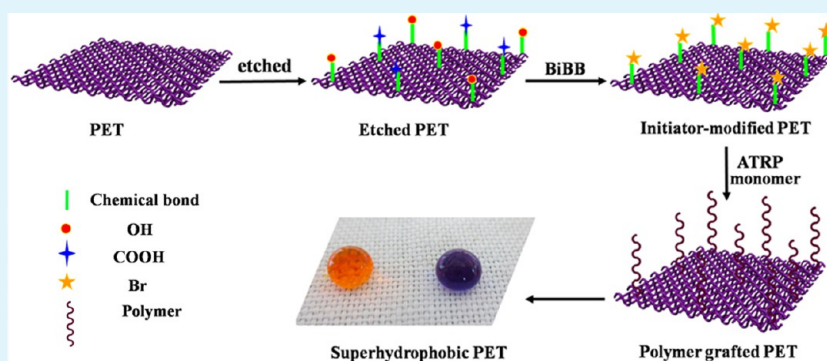


Fabrication of Robust and Antifouling Superhydrophobic Surfaces via Surface-Initiated Atom Transfer Radical Polymerization

Chao-Hua Xue,^{*,†,‡} Xiao-Jing Guo,[†] Jian-Zhong Ma,^{†,‡} and Shun-Tian Jia[†]

[†]College of Resource and Environment, Shaanxi University of Science and Technology, Xi'an 710021, China

[‡]Shaanxi Research Institute of Agricultural Products Processing Technology, Shaanxi University of Science and Technology, Xi'an 710021, China



ABSTRACT: Superhydrophobic surfaces were fabricated via surface-initiated atom transfer radical polymerization of fluorinated methacrylates on poly(ethylene terephthalate) (PET) fabrics. The hydrophobicity of the PET fabric was systematically tunable by controlling the polymerization time. The obtained superhydrophobic fabrics showed excellent chemical robustness even after exposure to different chemicals, such as acid, base, salt, acetone, and toluene. Importantly, the fabrics maintained superhydrophobicity after 2500 abrasion cycles, 100 laundering cycles, and long time exposure to UV irradiation. Also, the surface of the superhydrophobic fabrics showed excellent antifouling properties.

KEYWORDS: superhydrophobic, antifouling property, alkali treatment, SI-ATRP

1. INTRODUCTION

Nature-inspired superhydrophobic surfaces, showing a water contact angle (CA) higher than 150° and a sliding angle (SA) lower than 10° , have attracted tremendous attention over the past decade in both academic and industrial areas.^{1–13} Their emerging applications include antireflective glass,¹⁴ oil–water separation,^{15,16} protection of electronic devices,¹⁷ anti-icing,¹⁸ and avoiding fluid drag in microfluidic devices.¹⁹ Compared with other artificial superhydrophobic surfaces, water repellent fabric is considered to be among the most promising ones. However, many superhydrophobic surfaces lose easily their superhydrophobicity due to suffering from special chemical environments, strong light, or physical rubbing.^{20,21} Therefore, fabrication of durable, robust superhydrophobic fabrics becomes one of the hotspots of academic research.^{6,22}

Up to date, several methods have been proposed to fabricate mechanically robust and laundering-durable superhydrophobic fabrics. One approach involves simple coating of low-surface-energy materials on the roughening fibrous substrates.^{23–25} The other strategy is to bond hydrophobic compounds covalently into/onto the fibers.^{26–29} Forming covalent bonds between fibers and low-surface-energy compounds is considered to be an effective way to enhance the abrasion and laundering

durability of the superhydrophobicity and, as a consequence, to prolong the lifespan of the superhydrophobic fabrics.

The “grafting from” technique is an important method to bonding polymers covalently onto substrates, in which polymer chains grow from initiating sites or immobilized initiators on the surfaces. This is, in most cases, called surface-initiated polymerization, which can be conducted by atom transfer radical polymerization (ATRP). As one of the most widely used controlled/living radical polymerizations, ATRP is a versatile and compatible method for a wide range of vinyl monomers and solvents, providing polymers with controlled molecular weights and low polydispersities.^{30–33} Surface-initiated ATRP (SI-ATRP), as a kind of surface modification method, has also been used for the modification of a variety of other substrates,^{13,34–40} thus it should be suitable for adjusting the hydrophobicity of fabrics by controlling the polymerization.

In this work, we report the modification of poly(ethylene terephthalate) (PET) fabrics by chemical etching of the fiber surfaces and grafting of fluorinated methacrylate polymers via SI-ATRP, as shown in Figure 1. The hydrophobicity of the PET

Received: February 13, 2015

Accepted: April 2, 2015

Published: April 2, 2015

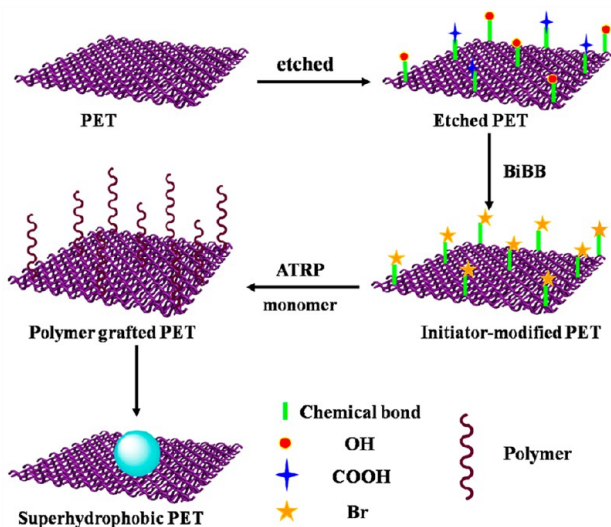


Figure 1. Schematic illustration of the fabrication of superhydrophobic fabrics.

fibers was tuned by controlling the polymerization to obtain superhydrophobic fabrics. Wettability tests showed that the superhydrophobic fabrics were robust to different chemicals and maintained superhydrophobicity after severe abrasion, laundering, and long time exposure to UV irradiation. And the

surface of the superhydrophobic fabrics showed excellent antifouling properties.

2. EXPERIMENTAL SECTION

2.1. Materials. PET fabric was purchased from a local factory. α -Bromoisobutyryl bromide (BiBB, 98%), ethyl 2-bromoisobutyrate (EBiB, 98%), copper(I) bromide (Cu(I)Br, 99%), and bipyridine (bpy) were purchased from Aladdin. 2,2,2-Trifluoroethyl methacrylate (TFEMA) was purchased from Harbin Xeogia Fluorine–Silicon Material Co., Ltd. (China). Glucose and sodium hydroxide were purchased from Tianjin Hengxing Chemical Reagent Co., Ltd.

2.2. Chemical Etching of PET Fabrics. First, the PET fabrics (7.5 g, 15 cm \times 25 cm) were washed with deionized water to remove the impurities and immersed in 25 g/L sodium hydroxide solution with a liquor-to-fabric ratio of about 35:1. Then the solution was heated at 120 $^{\circ}$ C for 60 min. At last, the fabrics were washed with an abundant amount of water until the pH of the fabric surfaces reached 7 and dried at 80 $^{\circ}$ C without any tension. The chemically etched sample was denoted as E-PET.

