

## Fabrication of durable hydrophobic cellulose surface from silane-functionalized silica hydrosol via electrochemically assisted deposition

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**ABSTRACT:** Durable excellent hydrophobic surface on cellulose substrate was fabricated from the silica hydrosol functionalized with silane chemicals by a facile electrochemically assisted deposition technique. The silica hydrosol was synthesized using tetraethoxysilane (TEOS) as the precursor and sodium dodecylbenzene (SDBS) as the emulsifier under acidic conditions. The hydrophobic silane modifiers including octyltriethoxysilane (OTES), dodecyltriethoxysilane (DTES) and isooctyltriethoxysilane (iso-OTES) and the silane-coupling agent  $\gamma$ -mercaptopropyltriethoxysilane (MPTES) were used to dope the silica hydrosol for preparing durable hydrophobic cellulose surface. The cellulose surface modified with silane modifier iso-OTES exhibited the best hydrophobicity with water contact angle of  $162.3 \pm 0.5^\circ$  due to its non-polar and hydrolytically stable of  $-\text{Si}(\text{C}_8\text{H}_{17})$  groups. The addition of silane-coupling agent MPTES containing the  $-\text{SH}$  group led to good durability of hydrophobicity with water contact angle of  $130.0 \pm 1.2^\circ$  after 20 washing times. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42733.

**KEYWORDS:** applications; coatings; colloids; electrochemistry; textiles

Received 17 March 2015; accepted 14 July 2015

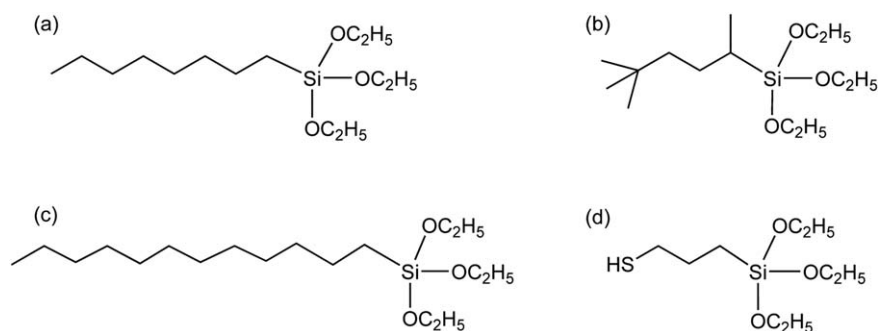
DOI: 10.1002/app.42733

### INTRODUCTION

Functional silica sol doped with long-chain silane agent can realize hydrophobic modification of substrate by creating a surface with certain degree of roughness and low surface free energy.<sup>1–3</sup> Regarding eco-friendly environment protection and cost-saving, fluoride-free long-chain silane agents have been chosen to create hydrophobic surfaces.<sup>4–6</sup> In general, sol-gel hydrophobic finishing process involves relatively large quantities of organic solvents like ethanol as the cosolvent to promote the compatibility of organic precursor and deionized water for preparing a homogeneous phase.<sup>7,8</sup> However, organic solvents are extremely flammable and high cost that limits the industrial production of sol-gel hydrophobic finishing. There have been some reports on the preparation of silica hydrosol without organic solvents. For example, Liu *et al.*<sup>9</sup> prepared silica hydrosol using cheap water glass (sodium silicate) with the acid catalyst and obtained superhydrophobic cellulose surface by dip-coating the silica hydrosol and self-assembling hexadecyltrimethoxysilane (HTMS). But the silica hydrosol prepared with water glass is unstable and easy to gel. Meng *et al.*<sup>10</sup> reported a one-step emulsion polymerization in aqueous solution to prepare highly monodisperse hybrid spherical nanoparticles from vinyltriethoxysilane (VTES). Xu *et al.*<sup>11</sup> investigated the preparation of silica hydrosol by the reaction of the precursor methyltrimethoxysilane (MTMS) under base condi-

tions via emulsion polymerization method. And excellent hydrophobic cellulose surface was obtained by the incorporation of basic silica hydrosol and subsequent hydrophobization with HTMS. The approach presents the silica hydrosol prepared via emulsion polymerization method can be used to fabricate hydrophobic textiles.

