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Super Water Repellent Fabrics Produced by Silica Nanoparticle-containing Coating

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ABSTRACT

In this paper, we report on superhydrophobic fabrics (polyester, wool and cotton) produced by a wet-chemical coating technique. The coating solutions were synthesized by the co-hydrolysis of two silane precursors, tetraethyl orthosilicate (TEOS) and an alkylsilane, in an alkaline condition. Without any purification, the as-hydrolyzed solutions were directly used to treat fabrics, and the treated fabrics had water contact angles (CA) as high as 170° and sliding angles (SA) as low as 5°. Three alkylsilanes have been used for the synthesis of the coating solutions, and all contain three hydrolysable alkoxy groups and one non-hydrolysable alkyl, but with different chain lengths (C1, C8 and C16). It was found that the CA value increased with an increase in the alkyl chain length, while the SA showed a reverse trend. When the functional group had a C16 alkyl, the treated fabric surfaces were highly superhydrophobic, with the CA not being affected much by the fabric type, while the SA values were slightly affected by the original wettability of the fabric substrates. The superhydrophobic feature was attributed to a highly rough surface formed by the particulate coating. Aside from the superhydrophobicity, the influence of the coating on the fabric softness was also examined.

Keywords: Superhydrophobic Fabrics, Core-shell Nanoparticle, Silica, Precursor

1. Introduction

“Superhydrophobicity” is typically used to describe surfaces with a water contact angle (CA) greater than 150° (Wenzel, 1936; Cassie & S. Baxter, 1944; Johnson & Dettre, 1964; Marmur, 2004).

Nature has imbued many plants, animals and insects, such as lotus leaves, butterfly wings and duck feathers, with a superhydrophobic surface to show water-repellent and self-cleaning functions. It is of great practical importance to create fabrics with superhydrophobic surfaces so that the fabrics can repel water/ice/snow and have anti-sticking, anti-contaminating and/or self-cleaning functions, while their moisture permeability is maintained.

Extensive research has been recently conducted to

realize superhydrophobicity on the surfaces of various substrates. It has been demonstrated that superhydrophobicity depends not only on the surface chemistry, but also on the surface topology. Two distinct theoretical models (Wenzel and Cassie-Baxter) (Wenzel, 1936; Cassie & S. Baxter, 1944) have been used to guide the generation of superhydrophobic surfaces by either roughening the surface (e.g. etching), or lowering the surface free energy, or both. Examples include using a micro-processing technique (Oener & McCarthy, 2000; Love et al., 2002; Feng et al., 2003; Morra et al., 1989; Chen et al., 1999; Burmeister et al., 2005; Khorasani et al., 2005; Samuel et al., 2004) to produce a rough surface and subsequent chemical treatment with silane (Chen et al., 1999) or fluoro-containing polymers (Samuel et al., 2004) to reduce the surface free energy. Alternatively, a superhydrophobic surface can be generated by imparting nanostructures to the surface through the use of chemical/

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electrochemical deposition (Ren et al., 2003; Li et al., 2003), self-assembly (Genzer & Efimenko, 2000; Gu et al., 2003; Li et al., 2005; Zhang et al., 2005), or sol-gel treatments (Tadanaga et al., 1997; Nakajima et al., 2001; Roig et al., 2004), followed by further chemical surface modification.

However, most of the above techniques involve a tedious and multiple-step procedure, which is impractical for fabrication of superhydrophobic surfaces on a large-scale. One-step solution treatments using appropriate micellar polymer solutions (Xie et al., 2004; Zhao et al., 2005), phase-separated polymers (Yabu & Shimomura, 2005), and nanofiller-added polymers or sol-gel solutions (Hikita et al., 2005; Wang et al., 2006) have been reported. These one-step solution methods are very promising because of the simplicity in both the process and the equipment involved.

Fabric materials have micrometer-scaled rough surfaces that arise from the fabric structure. Such a rough surface can increase the surface hydrophobicity if the fibers are made of a hydrophobic material. Despite that, conventional fabrics are seldom superhydrophobic. Many superhydrophobic techniques have been used to produce superhydrophobic fabrics. For example, carbon nanotubes (Hsieh et al., 2008), metal particles (Wang et al., 2007), silica particles (Ramaratnam et al., 2007) and zinc oxide (ZnO) nanorods (Xu & Cai, 2008) have been applied to various fabrics for superhydrophobic treatments, and chemical vapor deposition and plasma or laser treatment techniques (Li et al., 2007; Balu et al., 2008) have also been used to impart fabrics with superhydrophobicity.

