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Multifunctional Superamphiphobic Fabrics with Asymmetric Wettability for One-way Fluid Transport and Templated Patterning

Hui Liu[a] · Jianying Huang[a] · Feiyang Li[a], Zhong Chen[c], Ke-Qin Zhang[a,b] · Salem S. Al-Deyab[d] · Yuekun Lai[a,b*]

[a]National Engineering Laboratory for Modern Silk, College of Textile and Clothing Engineering, Soochow University, Suzhou 215123, China.
[b]Research Center of Cooperative Innovation for Functional Organic / Polymer Material Micro/Nanofabrication, Soochow University, Suzhou, Jiangsu 215123, China.
[c]School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore.
[d]Petrochemical Research Chair, Department of Chemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia.
Corresponding author email: yklai@suda.edu.cn.

Abstract In this work, multifunctional superamphiphobic fabrics with special wettability were constructed by a facile dip-coating or electrospraying process using easily available materials, *viz.* silica nanoparticles, heptadecafluorononanoic, and fluoroalkyl silane. The obtained HFA-FAS-SiO_2 NPs@surface exhibited a contact angle (CA) of 166.4±3.7° and 155.9±2.1° to water and hexadecane, respectively. In addition, this surface also showed stable repellency toward various corrosive droplets at a wide range of pH values, including HCl (pH=1), NaCl (pH=7), and NaOH (pH=14) solutions. After immersion in the strong acid and base solutions for 24 h, the cotton surface still maintained excellent anti-wetting property. The surface was durable enough to withstand 120 cycles of abrasion and 5 cycles of accelerated standard laundry and still kept a water CA higher than 140° and an oil CA higher than 120°. Another treatment method adopted in this work, electrospraying has been proved to be able to realize asymmetric wetting with one side displaying highly anti-wetting behavior and the other side retaining the inherent hydrophilic and oleophilic nature of the pristine cotton fabric. Based on this special wettability, the obtained fabric could display a one-way directional transport feature. This method can also be extended to create hydrophilically and oleophilically patterned superamphiphobic cotton fabrics using a template. This novel fabric is useful for the development of intelligent cellulose-based substrates for various applications.

Keywords Superamphiphobic · Dip-coating · Electrospraying · Asymmetric wettability · Patterned fabric

Introduction

Superamphiphobic surfaces with large contact angles (CA > 150°) toward various water and oil liquids have gained increasing attention due to their wide range of practical applications, such as anti-fouling, self-cleaning, anti-icing, fluidic devices and anti-corrosion coating (Wang et al. 2015; Lai et al. 2016; Liu et al. 2016; Cao et al. 2016; Waghmare et al. 2014; Valipour et al. 2014). Over the last two decades, superhydrophobic surfaces inspired from lotus leaves have been widely investigated by various materials and fabrication methods. Superoleophobicity was firstly discovered on the skin of marine animals with self-cleaning property, which can remove various contaminates (Cai et al. 2014). The fabrication of superamphiphobic surfaces is based on two key factors: appropriate geometrical structures to enhance the roughness and particular chemical component to decrease the surface energy. So far, numerous construction approaches and various materials have been employed, including design of the re-entrant structures (Zhao et al. 2012; Zhao et al. 2011; Shateri-Khalilabad et al. 2013; Xue et al. 2016), preparation of overhung structures (Deng et al. 2012), and use of nanoparticles to create hierarchical micro / nanoscale structures (Bellanger et al. 2013; Saifaldeen et al. 2014; Guo et al. 2011; Khedir et al. 2014). Song et al. fabricated superoleophobic surfaces by constructing re-entrant micro-scale and nano-scale structures to enhance roughness of Al substrates via electrochemical etching and dipping in $[Ag(NH_{3})_2]^+$ solution. The as-obtained surfaces displayed superior repellency toward oil with a contact angle of about 160.0° (Song et al. 2013). Liu et al. constructed an extraordinary hierarchical re-entrant structure that enabled very low liquid-solid contact fraction, and endowed the surface with super-repellency by the combination of physical deposition, chemical etching and plasma etching (Liu et al. 2014). It has been experimentally verified that the surface chemical functionalization with fluorinated groups and rough surface construction with re-entrant structures are crucial for superamphiphobic property (Bellanger et al. 2013; Saifaldeen et al. 2014; Si et al. 2015; Wang et al. 2014; Xue et al. 2015).

There has been a high demand for superamphiphobic fabrics with super-repellency toward various liquids in the textile industry. With retained breathability and comfortableness, fabrics endowed with super antiwetting ability are of remarkable potential for the development of protective clothing against harmful liquids and other contaminants. Pereira et al. (Pereira et al. 2011) have reported the preparation of superamphiphobic fabrica by synthesizing mesoporous silica nanoparticles functionalized with tridecafluorooctyltriethoxysilane and incorporating them onto cotton fabrics. So far, some significant progress in superamphiphobic surface has been made, however, for a long time, two major difficulties have severely limited the practical use of superamphiphobic surface in daily life and industry. Firstly, many surfaces are still easily contaminated by those low surface tension fluids, especially the ones below 30 mN m^{-1}. Secondly, as a vital factor to fabricate antiwetting surface, rough surface topography is easy to be destroyed during abrasion or washing process, resulting in the poor durability of the surfaces. Therefore, to construct superamphiphobic surfaces with robust durability which repel various liquids is very urgent. To our delights, some progress in these aspects have made recently. Verho et al. (Verho et al. 2011) have demonstrated increased wear resistance by exploiting hierarchical roughness where nanoscale roughness is protected to some degree by the larger scale features, and avoiding the use of hydrophilic bulk materials to prevent the formation of hydrophilic defects. Zhou et al. (Zhou et al. 2015) have prepared superamphiphobic fabrics via one-step dip-coating on fabrics using a coating solution consisting of poly(vinylidene fluoride-co-hexafluoropropylene), fluoroalkyl silane, and a volatile solvent. The as-prepared surface has excellent durability against repeated wash and abrasion.