2.3. Immobilization of ATRP Initiators on the Etched PET Fabrics. A solvent-free condition was used to immobilize ATRP initiators on the E-PET fabrics. First, E-PET fabrics were placed into a container with only 0.02 mL of BiBB added. The container was sealed and mounted in an infrared-ray heating machine which is commonly used to dye fabrics in our lab as well as in a fabric dyeing manufactory for sampling before large-scale production. Then, the reaction temperature was programmed for heating to 90 $^{\circ}$ C and held for 1.5 h, according to the reported procedure.³⁶ Finally, the samples were taken out, washed successively with anhydrous ethanol and deionized

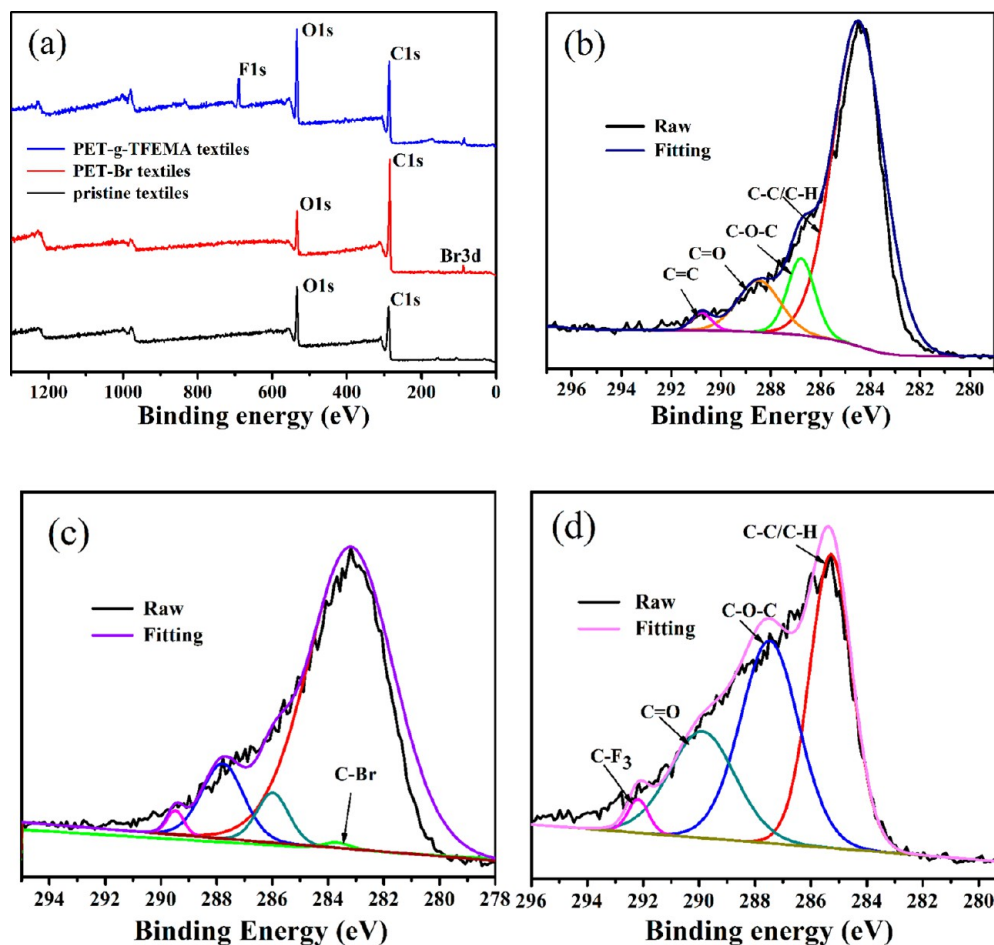


Figure 2. (a) XPS spectra of the pristine PET, PET-Br, and PET-g-P(TFEMA) fabrics. C 1s XPS spectra with fitting curves of the (b) pristine PET, (c) PET-Br, and (d) PET-g-P(TFEMA) fabrics.

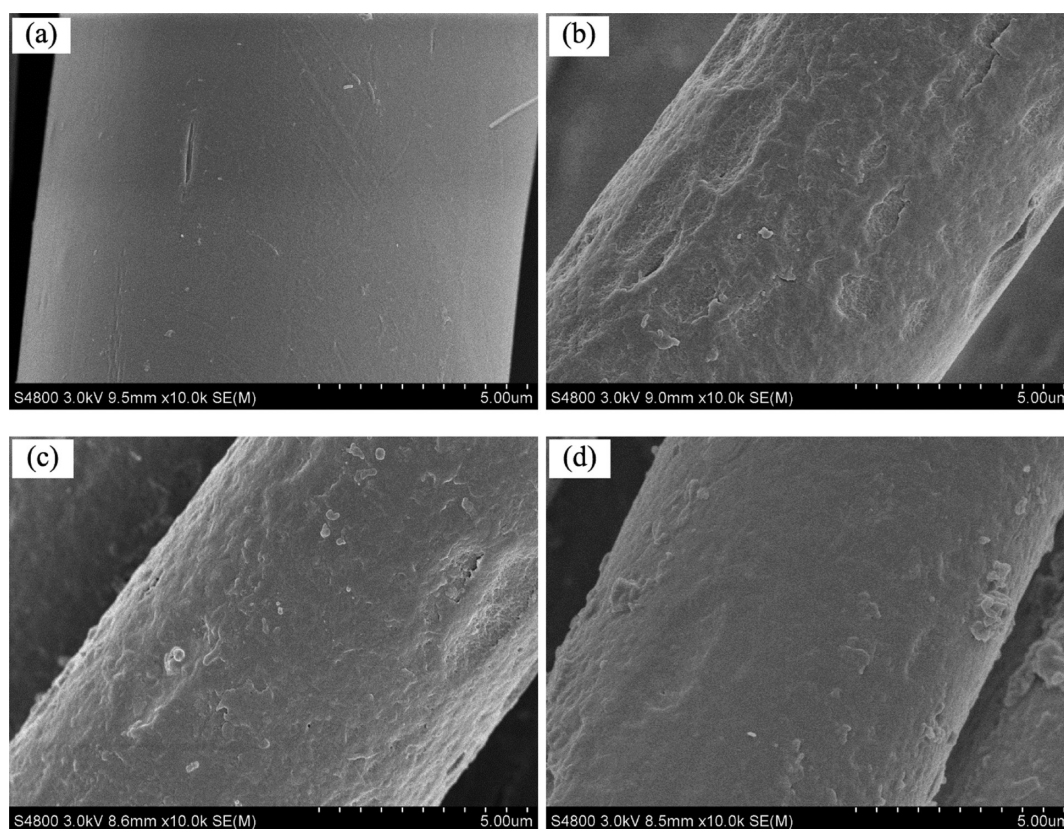


Figure 3. SEM images of (a) pristine PET, (b) E-PET, (c) PET-g-P(TFEMA) (4 h), and (d) PET-g-P (TFEMA) (8 h).

water, and dried at 80 °C to obtain initiator immobilized fabrics, denoted as PET-Br.