However, most of the work only focused on the static CA of the fabric superhydrophobicity, which is not sufficient to guarantee a low sliding angle (SA) for self-cleaning behavior. Also, there is very limited information about how a superhydrophobic coating influences the fabric handle property.

In this paper, we report on a simple coating technique to prepare superhydrophobic fabrics through the use of a coating solution synthesized by one-step co-hydrolysis and co-condensation of tetraethyl orthosilicate (TEOS) and alkyl silane. The effect of the type of organic silane on both water CA and SA is examined. The fabric bending

modulus is also measured to examine how alkyl silane affects the fabric softness properties after the superhydrophobic treatment.

2. Experimental Section

2.1 Materials and Measurements

Ethanol, TEOS, and ammonium hydroxide (28% in water) were obtained from Aldrich. Methyltriethoxysilane (MTES), octyl triethoxysilane (OTES, Dynasylan), and hexadecyl trimethoxysilane (HDTMS, Dynasylan 9116) were supplied by Degussa. Polyester (plain weave, 168 g/m²), wool (plain weave, 196 g/m²), and cotton fabrics (plain weave, 160 g/m²) were used in the present work.

Electron microscopic images and energy-dispersive X-ray (EDX) mappings were taken on a scanning electron microscope (SEM), Leo 1530 and JSM-5910, respectively. A transmission electron microscope (TEM, JEM-200 CX JEOL) was used to observe the silica particles. Fourier transform infrared (FTIR) spectra were measured on a FTIR spectrophotometer (Bruker Optics) in attenuated total reflection (ATR) mode. Water contact angles were measured through the use of a contact angle meter (KSV CAM200 Instruments Ltd). X-ray photoelectron spectra (XPS) were collected on a VG ESCALAB 220-iXL spectrometer with a monochromated Al K α source (1486.6 eV) using samples of ca. 3 mm² in size. The X-ray beam incidence angle is 0° with respect to the surface normal, which corresponds to a sampling depth of ca. 10 nm. The obtained XPS spectra were analysed by the XPSPEAK41 software.

The bending modulus of each fabric sample was measured by the cantilever method using a M003B Shirley stiffness tester in accordance to BS 3356, BS9073 (Part 7) and ASTM D1388. The bending modulus Q (g/cm²) was calculated according to the equations below:

$$Q = \frac{12G \times 10^{-3}}{g^3}$$

$$G = MC^3$$

Here, G (mg cm) is the flexural rigidity of the fabric, and M (mg/cm²) is the mass of the fabric per

square centimeter. C (cm) and g (cm) are the bending length and fabric thickness, respectively. The thickness of the fabric was measured using a MESDAN micrometer for fabric. Measurements were carried out on samples of fabric 2.5 cm wide and 20 cm long, and cut in the course and wale directions.

