W. D.; Lim, H. *Microelectron. Eng.* **2013**, *111*, 404.

20. Wu, L.; Zhang, J. P.; Li, B. C.; Wang, A. Q. *J. Mater. Chem. B* **2013**, *1*, 4756.

21. Zhang, J. P.; Li, B. C.; Wu, L.; Wang, A. Q. *Chem. Commun.* **2013**, *49*, 11509.

22. Ma, M. L.; Mao, Y.; Gupta, M.; Gleason, K. K.; Rutledge, G. C. *Macromolecules* **2005**, *38*, 9742.

23. Roach, P.; Shirtcliffe, N. J.; Newton, M. I. *Soft Matter* **2008**, *4*, 224.

24. Li, G.; Zheng, H. T.; Wang, Y. X.; Wang, H.; Dong, Q. B.; Bai, R. *Polymer* **2010**, *51*, 1940.

25. Roach, P.; Shirtcliffe, N. J.; Newton, M. I.; Roach, P.; Shirtcliffe, N. J.; Newton, M. I. *Soft Matter* **2008**, *4*, 224.

26. Pan, G. Y.; Du, Z. J.; Zhang, C.; Li, C. J.; Yang, X. P.; Li, H. Q. *Polymer* **2007**, *48*, 3686.

27. Pham, M. C.; Piro, B.; Tran, L. D.; Ledoan, T.; Dao, L. H. *Anal. Chem.* **2003**, *75*, 6748.

28. Abdolmaleki, A.; Mallakpour, S.; Borandeh, S. *Appl. Surf. Sci.* **2011**, *257*, 6725.

29. Lin, J.; Wu, X.; Zheng, C.; Zhang, P. P.; Li, Q. Y.; Wang, W.; Yang, Z. R. *J. Polym. Res.* **2014**, *21*, 435.

30. Anastasescu, C.; Anastasescu, M.; Teodorescu, V. S.; Gartnera, M.; Zaharescu, M. *J. Non Cryst. Solids* **2010**, *356*, 2634.

31. Jung, K. Y.; Park, S. B. *Appl. Catal. B* **2000**, *25*, 249.

32. Lin, J.; Wu, X.; Zheng, C.; Zhang, P. P.; Huang, B. W.; Guo, N. H.; Jin, L. Y. Z. *Appl. Surf. Sci.* **2014**, *303*, 67.

33. Mikhaylova, Y.; Adam, G.; Häussler, L.; Eichhorn, K. J.; Voit, B. *J. Mol. Struct.* **2006**, *788*, 80.

34. Chua, L. L.; Zaumseil, J.; Chang, J. F.; Ou, E. C. W.; Ho, P. K. H.; Sirringhaus, H.; Friend, R. H. *Nature* **2005**, *434*, 194.

35. Innocenzi, P. *Chem. Mater.* **2003**, *15*, 4790.

36. Gao, J. Z.; Wang, X. M.; Wei, Y. X.; Yang, W. *J. Fluor. Chem.* **2006**, *127*, 282.

37. Chung, C.; Lee, M.; Choe, E. K. *Carbohydr. Polym.* **2004**, *58*, 417.

38. Hare, E. F.; Shafrin, E. G.; Zisman, W. A. *J. Phys. Chem.* **1954**, *58*, 236.