2.4. Grafting of Fluorinated Methacrylate Polymers from PET-Br. The polymer coated PET fabric was prepared according to a modified procedure reported previously.³¹ PET-Br fabric was immersed in a container with added THF (100 mL), TFEMA (9.5 g, 56.5 mmol), Cu(I)Br (3.8 mg, 0.017 mmol), bpy (7.6 mg, 0.05 mmol), glucose (0.04 g, 0.2 mmol), and EBiB (13.3 mg, 0.068 mmol). Then the container was sealed and mounted in the infrared-ray heating machine, heated at 60 °C for a given time. Finally, the sample was rinsed with THF, anhydrous ethanol, and water. The resultant fabric was dried at 80 °C and denoted as PET-g-P (TFEMA).

The growth kinetics of the polymers from the PET-Br fabrics via SI-ATRP was investigated by degree of grafting (DG). DGs of the grafted fabrics were determined as the weight increase of the samples, according to the following equation:

$$\text{DG (\%)} = \frac{w_1 - w_0}{w_0} \times 100$$

where w_1 and w_0 are the weights of the samples after and before grafting, respectively.

2.5. Characterization. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4800 field emission scanning electron microscope. Samples were sputter-coated with gold prior to examination. X-ray photoelectron spectra (XPS) on the surfaces were obtained by using a K-alpha thermo Fisher Scientific. Water contact angles (CA) of the fabrics were measured with a deionized water droplet of 5 μL on a video optical contact angle system (OCA 20, Data Physics, Germany) at room temperature. The reported values of CA and SA were determined by averaging values measured at six different points on each sample surface.

2.6. Chemical and Mechanical Resistance of Superhydrophobic PET Samples. The chemical durability of the superhydrophobicity was evaluated by immersing the samples into aqueous solutions of different pH values and into various organic solvents. The samples were rinsed and dried at 80 °C for CA measurement after

immersion into the liquid for 72 h. The chemical durability of the superhydrophobicity was also evaluated by extracting the samples with THF, ethanol, and acetone for 24 h, followed by rinsing with water and drying at 80 °C.

The abrasion tests were performed according to a modified procedure based on the AATCCA Test Method 8-2001. Using a pure nylon fabric cloth as the abrasion partner, the sample was fixed onto the stainless steel column and moved repeatedly with a load pressure of 45 kPa (20 cm for one cycle).

The washing durability was tested by a standard procedure according to AATCC Test Method 61-2003 Test No. 1A. Samples were washed using a laundering machine (SW-12 E, Fang Yuan, China) at 40 °C in the presence of 10 stainless steel balls with the existence of 0.37 wt % soap powder. One washing cycle (45 min) is approximate to five instances of commercial laundering. The washed fabrics were rinsed with abundant water to remove the residual detergent and dried at 80 °C.

UV-Durability was conducted by irradiation using an artificial light source (UV lamp, Osram Ultra Vitalux 300 W) emitting a Gaussian-shaped spectrum which peaked at 370 nm with a cutoff at 290 nm. Fabrics were placed under the UV lamp for continuous irradiation.

3. RESULTS AND DISCUSSION

3.1. Characterization of the SI-ATRP Modified Fabrics.

In order to immobilize the initiator successfully, PET fabrics were treated with sodium hydroxide to produce hydroxyl and carboxyl groups at the fiber surface due to the breaking down of ester groups of PET polymers.²⁶ BiBB can react both with the hydroxyl groups at the fiber surfaces caused by alkaline hydrolysis and with end groups of PET macromolecules under solvent-free conditions, resulting in covalent bonding of BiBB on fibers to form initiator immobilized fabrics, namely PET-Br. After immobilization of the initiator, grafting of

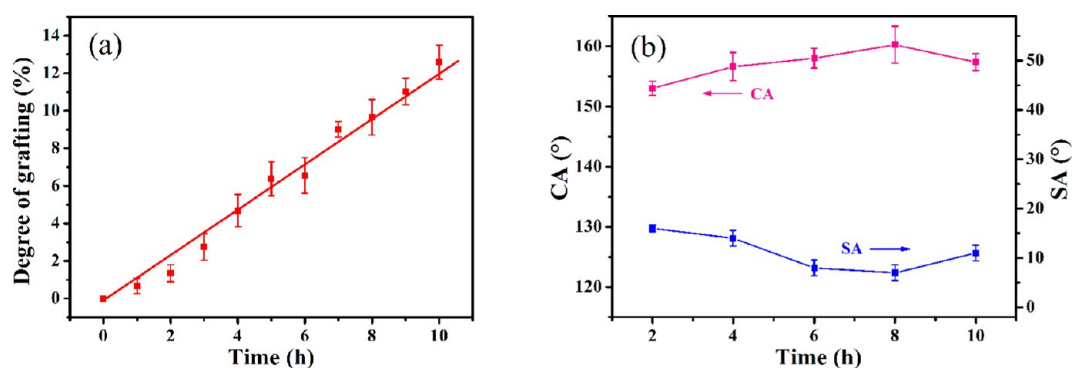


Figure 4. (a) The relationship between the DG and the SI-ATRP time. (b) The relationship between the CA/SA and the SI-ATRP time.

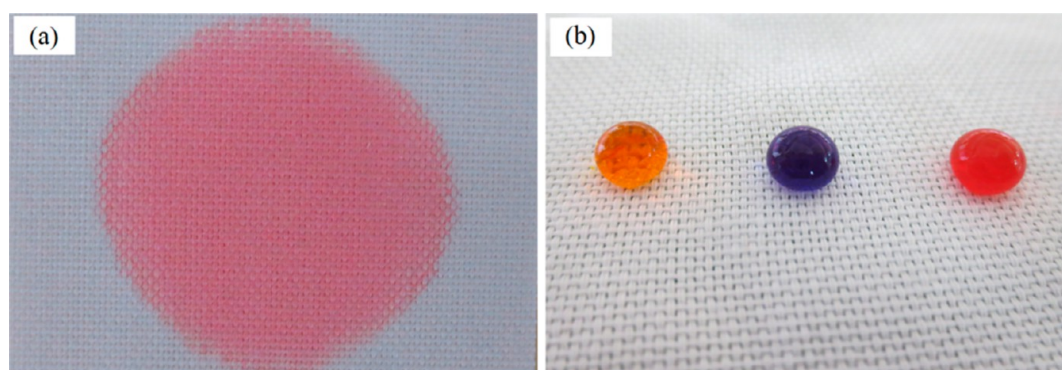


Figure 5. Digital images of dyed water droplets on (a) pristine and (b) PET-g-P(TFEMA) (8 h) fabrics.

polymers from fibers got easier via SI-ATRP with different monomers to tune the hydrophobicity of the fabrics.