2.2 Synthesis of Coating Solution

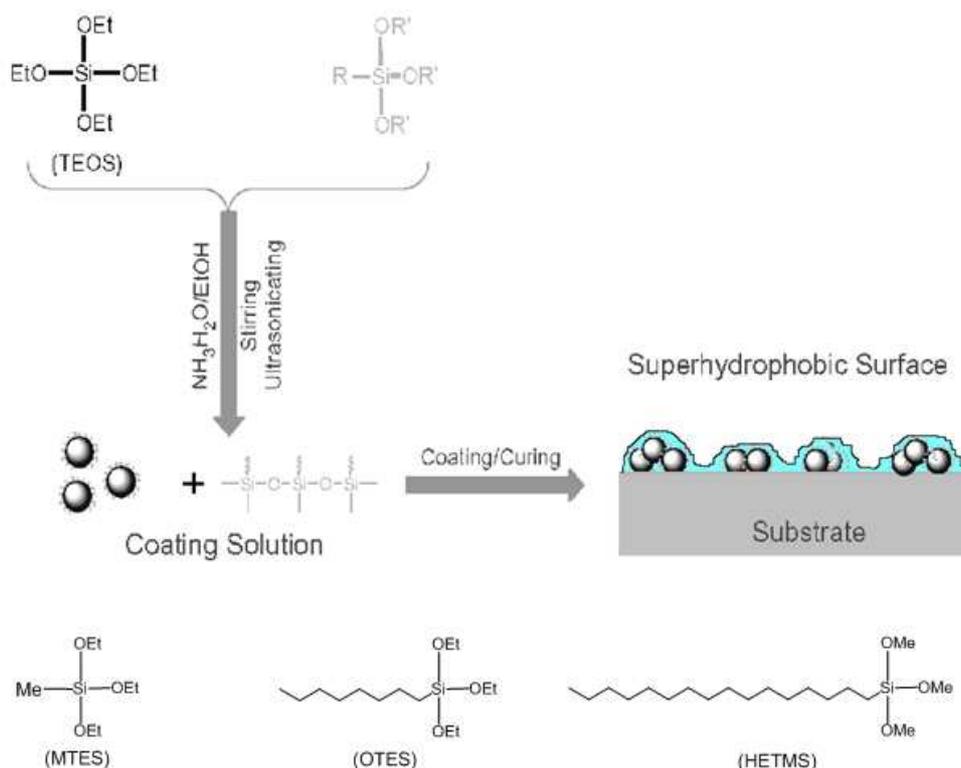
The typical sol preparation and coating procedure are as follows (Wang et al., 2008): TEOS (5 ml), together with an appropriate amount of silane, was dissolved in 25 ml of ethanol. The solution was mixed with an ammonium hydroxide/ethanol solution (6 ml of 28% $\text{NH}_3 \cdot \text{H}_2\text{O}$ in 25 ml of ethanol), and stirred intensively at room temperature for 12 hours. The mixture solution was then ultrasonicated (VCX750 Sonics & Materials Inc.) for 30 minutes to produce a homogeneous suspension.

2.3 Coating Procedure

The as-prepared solution was padded onto the fabric samples and dried at room temperature. Upon drying at room temperature, the treated substrate was further cured at 110°C for 1 hour.

3 Results and Discussion

The coating solution containing silica nanoparticles and silica resin was synthesized by co-hydrolysis and co-condensation of TEOS with an organic silane that has a non-hydrolyzable alkyl and three alkoxy groups in an $\text{NH}_3 \cdot \text{H}_2\text{O}$ -ethanol solution. Without any purification, the as-hydrolyzed reaction solution can be applied directly onto fabrics using a fabric coating technique, such as padding, dip-coating or spraying, to form a transparent coating on the fabrics. The procedure for preparation and fabric coating, and the structure of silane precursors are depicted in Scheme 1.



Scheme 1. Reaction route of silica sol preparation and coating procedure, and structures of silane precursors.

To understand the particle formation in the preparation, the two silane precursors were hydrolyzed separately under the same condition. It was observed that TEOS in the $\text{NH}_3\cdot\text{H}_2\text{O}$ -ethanol solution hydrolyzed quickly into silica particles that turned the solution milky, while the organic silane typically formed a thick and clear resin that phase-separated out from the solution, indicating that the hydrolysis of alkyl silane was much slower than that of TEOS. The resin-like hydrolysis product can be used to immobilize the particles on the fibre surface. When the two silane precursors were co-hydrolyzed, the quickly formed silica particles were covered with the slowly-hydrolyzed organic silane resin. There was no separated resin found in the solution even after 12 hours of reaction time.

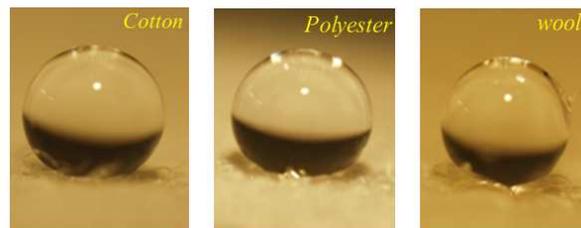


Fig. 1. Photos of water drop on the treated fabrics (Silanes TEOS/HETMS).

Figure 1 shows the highest superhydrophobicity achieved by the solution coating on different fabrics. The images clearly indicated that a nearly sphere-like water droplet (4 μl) was formed on the fabrics, and the droplet can stay on the treated fabric for a long period of time.