In the past decades, various techniques had been applied to construct superhydrophobic or superoleophobic surface such as sol-gel process (Fu et al. 2014), anodic oxidation (Vengatesh et al. 2015), chemical vapor deposition, electrodeposition (She et al. 2013; Liu et al. 2014) and so on. Among these methods, electrospraying was considered as a potential and economical solution to construct surfaces with appropriate morphology and structure because of its low-cost, simple operation and its application to various substrate surfaces. Electrospraying is a facile and convenient technique to achieve multifunctional coating on substrate, which is based on the atomization of droplet under a strong electrical field. Liquid drops split into tiny droplets and then deposit on the substrate (Islam et al. 2011; Kim et al. 2015). Between a nozzle and a collector, an electrical potential is applied. In general, the solution was extruded at a low rate to produce a droplet at the tip of the syringe needle because of the surface tension. However, if the applied electric voltage is high enough, the surface tension would be overcome by electrostatic repulsion between the charges and then a thin jet was formed. Once the viscosity of the jet was sufficiently low, the liquid would deposited on the substrate in a tiny droplet shape to form a multifunctional coating (Kim et al. 2011; Wang et al. 2014). Kim et al. have reported an easy method to prepare anti-wetting SiO_2 coating with a micro-scale and nano-scale hierarchical rough structure by combining electrospraying with a sol-gel process (Kim et al. 2013). Wang et al. have successfully applied an advanced conveyor belt and an electrosraying device to fabricate the superhydrophobic composite films with reinforced tensile performances by the combination of PAN fibers, porous PS microspheres and bead-on-string PVDF fibers (Kim et al. 2013).

Spontaneous, directional fluid transport is highly desirable for various applications such as microfluidics, oil-water separation, water harvesting, and so on (Zhou et al. 2013; Tian et al. 2014; Wang et al. 2010). One-way fluid transport is often driven by opposite wettability on two sides. Stenocara beetle is a typical example, which is able to collect tiny water droplet from the air implausibly to survive in Namib Desert (Zhai et al. 2006). Recently, fabrics imbibed with directional one-way fluid transport property have been reported. In common, the directional one-way fluid transport fabrics would be prepared according to the following two basic strategies. Firstly, creating a graded change of hydrophobicity-to-hydrophilicity or oleophobicity-to-oleophilicity from one side of fabric to the other side. Secondly, forming a hydrophobic or oleophobic layer on the surface. Zeng et al. (Zeng et al. 2016) have proved that the fabrics with a thin layer of SU-8 on one surface could display a one-way water transport property and were durable enough to withstand repeated washing. Wang et al. (Wang et al. 2015) have reported a one-way oil transport fabrics and their application in testing liquid surface tension. So far, patterns with special wettability have already been reported on various substrates, such as polymers, paper, and woven silk. Water and oil fluids can permeate selectively through the hydrophilic and oleophilic regions of the patterned fabrics (Yetisen et al. 2013; Kobaku et al. 2012). These obtained patterned surfaces have been applied to manage fluid transport and realize the self-assembly of microscale or nanoscale particles.

In this work, superamphiphobic fabrics have been constructed by dip-coating or electrospraying using conventional sources consisting of silica nanoparticles, heptadecafluorononanoic, and fluoroalkyl silane. In view of the application for fabrics, out-standing laundering and abrasion durability is essential. The obtained HFA-FAS-SiO_2 NPs@ fabrics by dip-coating maintain good hydrophobic and oleophobic after 120 cycles of abrasion and 5 cycles of standard accelerated laundry. As a facile and convenient technique, electrospraying has been employed to construct two-dimensional (2D) Janus fabrics with anisotropic wettability in this study. Water and oils transport through 2D Janus fabrics can be realized, and site-selective liquid wetting pattern on the same side of post-functionalized fabric can be obtained after a template-assisted electrospraying process. These types of post-functionalized fabrics, constructed by facile dip-coating or electrospraying of modified hydrophobic silica particles, have great potential applications for droplet manipulation, liquid transportation and separator, and wetting template.

Experimental Work

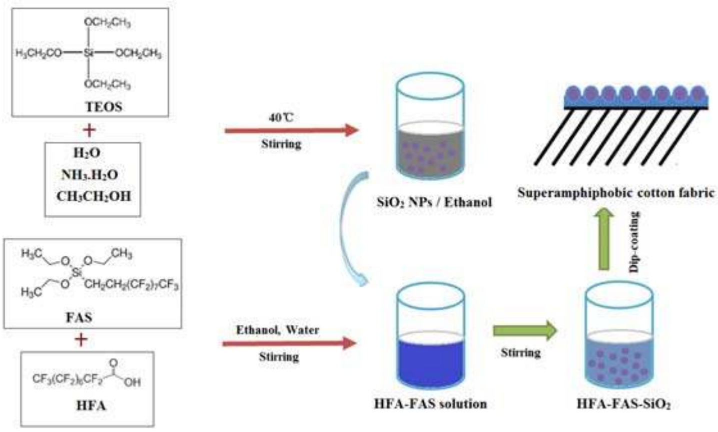
Materials and reagents: Tetraethyl orthosilicate (TEOS), heptadecafluorononanoic acid (HFA), fluoroalkylsilane (FAS), ethanol, methylene blue, oil red, hexadecane, ammonium hydroxide (25%), ethanol, cotton fabric.