The chemical composition of the fabric surfaces was determined by X-ray photoelectron spectroscopy (XPS; Figure 2). The surface of pristine PET fabrics shows the C 1s and O 1s signals, while the surfaces of PET-Br and PET-g-P(TFEMA) dominate new Br 3d and F 1s signals (Figure 2a). This demonstrated that BiBB and TFEMA were successfully incorporated onto the surface of the PET fibers. Figure 2b shows that the C 1s core-level spectra of pristine PET fiber can be curve-fitted into four peak components with binding energies (BEs) at about 284.6, 286.6, 288.7, and 290.7 eV, attributable to the C–H, C–O–C, C=O, and C=C of benzene species, respectively. A Br 3d signal at BE of about 71 eV, characteristic of covalently bonded bromine, appeared in the PET-Br fabrics. The weak Br 3d signal for the PET-Br surfaces is consistent with the nature of the single BiBB monolayer on the PET-Br fabric surface. And a new curve-fitted peak component with BE at about 284 eV appeared, attributable to C–Br. Figure 2d corresponds to the C 1s core-level spectra of PET-g-P(TFEMA) fabrics. Different from Figure 2b and c, the sample displayed a new peak belonging to C–F (292.3 eV), and the peak of C=C disappeared. The above results indicated that P(TFEMA) brushes have been successfully grafted on the fabric.

Scanning electron microscopy (SEM) was employed to characterize the pristine PET, E-PET, and PET-g-P(TFEMA) fabrics. It was found that the fibers of the pristine PET fabric were smooth with an average diameter of about 11.5 μm (Figure 3a). However, after treatment with sodium hydroxide, pits were formed on the fibers with the diameter reduced to 8.5 μm . It should be noted that modification with BiBB changed the morphology of the fiber surfaces little because BiBBs are

small molecules which form a single molecular layer by covalently binding on the etched fibers surface. Figure 3c suggests that graft polymerization with TFEMA for 4 h leveled small pits of the etched fibers and resulted in small lumps on the fiber surfaces which were caused by the accumulation of graft chains. Further polymerization to 8 h increased the diameter of the fibers to 9.5 μm and coated the fibers densely with polymer brushes, decreasing the surface roughness a little.

3.2. Hydrophobicity Property of SI-ATRP Modified Fabrics. The hydrophobicity of surfaces can be tuned by controlling the amount or chain length of the hydrophobic molecules. ATRP is a very robust and versatile synthetic technique for preparation of polymers with precisely controlled architecture and site specific functionality. By immobilizing initiators on fiber surfaces, the hydrophobicity of the fabrics could be adjusted by controlling the polymerization of fluorinated methacrylates. In this experiment, the amount of monomers was overloaded; therefore an approximately linear increase in DG of the P(TFEMA) on the initiator-modified PET fabrics was observed with increasing polymerization time, as shown in Figure 4a. And the CA of the fabrics with water was increased correspondingly, converting the hydrophilic fabrics (Figure 5a) to superhydrophobic ones (Figure 5b) with a CA of $160.5^\circ \pm 3^\circ$ and SA of $7^\circ \pm 2^\circ$, making water droplets roll easily. However, further prolonging the time of polymerization decreased the CA and increased the SA, although the DG increased. This might be because that further increase of DG caused dense and uniform coating of fibers, resulting in leveling of the pits of the etched fibers and lowering of the roughness of the fabrics.

In order to show visually the water repellency of the superhydrophobic PET fabrics, pristine and PET-g-P(TFEMA) fabric samples were immersed into water. It is interesting that

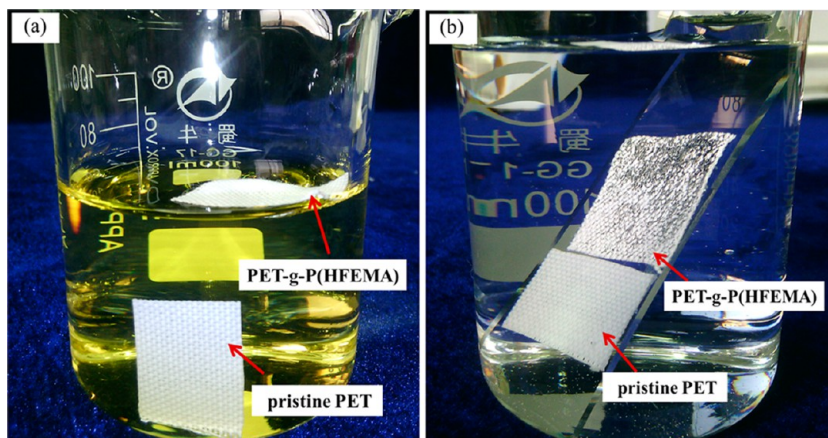


Figure 6. (a) Free immersion of pristine PET and PET-g-P(TFEMA) fabrics in dyed water. (b) Immersion of pristine PET and PET-g-P(TFEMA) fabrics stuck on glass.

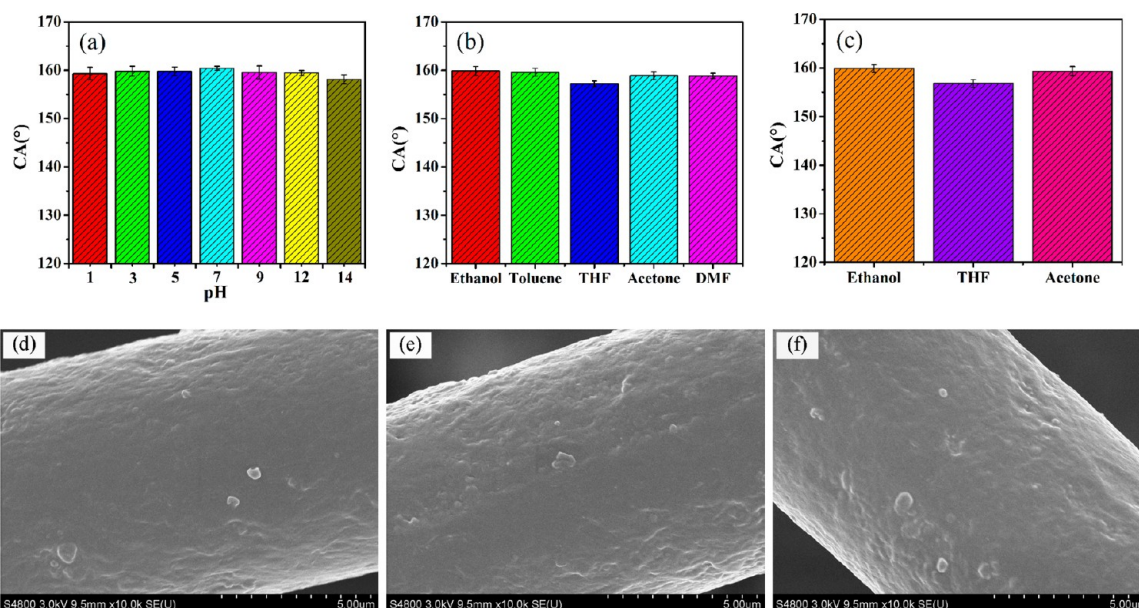


Figure 7. CA of the PET-g-P(TFEMA) fabrics treated by (a) immersion in different pH solutions for 72 h, (b) immersion in various organic solvents for 72 h, and (c) extraction with different solvents for 24 h. SEM images of PET-g-P(TFEMA) fabrics after soaking in (a) sulfuric acid solution, pH = 1; (b) sodium chloride solution, pH = 7; (c) sodium hydroxide solution, pH = 14.