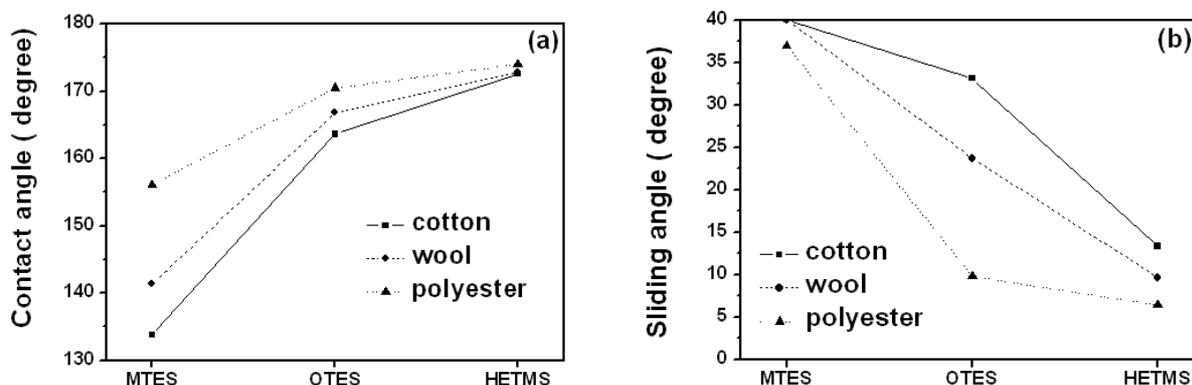


Fig. 2. Water CAs and SAs of the silica coated fabrics

The CA measurements indicated that the treated fabrics had a water CA of 174, 172 and 172.6° for the polyester, cotton and wool fabrics, respectively, when they were coated with a solution prepared from TEOS/HETMS. In contrast, the pristine fabric surface cannot support the formation of any spherical water droplet because of its lower water CA (117.1, 37.9 and 108° for the respective fabrics). The water CAs of the treated polyester, cotton and wool fabrics are shown in Figure 2a.

The SA for the coated fabric is shown in Figure 2b. For the fabrics treated with a thin layer of TEOS/HETMS hydrolysis product, the SAs for the treated fabrics were quite similar (less than 13 °), for the polyester, cotton and wool fabrics, although the coating loading varied in the range of 3.4~6.8 mg/cm^2 . These results suggested that when TEOS/HETMS sol was applied to the fabrics, the

surface properties were dominated by the feature of the silica coating,

The CA and SA values for the fabrics treated with other silane systems are also shown in Figure 2. It was interesting to note that the silica treatments did not make all the fabrics superhydrophobic. The treatment from MTES/TEOS solution only made the polyester fabric superhydrophobic. Although the treated cotton and wool fabrics showed a considerable increase in CA, the values were below 150°. Most treated cotton fabrics showed a lower CA value than did the wool and polyester fabrics, suggesting that both silane and fabric types influenced CA values.

The main difference among the MTES, OTES and HETMS is the chain length of the non-hydrolysable alkyl. The alkyl chain length for MTES, OTES and HETMS is C1, C8 and C16,

respectively. By associating the length of the alkyl chain with the water CA value, it is clear that increasing the alkyl chain length increases the CA value. Besides the water CA, the SA was also affected by the silane and fabric type. As shown in Figure 2b, the SA of all the MTES/TEOS-coated fabrics is greater than 35°. Due to instrument limitation, SAs greater than 40° were not obtainable. The SAs for the fabrics treated by TEOS/HDTMS sol solutions were lower than that treated by the TEOS/OTES solution. For MTES, OTES and HETMS, with the increase in the alkyl chain length, the coated fabric showed a reduced SA, which has a reverse trend to the CAs.

Figure 3 shows a typical surface morphology of silica coating on wool fibres. Particle-like materials were clearly observed after the coating treatment. These particles have an average size of ca.150-300 nm, and they aggregated randomly over the coated area and were immobilized by resin hydrolyzed from the alkyl silane. The size of the particles from different systems varied, being 240 ± 12 , 230 ± 46 and 190 ± 36 nm for the silane systems MTES, OTES and HETMS, respectively. The particulate/resin structure was also observed from other silane systems, and the particles had a similar size range (Figure 3b). This suggested that the particle size was mainly controlled by TEOS, and the long alkyl silane slightly influenced the particle size. The TEM image in Figure 3a shows that the nanoparticles were encapsulated with resin product, and some particles were stuck by the silane resin.