Synthesis of silica nanoparticles: Firstly, in a solution composed of 3.0 mL ammonium hydroxide (25%), 1.0 mL deionized water and 50 mL ethanol, 1.5 mL TEOS was added under magnetic stirring. Then the obtained mixture was stirred at 40°C. After 4 h, 1.0 mL TEOS was added again and magnetically stirred for another 12 h. Finally, the obtained suspension was centrifuged and solid particles were dried in oven for further use.

Preparation of superamphiphobic coating: A solution of 200 µL FAS in 2.5 ml ethanol was slowly added dropwise into a solution of 0.25 g HFA in 10 ml ethanol under vigorous stirring. The mixture was added with 27 µL of deionized water and then kept vigorously stirred for 2 h at room temperature. To this as-prepared solution, the suspension of silica nanoparticles in ethanol with different concentrations was added. Subsequently, cotton fabrics were dip-coated in this solution (denoted as HFA-FAS-SiO_2 NPs solution thereafter) for 4 h. Finally, the fabrics were dried at 120 °C for 30 min.

Application of an electrospraying technique: An electrospraying technique was applied to deposit the superamphiphobic HFA-FAS-SiO_2 NPs solution on one side of the untreated cotton fabric to obtain a one-way fluid transport fabric. As for the patterned cotton fabric, a paper pattern was stuck on the cotton substrate before the spraying. The feeding rate was set at 1.0 mL/h, and the receiving distance from nozzle to collector was 13.0 cm. A constant positive high voltage at 2o kV was maintained throughout.

Characterization:
The surface nano-scale and microscale structures of the cotton fabric before and after coating were characterized by Hitachi S-4800 field emission scanning electron microscope (FESEM). Elemental analysis was performed by energy dispersive spectroscopy (EDS). A Kratos Axis-Ultra HAS X-ray photoelectron spectrometer (XPS) with a 100 W Al Kα X-ray source was applied for the investigation of the surface chemical composition. A Nicolet 5700 Fourier transform infrared (FTIR) spectrometer was used to record the infrared spectra of the cotton fabric before and after HFA-FAS-SiO_2 NPs coating. The root mean squared (RMS) roughness value was obtained by an atomic force microscope (AFM, Dimension Loon, Bruker Company). The water and oil contact angles were measured by an optical contact angle meter system of Krüss DSA100 with 6 µl droplets. The abrasion durability was tested in a Y571B colour fastness rubbing tester using a blank cotton fabric as the abrasive. The laundering durability test was performed following the American Association of Textile Chemists and Colourists (AATCC 61-2006) standard method under conditions of 2A.



Scheme 1 Schematic illustration of the preparation procedure for the superamphiphobic cotton fabric by dip-coating.

Results and discussion

Scheme 1 illustrates the preparation of superamphiphobic coating. The HFA-FAS solution was prepared by mixing HFA, FAS and H_2O in ethanol, in which both silicon carboxylate coordination complexes and Si-O-Si networks were formed. SiO_2 NPs were then added to the solution to form a coating solution (Xu et al. 2015). Fig. 1d showed the EDS spectrum of the superamphiphobic surface by dip-coating. The table displayed the corresponding elements composition and relative contents on the coated cotton. It exhibited that the atomic ratio of C/O/F/Si/Au was about 43.53%/40.47%/10.97%/4.50%/0.543%. Compared with the pristine cotton, which detected mainly C and O elements, the F and Si elements appeared on the cotton surface only after the successful surface treatment.. To further investigate the surface chemical components of cotton fabrics before and after HFA-FAS-SiO_2 NPs coating, X-ray photoelectron spectroscopy (XPS) was performed. Figure 2 displays the survey spectra and Si 2p, and F 1s high-resolution spectra of fabrics before and after HFA-FAS-SiO_2 NPs modification. As showed in Fig. 2a, the XPS survey spectra indicates that the blank cotton fabric consists of C and O elements. After the HFA-FAS-SiO_2 NPs coating, three additional characteristic peaks corresponding to Si 2p, Si 2s and F 1s at binding energies (BEs) of 101.0, 152.0 and 689.0 eV respectively, were clearly observed. In the FTIR spectra in Fig. 1e, the bands appeared at 1218 cm^{-1} were due to the C-F bond stretching. The band at 1684 cm^{-1} can be assigned to the carboxylate stretching. The increase in peak intensity at 1093 cm^{-1} was due to Si-O-Si asymmetric stretching vibrations. The peaks at 799 cm^{-1} and 467 cm^{-1} were ascribed to the stretching vibration and bending vibrations of the Si-O bonds. These results all indicate that the HFA-FAS-SiO_2 NPs coating has been successfully applied on the fabrics.

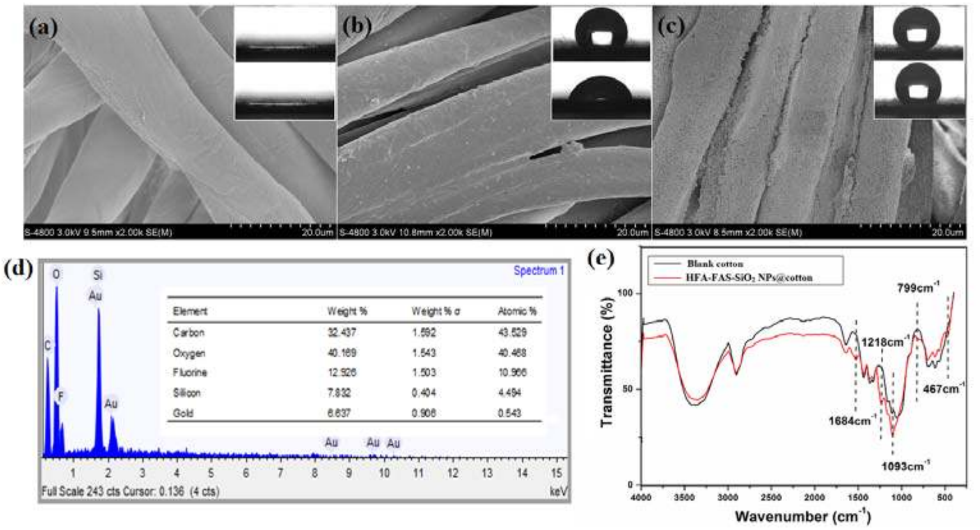


Fig. 1 SEM images of (a) pristine cotton, (b) HFA-FAS @ cotton by dip-coating and (c) HFA-FAS-SiO_2 NPs@ cotton by dip-coating; Insets of (a), (b) and (c) are the water and oil droplet images on the corresponding cotton surface. (d) EDS spectrum and elements proportion of the superamphiphobic coating; (e) FTIR spectra of the blank cotton and the coated cotton.