the pristine fabric sunk under water, while the PET-g-P(TFEMA) sample floated on the surface of water after release of force (Figure 6a). When the samples were stuck on a glass plate and put into the water, there is an obvious bright plastron layer on the surface of the PET-g-P(TFEMA) fabric, due to the total reflectance of light at the air layer trapped on the surface. This trapped air can effectively prevent a wetting on the fabric surface underwater. By contrast, pristine PET displayed no bright plastron layer. This phenomenon indicated that the PET-g-P(TFEMA) fabrics possessed typical Cassie mode superhydrophobicity.

3.3. Stability of the Superhydrophobic Fabrics. For practical applications, the durability of superhydrophobic surfaces is a major consideration. Figure 7a shows that the CAs of PET-g-P(TFEMA) fabrics remained above 150° after immersion in different pH solutions for 72 h, although a slight decrease of CA after immersion in a solution at pH 14 was observed, which might be caused by some hydrolysis of the ester groups of polymeric fluorinated methacrylates under

strong alkaline conditions. The SEM images of PET-g-P(TFEMA) fabrics after immersion in solutions of pH 1, pH 7, and pH 14 were also given, and surface morphologies did not alter significantly before and after soaking (Figure 7b,c,d). Additionally, immersion for 72 h (Figure 7b) and even extraction for 24 h (Figure 7c) of the superhydrophobic PET-g-P(TFEMA) with various organic solvents did not greatly change the CAs. The CAs of the samples remained above 155° , although the superhydrophobic PET-g-P(TFEMA) fabrics showed weaker resistance against THF solution than other organic solvents.

Figure 8 shows the CA changes of superhydrophobic PET-g-P(TFEMA) fabrics with UV irradiation time. It was found that the CA increased a little from $160.5^\circ \pm 3^\circ$ to $163.7^\circ \pm 2^\circ$ after the first 144 h of UV exposure, which might be due to the migration of fluoroalkyl chains caused by the temperature rising under UV exposure. However, the CA and SA showed no great change for further irradiation, indicating excellent resistance of the PET-g-P(TFEMA) to UV light.

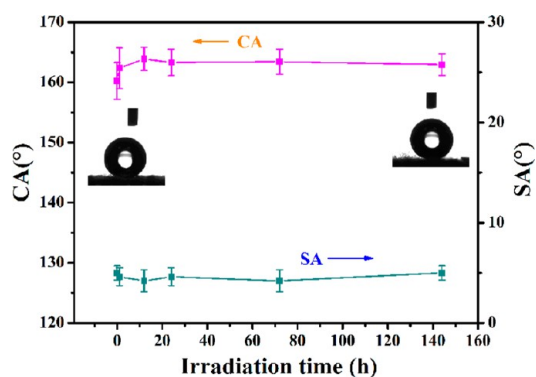


Figure 8. CA and SA changes of superhydrophobic PET-g-P(TFEMA) fabrics with UV irradiation time.

The resistance against mechanical damage of the superhydrophobic PET fabrics was further evaluated by a laundering test with 0.37 wt % of detergent (Figure 9). It was found that the superhydrophobicity was maintained after the superhydrophobic PET fabrics were laundered for 20 cycles, approximate to 100 cycles of commercial laundering. Figure 9a shows that polymers on the fabric surface were partially removed after 100 cycles of commercial laundering, causing only a slight decrease of CA, as shown in Figure 9c. However, the SA increased from $7^\circ \pm 2^\circ$ to $57^\circ \pm 1^\circ$. There are two reasons for this phenomenon. On the one hand, as laundering cycles increased, the amount of polymer on the PET-g-P (TFEMA) surface decreased. On the other hand, with severe mechanical laundering, some protruding fuzzes appeared on the surface of the sample, causing some force or adhesion to the

water on the fabric. Thus, the SA increased with increasing the laundering cycles. Figure 9b showed that water droplets remained spherical on the fabric surface both before and after laundering.

We also tested the mechanical stability of the modified PET fabrics by abrading the superhydrophobic samples back and forth under 45 kPa of force for repeated cycles (Figure 10). After the modified PET fabric was abraded over given friction cycles, the sample was carefully cut into strips (1 cm \times 6 cm) including the abraded area and attached to a glass slide with double-sided adhesive tape. The reported value was the average of at least six trials measured using deionized water droplets that were placed at a different collapsed position on the sample. It was found that the CA of the PET-g-TFEMA fabrics decreased from $160.5^\circ \pm 3^\circ$ to $155.6^\circ \pm 1^\circ$ (Figure 10d), which is ascribed to the partial removal of the polymer at the fiber surface (Figure 10b). Although severe abrasion of 2500 cycles broke and distorted some of the fibers and made the sample worn out, increasing the SA from $7^\circ \pm 2^\circ$ to $55^\circ \pm 2^\circ$, the water droplet maintained a spherical form on the worn part. The results further confirmed that the prepared superhydrophobic surface had excellent resistance against mechanical damage.

All of these results have demonstrated that the superhydrophobic PET-g-P (TFEMA) fabrics by SI-ATRP were highly stable and robust. And the preparation process of superhydrophobic fabrics has the following characteristics: (1) Preparation was done without using any nanoparticles in construction of the rough structure. (2) A solvent-free condition was used to immobilize ATRP initiators on the E-PET fabrics. (3) In comparison with other highly fluorinated