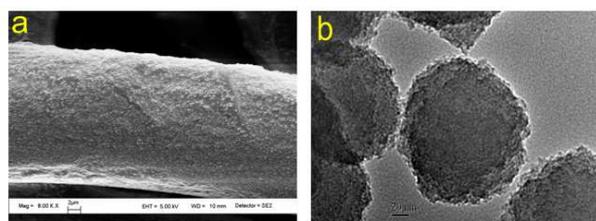


Fig. 3. SEM and TEM images of the coating surface and particles (Silanes: TEOS/HETMS).

The coverage of the coating was studied by SEM-EDX mapping. As shown in Figure 4, the coated fabric (TEOS/HETMS) surface reveals the presence of elements oxygen (O) and silicon (Si) in addition to the bulk carbon (C). Also, the coating covered the fabric surface uniformly. Similar results were also found for fabrics coated

with other silane systems.

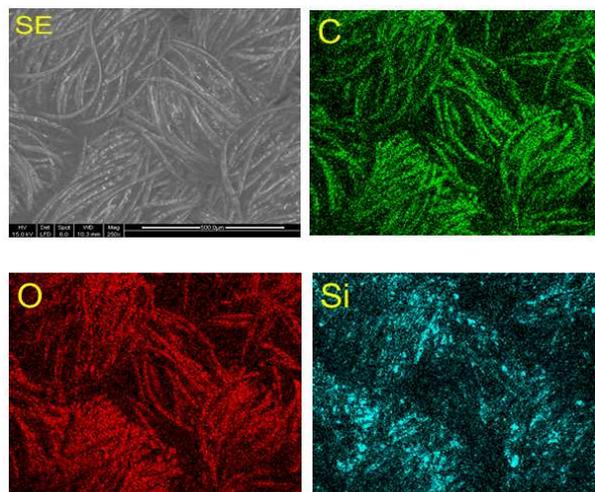


Fig. 4. SEM image and EDX mapping of elements O, Si, and C for the coated polyester fabric (Silanes TEOS/HETMS).

Apart from the microscopic investigation described above, the chemical nature of the fabric before and after the coating treatment has also been studied by FTIR and XPS (Figure 5). For all the coated surfaces, vibrations at 1087 and 810 cm^{-1} corresponding to the Si–O–Si asymmetric and symmetric vibrations, respectively, appeared in the FTIR spectra (Jeong et al., 2000).

The high resolution XPS C1s and Si2p spectra of the polyester fabric also showed the binding energies of 283, 285 and 288 eV after the coating treatment, which are typical for -CSi and -C-C/-CH and C-O moieties, respectively. The XPS peak at 104.6 eV is attributable to Si2p, which suggests that the fabric surface was indeed covered with silica. Other coated fabric showed similar characteristics.

The formation of the superhydrophobic surface derives from the hydrophobic silica nanoparticles immobilized onto the substrate to form a rough surface with a low free energy. The surface superhydrophobicity is highly influenced by the surface energy of silica particles which is associated with functional groups of the organic silane. The lower the surface energy is, the higher the superhydrophobicity. That is why alkyl with a longer alkyl chain could lead to higher water CAs and lower SAs.