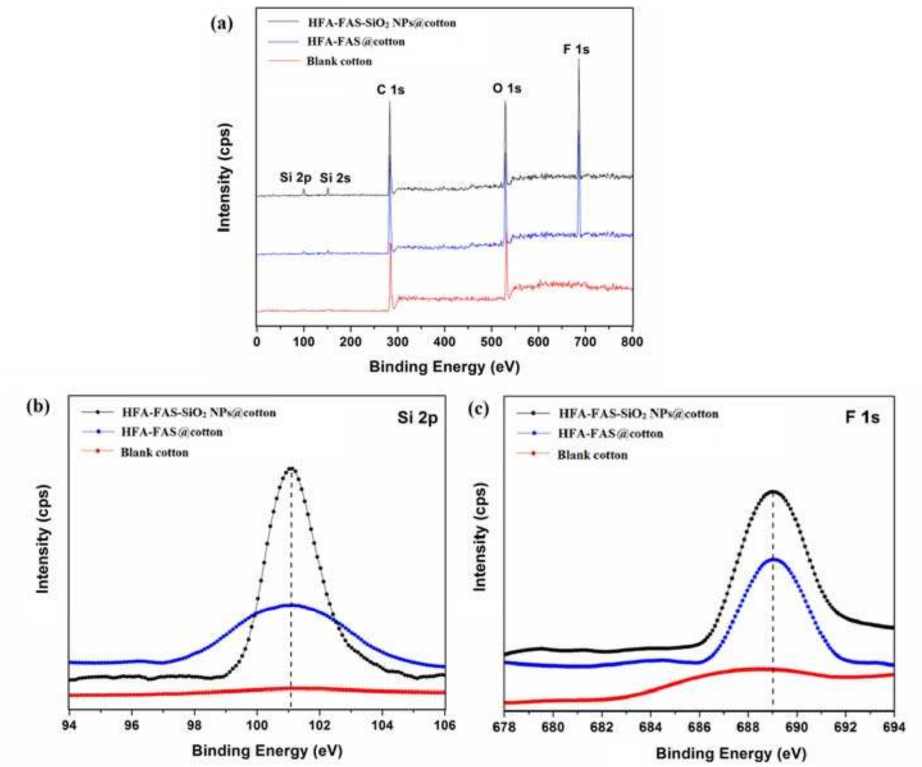


Fig. 2 (a) Survey XPS spectra of cotton fabric before and after HFA-FAS-SiO_2 NPs coating. High-resolution XPS spectra of (b) Si 2p, (c) F 1s.

As shown in Fig. 1a, the surface of blank cotton fabric is very smooth without any microscale or nanoscale features. To identify the influences of the SiO_2 NPs, the pristine cotton was firstly immersed in HFA-FAS solution and the water and oil drops gradually spread and finally wetted the obtained HFA-FAS@cotton (Fig. 1b) with a transient water CA of 140.5±3.3° and oil CA of 73.3±2.9° (Fig. S1c, d, Supporting Information). However, the CAs decreased to below 5° gradually within about 1 h both for water and oil, which is ascribed to the capillary effect of the fabric fibres. This indicats that such initial superamphiphobility of HFA-FAS@fabric was unstable and would lose its effectiveness later. After the addition of SiO_2 NPs to the solution, it was obvious that the cotton surface was uniformly covered by SiO_2 NPs and a thin layer of HFA-FAS (Fig. 1c). To our delight, the HFA-FAS-SiO_2 NPs coatings exhibited excellent superamphiphobility to water drops with CA of 166.4±3.7° and hexadecane with CA of 155.9±2.1° (Fig. S1e, f), and droplets of water and hexadecane both stayed nearly spherical (Fig. S2c). The hybrid HFA-FAS-SiO_2 NPs coating was proved to endow the fabric surfaces with stable superamphiphobility by increasing the roughness to a large extent. In contrast, pure SiO_2 NPs@cotton showed no hydrophilicity or oleophobicity at all with contact angle of 0º both for water and oil, suggesting that the pure HFA-FAS layer was also vital for achieving the superamphiphobicity. These results all indicate that the combination of the microscale roughness of the cotton weave structure and the nano-scale roughness of SiO_2 NPs, along with the fluorinated alkyl chain of HFA-FAS, has contributed to the observed superamphiphobicity. The surface roughness was further characterized by atomic force microscopy (AFM). The pristine cotton surface is comparatively smooth and has an RMS value of 13.7 nm (Fig. 3a). A noticeable surface morphology change could be observed in Fig. 3b. The RMS value of HFA-FAS-SiO_2 NPs@cotton increased to 63.4 nm after dip-coating, indicating a rougher surface. The enhanced RMS was obviously resulted from the incorporation of nano-structures of SiO_2 NPs.