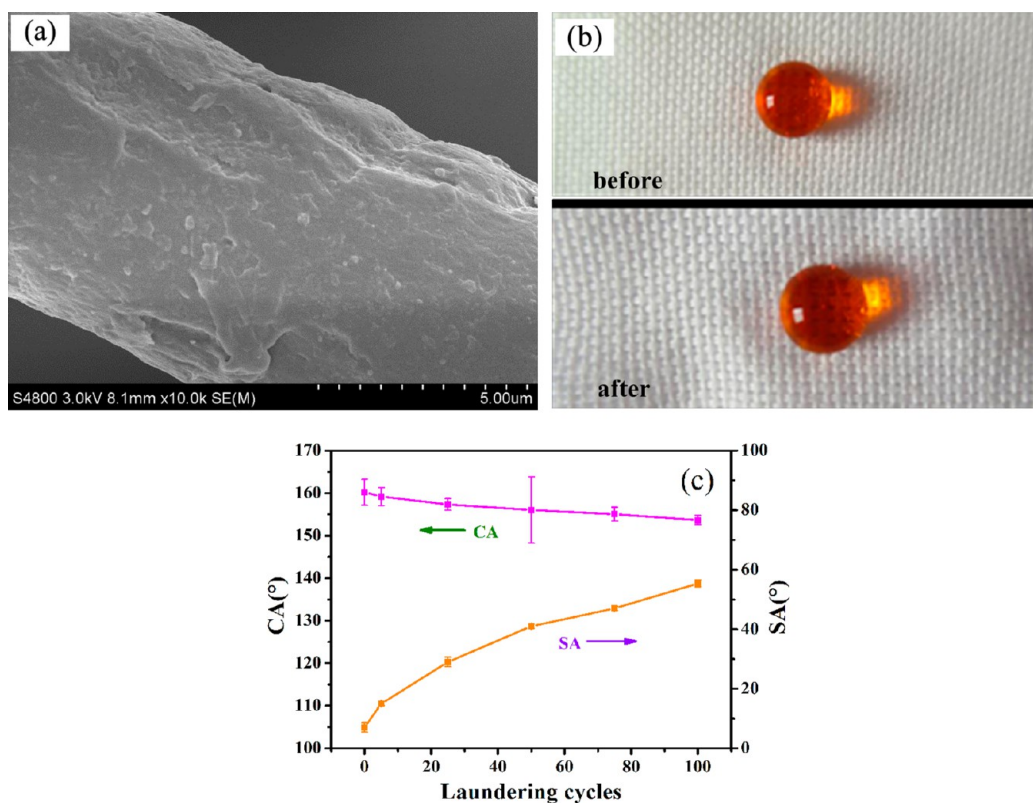


Figure 9. (a) SEM image of PET-g-P (TFEMA) fabrics after laundering test of 100 cycles. (b) Photograph of a water droplet on the PET-g-P (TFEMA) fabrics before and after laundering test. (c) Changes of CA and SA of PET-g-P(TFEMA) fabrics with washing cycles.

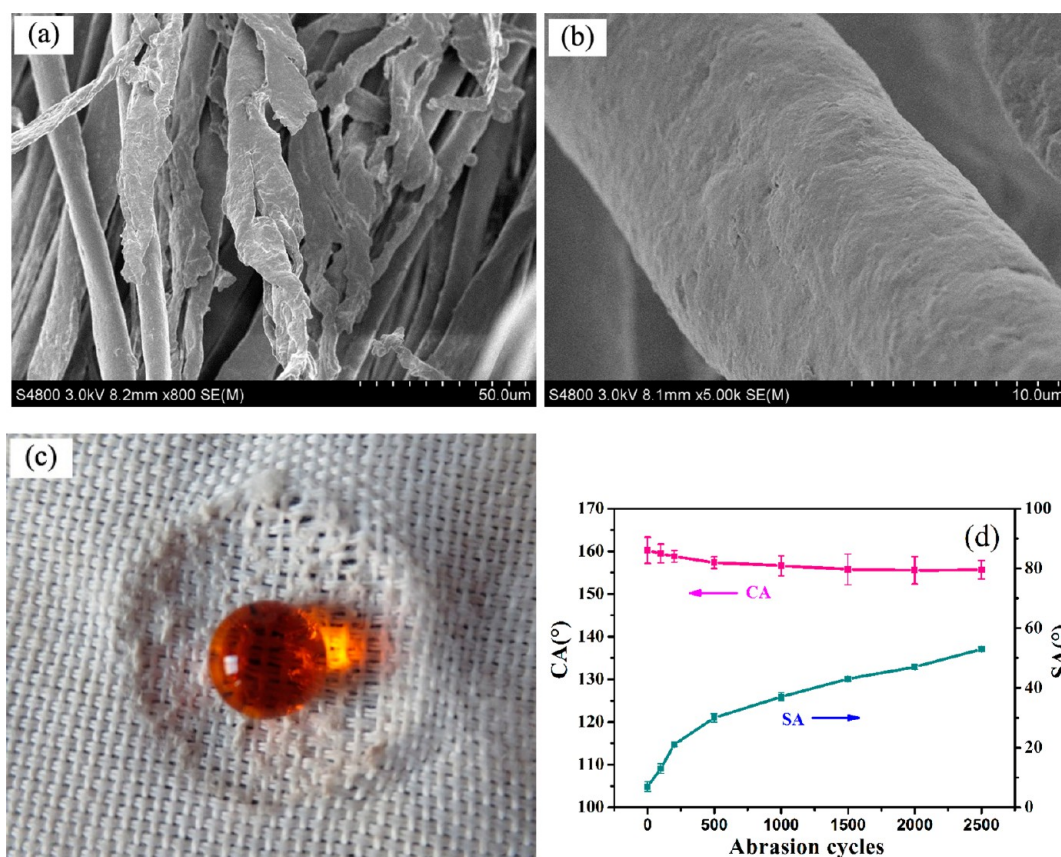


Figure 10. (a) SEM image of PET-g-P (TFEMA) fabrics after abrasion test of 2500 cycles. (b) Higher magnification of a. (c) Photograph of a water droplet on the PET-g-P (TFEMA) fabrics after 2500 cycles. (d) Changes of CA and SA of PET-g-P (TFEMA) fabrics with abrasion cycles.

polymers that are often used for fabricating superhydrophobic surfaces, P(TFEMA) polymers were both inexpensive and more environmentally friendly. (4) Most importantly, SI-ATRP is a surface modification method with mild reaction conditions.

3.4. Antifouling Property of the Superhydrophobic Fabrics. For a superhydrophobic surface to be antifouling, a sliding angle lower than 10° is necessary.^{41–45} As shown in Figure 11a, a coffee droplet maintained a spherical form on the PET-g-TFEMA fabric. To further investigate stain resistance, we immersed PET-g-TFEMA fabric in coffee with pristine fabric as the reference. After 12 h, the fabrics were taken out and dried. The result showed that the pristine fabric was stained heavier than the PET-g-TFEMA fabric (Figure 11c). Figure 11d showed, compared with the pristine fabric, that the PET-g-

TFEMA fabric was easily cleaned by water rinsing, with superhydrophobicity changed little. The excellent stain resistance of the PET-g-TFEMA fabric here suggests that it could be useful for the application of an antifouling material.

4. CONCLUSIONS

In summary, we have demonstrated a novel and general strategy, namely, SI-ATRP, for producing superhydrophobic PET fabrics. It was shown that the superhydrophobicity of the modified fabrics is resistant to UV irradiation, chemical etching, mechanical laundering, and abrasion. Importantly, the surface of the superhydrophobic fabrics showed excellent antifouling properties. This method might be suitable for other hydrophobic monomers for fabrication of superhydrophobic fabrics, paving a way for generating durable and robust superhydrophobic surfaces through chemical bonding between the hydrophobic substances and the substrates.