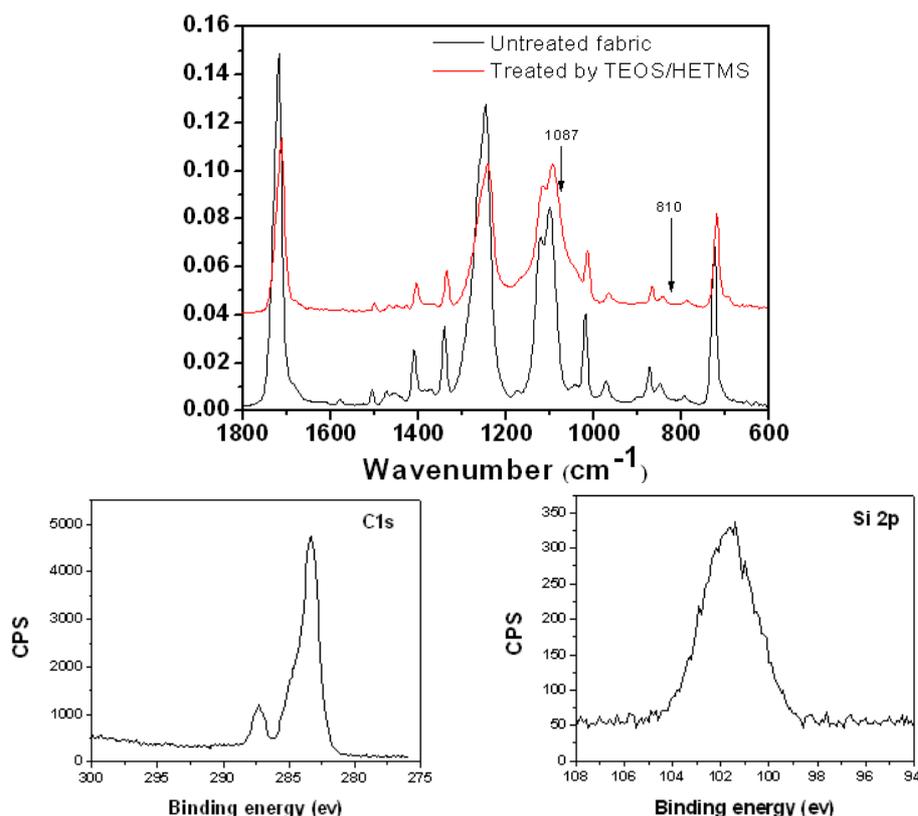


Fig. 5. FTIR spectra of fabric before and after the coating treatment, and XPS C and Si spectra of the silica coated fabric (Polyester, Silanes: TEOS/HETMS).

Besides the surface wettability, the bending modulus of the fabric before and after the coating treatment was also examined. The fabric bending modulus is an indication of the fabric comfort property. The higher the bending modulus, the more rigid the fabric was, and the fabric is less comfortable to wear. As shown in Figure 6, the coating increased the bending modulus and the silane type also influenced the modulus value.

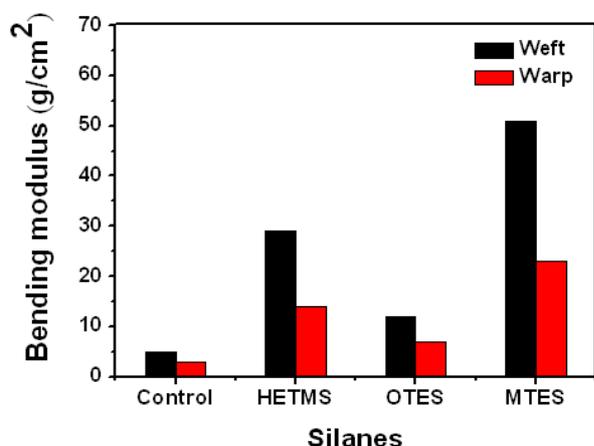


Fig. 6. Bending modulus of the polyester fabrics before and after the coating treatments.

Possible effect(s) of the substrate nature on the surface superhydrophobicity can be minimized by uniform coating (Wenzel, 1936; Cassie & S. Baxter, 1944), while the adhesion of particles to the substrate could be enhanced by the formation of interfacial chemical bonds (Arkles, 2001).

For the cotton fiber, the surface hydroxyl groups facilitated co-condensation with the partially hydrolyzed TEOS/silane (via Si-OH groups) to form interfacial Si-O-Si or Si-O-C bonds. On the other hand, polyester and wool could partially hydrolyze under alkaline condition to generate surface carboxylic groups for subsequent co-condensation with the Si-OH groups, leading to the formation of interfacial ester bonds.

4. Conclusion

We have demonstrated that coating solutions prepared by one-step co-hydrolysis and co-condensation of TEOS with an organic silane under alkaline condition can effectively generate superhydrophobic surfaces on different fabrics (e.g. polyester, wool and cotton). The alkyl chain length considerably influenced the surface hydrophobicity of the treated fabrics. For the silane bearing alkyl,

such as a long chain alkyl (C16), the resultant surface superhydrophobicity was little influenced by the intrinsic feature of the fabric substrate, and the treatment led to a high water CA ($> 170^\circ$) and a low SA ($< 15^\circ$). This work provides a simple, universal and cost-efficient method to produce a superhydrophobic surface on various fibrous substrates.

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