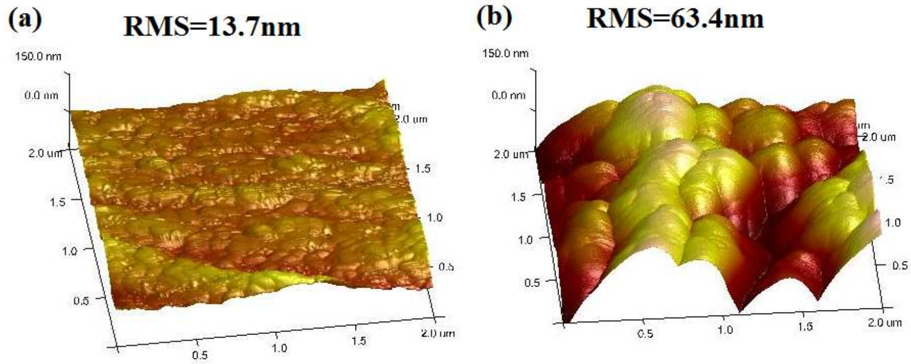


Fig. 3 AFM images of the surface of (a) pristine cotton fabric; (b) HFA-FAS-SiO_2 NPs @cotton by dip-coating.

To explore the influence of SiO_2 concentration on wettability, a series of experiments were systematically conducted. Fig. 4 exhibited SEM images of the cotton surface prepared in various SiO_2 concentrations. As shown in Fig. 4a and d, sparse nanoparticles were observed on the fiber surface at a low SiO_2 concentration (1.0 mol/L). With the increasing concentration of 1.5 mol/L (Fig. 4b and e), higher-density nanoparticles appeared. As the concentration increased from 1.5 to 2.0 mol/L (Fig. 4c and f), great changes have taken place obviously in the configuration and morphological structure of the fiber surface. The density of random nanoparticles markedly increased to a degree to render the cotton fabric surface with excellent liquid repellency. When the SiO_2 concentration was further increased to 2.5 mol/L, a thicker coating consisted of SiO_2 NPs was formed on the fiber surface. As the SiO_2 concentration further increased, SiO_2 NPs would undergo the secondary growth on the surface of the original nanoparticles, endowing cotton with rougher nanostructures. However, many cracks would form in the SiO_2 coating due to the continuous accumulation of internal stress, resulting in the decrease of mechanical properties and CA. Therefore, SiO_2 concentrations of 2.0 mol/L is the optimum condition to realize outstanding superamphiphobility.

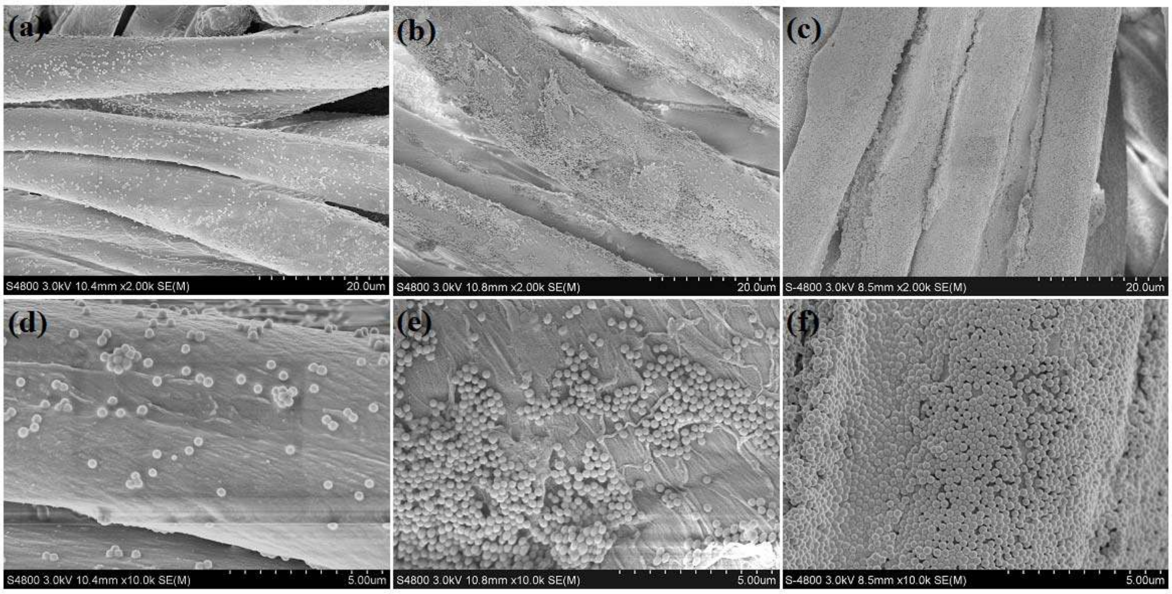


Fig. 4 FESEM images showing the as-prepared SiO_2 when cotton fabric was treated with various SiO_2 concentrations: (a) 1.0 mol/L; (b) 1.5 mol/L; and (c) 2.0 mol/L. (d), (e) and (f) are the corresponding high-magnification images of (a), (b) and (c).

Robust laundering durability is a basic requirement for reuse of textile fabrics in the industry, and in this work it was used to assess the stability of the superamphiphobicity of fabrics. The test was performed following the American Association of Textile Chemists and Colourists (AATCC 61-2006) standard method under the condition 2A. Fig. 5f showed the influence of repeated laundering on the CAs of water and oil. Before laundering, the as-prepared cotton samples exhibited outstanding anti-wetting property with water contact angle of 166° and oil contact angle of 155°. After laundering for the first cycle, an obvious decline on CAs of both water and oil occurred. However, in the following a few cycles, the decrease was quiet small.The decrease of the CA after the first cycle is likely to be due to the removal of some SiO_2 particles that are weakly binded to the fabric surface. The bonding between the remaining particles and the fabric surface is strong enough to resist the following laundering cycles, resulting in only a minor change in CAs. After 5 laundering cycles, the sample still retained its superhydrophobicity with a WCA higher than 150°, although the oleophobicity weakened from the original contact angle of 155.9±2.1° to 138.1±3.2°. The contact angles for water and oil both reached a plateau of about 150° and 138°, respectively, demonstrating the stability of the superamphiphobic surface. (Huang et al. 2015)