AUTHOR INFORMATION

Corresponding Author

*E-mail: xuech@zju.edu.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by National Natural Science Foundation of China (51372146), Program for New Century Excellent Talents in University (NCET-12-1042), Research Fund for the Doctoral Program of Higher Education of China (20116125110002, 20136125110003), Major Program of

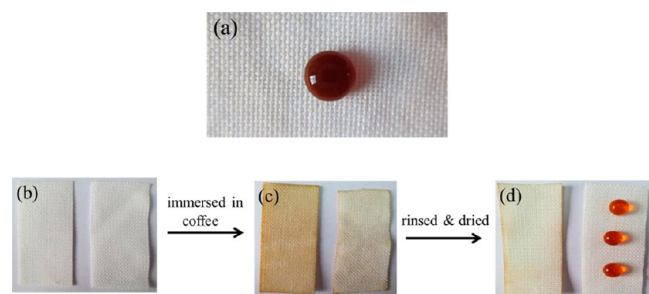


Figure 11. (a) Coffee droplets on the PET-g-P(TFEMA) fabric, photos of (b) pristine (left) and PET-g-P(TFEMA) (right) fabrics, (c) fabrics after being soaked in coffee solution and drying, (d) rinsed and dried fabrics.

Science Foundation of Shaanxi Province (2011ZKC05-7), Key Scientific Research Group of Shaanxi province (2013KCT-08), and Scientific Research Group of Shaanxi University of Science and Technology (TD12-03).

REFERENCES

- (1) Jeong, D.-W.; Kim, S.-J.; Park, J.-K.; Kim, S.-H.; Lee, D.-W.; Kim, J.-M. A Simple Route to Morphology-Controlled Polydimethylsiloxane Films Based on Particle-Embedded Elastomeric Masters for Enhanced Superhydrophobicity. *ACS Appl. Mater. Interfaces* **2014**, *6*, 2770–2776.
- (2) Sparks, B. J.; Hoff, E. F. T.; Xiong, L.; Goetz, J. T.; Patton, D. L. Superhydrophobic Hybrid Inorganic–Organic Thiol-ene Surfaces Fabricated via Spray-Deposition and Photopolymerization. *ACS Appl. Mater. Interfaces* **2013**, *5*, 1811–1817.
- (3) Vakarelski, I. U.; Patankar, N. A.; Marston, J. O.; Chan, D. Y. C.; Thoroddsen, S. T. Stabilization of Leidenfrost Vapour Layer by Textured Superhydrophobic Surfaces. *Nature* **2012**, *489*, 274–277.
- (4) Wang, H.; Ding, J.; Dai, L.; Wang, X.; Lin, T. Directional Water-Transfer through Fabrics Induced by Asymmetric Wettability. *J. Mater. Chem.* **2010**, *20*, 7938–7940.
- (5) Wang, M.; Chen, C.; Ma, J.; Xu, J. Preparation of Superhydrophobic Cauliflower-like Silica Nanospheres with Tunable Water Adhesion. *J. Mater. Chem.* **2011**, *21*, 6962–6967.
- (6) Xue, C.-H.; Ma, J.-Z. Long-lived Superhydrophobic Surfaces. *J. Mater. Chem. A* **2013**, *1*, 4146–4161.
- (7) Yong, J.; Chen, F.; Yang, Q.; Zhang, D.; Bian, H.; Du, G.; Si, J.; Meng, X.; Hou, X. Controllable Adhesive Superhydrophobic Surfaces Based on PDMS Microwell Arrays. *Langmuir* **2013**, *29*, 3274–3279.
- (8) Zhang, G.; Lin, S.; Wyman, I.; Zou, H.; Hu, J.; Liu, G.; Wang, J.; Li, F.; Liu, F.; Hu, M. Robust Superamphiphobic Coatings Based on Silica Particles Bearing Bifunctional Random Copolymers. *ACS Appl. Mater. Interfaces* **2013**, *5*, 13466–13477.
- (9) Zhao, Y.; Xu, Z.; Wang, X.; Lin, T. Photoreactive Azido-Containing Silica Nanoparticle/Polycation Multilayers: Durable Superhydrophobic Coating on Cotton Fabrics. *Langmuir* **2012**, *28*, 6328–6335.
- (10) Duan, W.; Xie, A.; Shen, Y.; Wang, X.; Wang, F.; Zhang, Y.; Li, J. Fabrication of Superhydrophobic Cotton Fabrics with UV Protection Based on CeO₂ Particles. *Ind. Eng. Chem. Res.* **2011**, *50*, 4441–4445.
- (11) Kong, Y.; Liu, Y.; Xin, J. H. Fabrics with Self-Adaptive Wettability Controlled by “Light-and-Dark”. *J. Mater. Chem.* **2011**, *21*, 17978–17987.
- (12) Su, F.; Yao, K. Facile Fabrication of Superhydrophobic Surface with Excellent Mechanical Abrasion and Corrosion Resistance on Copper Substrate by a Novel Method. *ACS Appl. Mater. Interfaces* **2014**, *6*, 8762–8770.
- (13) You, J. B.; Yoo, Y.; Oh, M. S.; Im, S. G. Simple and Reliable Method to Incorporate the Janus Property onto Arbitrary Porous Substrates. *ACS Appl. Mater. Interfaces* **2014**, *6*, 4005–4010.
- (14) Xu, L.; Geng, Z.; He, J.; Zhou, G. Mechanically Robust, Thermally Stable, Broadband Antireflective, and Superhydrophobic Thin Films on Glass Substrates. *ACS Appl. Mater. Interfaces* **2014**, *6*, 9029–9035.
- (15) Ge, J.; Ye, Y.-D.; Yao, H.-B.; Zhu, X.; Wang, X.; Wu, L.; Wang, J.-L.; Ding, H.; Yong, N.; He, L.-H.; Yu, S.-H. Pumping through Porous Hydrophobic/Oleophilic Materials: An Alternative Technology for Oil Spill Remediation. *Angew. Chem., Int. Ed.* **2014**, *53*, 3612–3616.
- (16) Xue, C.-H.; Ji, P.-T.; Zhang, P.; Li, Y.-R.; Jia, S.-T. Fabrication of Superhydrophobic and Superoleophilic Textiles for Oil-Water Separation. *Appl. Surf. Sci.* **2013**, *284*, 464–471.
- (17) Lee, S.; Kim, W.; Yong, K. Overcoming The Water Vulnerability Of Electronic Devices: A Highly Water-Resistant ZnO Nanodevice With Multifunctionality. *Adv. Mater.* **2011**, *23*, 4398–4402.
- (18) Ruan, M.; Li, W.; Wang, B.; Deng, B.; Ma, F.; Yu, Z. Preparation and Anti-icing Behavior of Superhydrophobic Surfaces on Aluminum Alloy Substrates. *Langmuir* **2013**, *29*, 8482–8491.
- (19) Ou, J.; Rothstein, J. P. Direct Velocity Measurements of the Flow past Drag-Reducing Ultrahydrophobic Surfaces. *Phys. Fluids (1994-present)* **2005**, No. 17, 103606–103616.
- (20) Li, Y.; Li, L.; Sun, J. Bioinspired Self-Healing Superhydrophobic Coatings. *Angew. Chem., Int. Ed.* **2010**, *49*, 6129–6133.
- (21) 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.
- (22) 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.
- (23) Wang, H.; Fang, J.; Cheng, T.; Ding, J.; Qu, L.; Dai, L.; Wang, X.; Lin, T. One-Step Coating of Fluoro-Containing Silica Nanoparticles for Universal Generation of Surface Superhydrophobicity. *Chem. Commun.* **2008**, 877–879.
- (24) Xue, C.-H.; Li, Y.-R.; Zhang, P.; Ma, J.-Z.; Jia, S.-T. Washable and Wear-Resistant Superhydrophobic Surfaces with Self-Cleaning Property by Chemical Etching of Fibers and Hydrophobization. *ACS Appl. Mater. Interfaces* **2014**, *6*, 10153–10161.
- (25) Zhou, H.; Wang, H.; Niu, H.; Gestos, A.; Wang, X.; Lin, T. Fluoroalkyl Silane Modified Silicone Rubber/Nanoparticle Composite: A Super Durable, Robust Superhydrophobic Fabric Coating. *Adv. Mater.* **2012**, *24*, 2409–2412.
- (26) Xue, C.-H.; Zhang, P.; Ma, J.-Z.; Ji, P.-T.; Li, Y.-R.; Jia, S.-T. Long-lived Superhydrophobic Colorful Surfaces. *Chem. Commun.* **2013**, *49*, 3588–3590.
- (27) Zou, H.; Lin, S.; Tu, Y.; Liu, G.; Hu, J.; Li, F.; Miao, L.; Zhang, G.; Luo, H.; Liu, F.; Hou, C.; Hu, M. Simple Approach towards Fabrication of Highly Durable and Robust Superhydrophobic Cotton Fabric from Functional Diblock Copolymer. *J. Mater. Chem. A* **2013**, *1*, 11246–11260.
- (28) Yoo, Y.; You, J. B.; Choi, W.; Im, S. G. A Stacked Polymer Film for Robust Superhydrophobic Fabrics. *Polym. Chem.* **2013**, *4*, 1664–1671.
- (29) Deng, B.; Cai, R.; Yu, Y.; Jiang, H.; Wang, C.; Li, J.; Li, L.; Yu, M.; Li, J.; Xie, L.; Huang, Q.; Fan, C. Laundering Durability of Superhydrophobic Cotton Fabric. *Adv. Mater.* **2010**, *22*, 5473–5477.
- (30) Hansson, S.; Östmark, E.; Carlmark, A.; Malmström, E. ARGET ATRP for Versatile Grafting of Cellulose Using Various Monomers. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2651–2659.
- (31) Carlmark, A.; Malmström, E. Atom Transfer Radical Polymerization from Cellulose Fibers at Ambient Temperature. *J. Am. Chem. Soc.* **2002**, *124*, 900–901.
- (32) Li, C. Y.; Xu, F. J.; Yang, W. T. Simple Strategy to Functionalize Polymeric Substrates via Surface-Initiated ATRP for Biomedical Applications. *Langmuir* **2012**, *29*, 1541–1550.
- (33) Östmark, E.; Harrison, S.; Wooley, K. L.; Malmström, E. E. Comb Polymers Prepared by ATRP from Hydroxypropyl Cellulose. *Biomacromolecules* **2007**, *8*, 1138–1148.
- (34) Morandi, G.; Heath, L.; Thielemans, W. Cellulose Nanocrystals Grafted with Polystyrene Chains through Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP). *Langmuir* **2009**, *25*, 8280–8286.
- (35) Hua, Z.; Yang, J.; Wang, T.; Liu, G.; Zhang, G. Transparent Surface with Reversibly Switchable Wettability between Superhydrophobicity and Superhydrophilicity. *Langmuir* **2013**, *29*, 10307–10312.
- (36) Kobayashi, M.; Terayama, Y.; Yamaguchi, H.; Terada, M.; Murakami, D.; Ishihara, K.; Takahara, A. Wettability and Antifouling Behavior on the Surfaces of Superhydrophilic Polymer Brushes. *Langmuir* **2012**, *28*, 7212–7222.
- (37) Carlmark, A.; Malmström, E. E. ATRP Grafting from Cellulose Fibers to Create Block-Copolymer Grafts. *Biomacromolecules* **2003**, *4*, 1740–1745.
- (38) Schmidt, V.; Giacomelli, C.; Lecolley, F.; Lai-Kee-Him, J.; Brisson, A. R.; Borsali, R. Diblock Copolymer Micellar Nanoparticles