In addition to the laundering durability discussed above, the HFA-FAS-SiO_2 NPs@cotton also presented satisfactory abrasion durability. In the abrasion experiment, the tested sample was rubbed in one direction at a rate of 3 cm/s against the pristine cotton fabric as the abrasive. As expected, the contact angle was gradually decreased with the increase of abrasion times at the beginning due to the partial remove of SiO_2 NPs (Fig. S4) and the fluorine-containing compounds. However, further increasing the abrasion time, the contact angle did not show further change and slowly approached plateaus with a WCA of 141.6±3.2° and an oil CA of 126.5±1.9°. These results demonstrated excellent anti-wetting ability of robust post-functionalized fabrics, because of the preservation of rough surface morphology of the HFA-FAS-SiO_2 NPs@cotton fabric in spite of the removal of a small fraction of SiO_2 particles on the outermost surface after repeatedly abrasion.

To further investigate their stability against a pressure-induced wetting, an immersion test was performed. When immersed in water by an external force, the superhydrophobic cotton surfaces displayed like a silver mirror, which is caused by the triapped air bubbles on the surface (Fig. 5a). This phenomenon was not observed on the pristine cotton surface. After the external force was removed, the superhydrophobic cotton bounced back immediately and floated on the water surface without absorbing any water (Fig. 5b). By contrast, the pristine cotton fabric just sank below the water interface due to its strong absorption of water, as shown in in Fig. 5c. In addition to the water repellency, the obtained fabric also showed stable repellency toward various liquids at all pH values, such as acidic, alkali and salt solutions. Fig. 5d showed the image of HCl (pH=1), NaCL (pH=7), and NaOH (pH=14) droplets on the obtained cotton surface. These three droplets all displayed perfect spherical shapes uniformly on fabric surfaces, displaying robust anti-wetting even toward strongly corrosive liquids (Jin et al. 2014).

In addition, the chemical durability of the superamphiphobic coating was also evaluated. After being immersed into NaOH solution of pH 14 (Fig. S5a) and HCl solution of pH 1 (Fig. S5b) for 24 h, the cotton still preserved superhydrophobicity and highly oleophobicity with the CA of water larger than 155° and CA of oil larger than 145°.

These results indicate that the HFA-FAS-SiO_2 NPs coating displayed superior stability and excellent durability under various harsh environmental conditions.

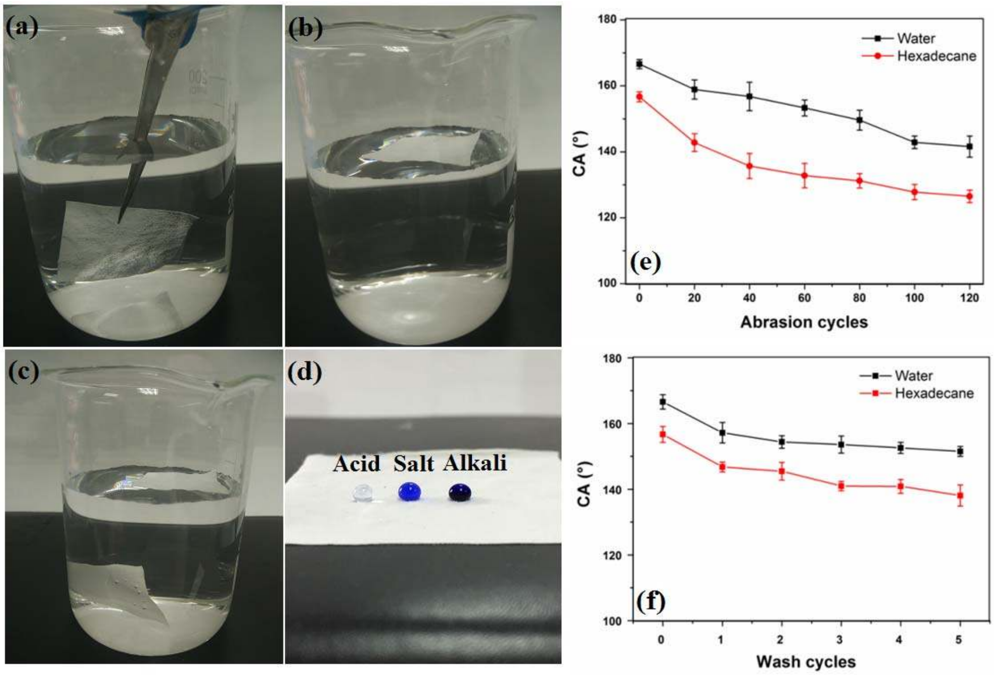


Fig. 5 (a) Superhydrophobic cotton fabric immersed in water by an external force with a silver mirror-like phenomenon. (b) Superhydrophobic cotton fabric floating on water after releasing the external force. (c) The pristine cotton fabric floating below the water interface and the superhydrophobic cotton fabric standing on the water. (d) The droplets of the HCl solution (pH 1), NaCl solution (pH 7), and NaOH solution (pH 14) droplets on the superhydrophobic surface staying nearly spherical. The correlation of contact angle with (e) abrasion cycles and (f) wash cycles on dip-coated cotton surface.

Fig. 6a showed another fabric treatment procedure in this work. The superamphiphobic coating solution was selectively applied on one side of the pristine substrate via an electrospraying process, which is a simple, straightforward, and time-saving approach to construct a robust superhydrophobic or superoleophobic surface on any kind of substrates. By controlling the spraying conditions, the exposed face could exhibit amphiphobicity while the opposite face retained amphiphilicity. As shown in Fig. 6b and c, after the one-side electrospraying with a feeding rate at 1.0 mL/h, a constant electrical potential of 20 kV and the receiving distance from syringe needle to collector at 13.0 cm, the sprayed surface exhibited highly anti-wetting property with droplets of water and hexadecane both staying nearly spherical, whereas the unexposed face still maintained the primitive hydrophilic and oleophilic nature and the droplets spread onto the surface. In Fig. 6d and 6e, SEM images show that the sprayed fiber surface was coated with a layer of thin gel coating containing SiO_2 NPs. The anisotropic surface morphology through Janus cotton gave rise to one-way directional fluid gating performance. Fig. 7a, b display a group of frames to show water and oil transport behaviour (volume, 40 μL) on the 2D Janus fabrics. Once the fluid contacted the sprayed side, it moved up to penetrate through the cotton and then started to spread on the other side. The complete transfer times for the water and oil droplet were approx. 4.6 s and 10.0 s, respectively. However, when fluid was dropped onto the non-sprayed side, it did not penetrate the fabric at all, instead they just spread onto the surface layer. It took about 3 s for water and 5 s for oil to spread out completely. These specific 2D Janus fabrics with directional liquid transportation would be potentially useful for microfluidic gate device or one-way liquid transport membranes.

Fig. 7c showed CA changes during dripping droplets on the electrosprayed cotton. On the electrosprayed side, it took around 5 s for contact angle of water to decrease from 137° to 0°, while the contact angle of oil dropped from 135° to 0° within 10 s. On the other non-sprayed side, the CA of water and oil decreased from about 135° to 0° quickly. Although CAs of water and oil on both faces exhibited a decreasing trend, the transport features they were based on were different. When droplets were placeed on the electrosprayed side, they fully wicked into the coating and penetrate to another unsprayed side. However, when droplets were dropped on the unsprayed side, they quickly spread into the fibers due to the hydrophilic and oleophilic property of the original cotton. These results clearly indicated that the cotton fabric after one-side electrospraying post-functionalization possesses an excellent one-way fluid-transport ability (Zeng et al. 2016). This 2D Janus fabric with the feature of directional gating of continuous water and oil flow, as displayed in Fig. 7, is very desirable for application in the fluid diode for directional one-way liquid/heat flow regulation.

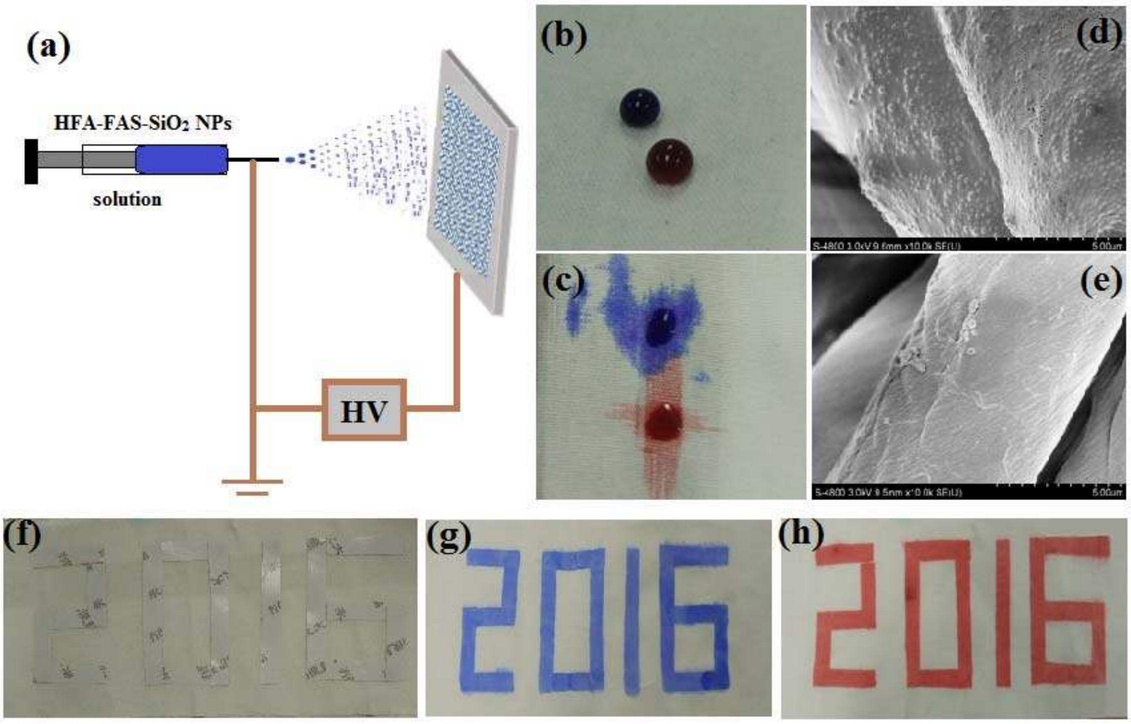


Fig. 6 (a) Schematic illustration of one-side electrospraying coating; photos of droplets of water and hexadecane on the fabric surface with (b) or without (c) electrospray coating; SEM images of the fabric surface with (d) or without (e) electrospray coating; (f) mask pattern covered on the cotton substrate; (g) water micropatterned cotton surface; (h) oil micropatterned cotton surface.

The phenomenon above was under the condition that the fabric was electrosprayed for 1 h. The HFA-FAS-SiO_2 NPs coating weight on the fabric varied with different electrospraying time. It was found that the change of electrospraying time on one face endowed the cotton with different fluid one-way transportation features, as shown in Table 1. With increasing electrospraying time, there is an increase in the amount of coating solution on the sprayed side and the solution would gradually penetrate through the fabric to the other side because of the capillary force, resulting in the increase of CAs on the unsprayed side. Interestingly, when the time of electrospraying procedure on one side of the fabric was between 20 and 60 mins, the one-way directional fluid transportation appeared. If the time was less than 20 mins, the fabric exhibited two-way transport feature. By contrast, if the time was longer than 60 mins, the fabric showed no transport and droplets could not penetrate through the fabric from either side.