Decorated with Annexin-A5 Proteins. *J. Am. Chem. Soc.* **2006**, *128*, 9010–9011.

(39) Nyström, D.; Lindqvist, J.; Östmark, E.; Antoni, P.; Carlmark, A.; Hult, A.; Malmström, E. Superhydrophobic and Self-Cleaning Bio-Fiber Surfaces via ATRP and Subsequent Postfunctionalization. *ACS Appl. Mater. Interfaces* **2009**, *1*, 816–823.

(40) Rastogi, A.; Nad, S.; Tanaka, M.; Mota, N. D.; Tague, M.; Baird, B. A.; Abruña, H. D.; Ober, C. K. Preventing Nonspecific Adsorption on Polymer Brush Covered Gold Electrodes Using a Modified ATRP Initiator. *Biomacromolecules* **2009**, *10*, 2750–2758.

(41) Bixler, G. D.; Theiss, A.; Bhushan, B.; Lee, S. C. Anti-Fouling Properties of Microstructured Surfaces Bio-Inspired by Rice Leaves and Butterfly Wings. *J. Colloid Interface Sci.* **2014**, *419*, 114–133.

(42) Wu, G.; An, J.; Tang, X. Z.; Xiang, Y.; Yang, J. A Versatile Approach towards Multifunctional Robust Microcapsules with Tunable, Restorable, and Solvent-Proof Superhydrophobicity for Self-Healing and Self-Cleaning Coatings. *Adv. Funct. Mater.* **2014**, *24*, 6751–6761.

(43) Razmjou, A.; Arifin, E.; Dong, G.; Mansouri, J.; Chen, V. Superhydrophobic Modification of TiO₂ Nanocomposite PVDF Membranes for Applications in Membrane Distillation. *J. Membr. Sci.* **2012**, *415*, 850–863.

(44) Zhang, X.; Guo, Y.; Zhang, Z.; Zhang, P. Self-Cleaning Superhydrophobic Surface Based on Titanium Dioxide Nanowires Combined with Polydimethylsiloxane. *Appl. Surf. Sci.* **2013**, *284*, 319–323.

(45) Brown, P. S.; Bhushan, B. Mechanically Durable, Superoleophobic Coatings Prepared by Layer-by-Layer Technique for Anti-Smudge and Oil-Water Separation. *Sci. Rep.* **2015**, *5*, 8701.