Table 1 Effect of electrospraying time on water and oil transport feature

electrospraying time (min)	fluid transport features	WCA/ OCA	
		sprayed side	unsprayed side
0	**Two-way transport**	**0°/ 0°**	**0°/ 0°**
10	**Two-way transport**	**34.5° / 23.7°**	**7.9° / 4.8°**
20	**One-way transport**	**89.6° / 85.4°**	**40.3° /34.6°**
60	**One-way transport**	**122.3° / 115.6°**	**55.6° / 50.2°**
70	**None transport**	**143.1° / 140.7°**	**78.6° / 67.9°**
Dip-coating	**None transport**	**166.4°/ 155.9°**	**166.4°/ 155.9°**

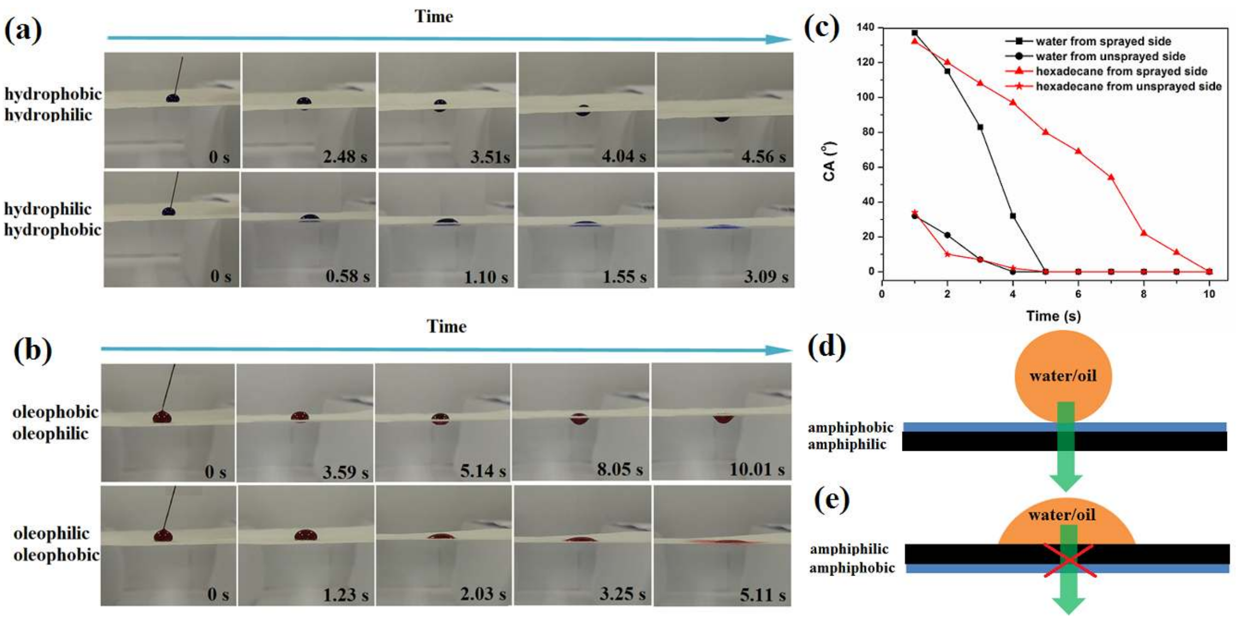


Fig. 7 Frames from a video to show dropping blue-dyed water (a) and red-dyed oil (b) on electrosprayed cotton fabric and on the unsprayed back surface and corresponding schematic illustrations (d) and (e); (c) CA changes during the dropping of water or oil onto the fabric with or without electrospraying treatment.

The method to prepare hydrophilic and oleophilic patterned superamphiphobic cotton fabrics has been illustrated in Fig. 6. Firstly, before the electrospraying, mask with patterns of “2016” was pasted on one side of the pristine cotton fabric (Fig. 6f). Then, this face of the cotton fabric was spraying for 1 h, and the spraying has caused the formation of the superamphiphobility on the exposed region. While the unexposed region retained the inherent hydrophilic and oleophilic nature. As shown in Fig. 6g and h, the unsprayed region readily absorbed water and oil, which was repelled by the sprayed superamphiphobic domains. This was due to the selective permeation of fluid in the amphiphilc regions.(Wang et al. 2014)

Conclusions

In summary, we have successfully prepared robust superamphiphobic fabrics via a facile dip-coating process to anchor the modified hydrophobic silica nanoparticles on the fabric surface. The robust superamphiphobic fabrics were able to maintain good anti-wetting performance after 120 cycles of abrasion and 5 cycles of standard accelerated laundry. In addition, the novel 2D Janus fabrics with anisotropic wettability could be successfully constructed via the selective electrospraying coating of the HFA-FAS-SiO_2 NPs on the original superamphiphilic fabrics. The 2D Janus fabrics with directional liquid transportation features demonstrated promising one-way liquid transport ability for both water or oil droplets. Water or oil wetting micropatterns on superamphiphobic cotton fabric can also be created by site-selective electrospray coating. This simple and effective superamphiphobic post-functionalization process could be easily applied to various cellulose-based substrates and can also be easily scaled up in production. We believe that these robust uniform superamphiphobic fabrics or Janus fabrics with anisotropic wettability are useful for various promising applications, e.g. self-cleaning, anti-fouling, intelligent fluidic gate /sensors, and templated wetting.

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