Conventionally, self-assembly-like methods including dip-coating, spray-coating and spin-coating are utilized to fabricate silica-based sol-gel films.<sup>12</sup> The driving force between the silica sol and the substrate surface by these self-assembly-like methods is limited. And it is not easy to deposit better hydrophobic film on the substrate surface.<sup>13,14</sup> Recently, the electrochemically assisted deposition technique has been used to fabricate sol-gel-derived hydrophobic silica films.<sup>15–17</sup> In the electrochemically assisted deposition process, a pH increase occurred in the micro acid silica sol near the negative electrode surface when applying an additional potential. It was attributed to the catalytic effect of cathodically generated  $\text{OH}^-$  ions via the reduction of oxygen or water splitting. This accelerated the condensation reactions of silane agents and sol, and caused the immediate deposition of the sol on the substrate surface. As a result, the film-forming of silica sol was promoted. For example, Luna-Vera *et al.*<sup>18</sup> successfully employed sol-gel electrochemistry to prepare highly rough inorganic silica films from alcohol silica sol. Wu *et al.*<sup>19</sup>



**Figure 1.** Molecular structures of (a) OTES, (b) iso-OTES, (c) DTES, and (d) MPTES.

reported a novel one-step sol-gel electrochemistry route to fabricate superhydrophobic surface on indium-doped tin oxide glass with a mixed alcohol sol solution containing tetraethoxysilane (TEOS) and HTMS. So far, there is not any report that combines the electrochemically assisted deposition technique and silica hydrosol for the fabrication of excellent hydrophobic cellulose surface. And the silica coating on the substrate surface performs poor washing durability of hydrophobic properties because of low compatibility and adhesion between the substrate surface and the silica gel coating. Silane agents<sup>20–22</sup> and synthesized silane polymers<sup>23,24</sup> containing functional groups have been proved to be the coupling agents to improve the washing durability of hydrophobicity.

In this article, a silica gel coating was deposited on cellulose substrate by the electrochemically assisted deposition technique with the functional silica hydrosol. The functional silica hydrosol was prepared with emulsifier sodium dodecylbenzene (SDBS), precursor TEOS and hydrophobic silane modifiers including octyltriethoxysilane (OTES), dodecyltriethoxysilane (DTES) and isooctyltriethoxysilane (iso-OTES). And the silane-coupling agent  $\gamma$ -mercaptopropyltriethoxysilane (MPTES) was employed as the crosslinker to improve the washing durability of hydrophobicity.

## EXPERIMENTAL

### Materials

Singed, desized, scoured, bleached and mercerized 100% woven cellulose fabrics weighting 141.0 g/m<sup>2</sup> were produced by Jiangsu Hongdou Industrial Co. (China). The OTES and DTES were purchased from Shandong Qufu Chenguang Chemical Co. (China). The iso-OTES and MPTES were gained from Hubei Jiangnan Fine Chemical Co. (China). The TEOS, SDBS and hydrochloric acid (HCl, 37%) were obtained from Sinopharm Chemical Reagent Co. (China). All the chemicals were analytical reagent grade. The molecular structures of main chemicals are listed as Figure 1.

### Preparation of Silica Hydrosol

The silica hydrosol was prepared via acidic hydrolysis of TEOS dispersed in a mixture of SDBS and deionized water. TEOS (6.0 g) and SDBS (0.4 g/L) were added to 100.0 g deionized water under magnetic stirring at room temperature for 1 h until an emulsion formed. Then 3 mL of HCl (0.1 mol/L) was added dropwise to the above mixture emulsion. The acid silica hydrosol was obtained after stirred at room temperature for 3 h and aged for 24 h.

### Electrochemically Assisted Deposition of Fabrics

The silica gel coating was directly *in-situ* deposited on cellulose substrate by electrochemistry from silica hydrosol doped with 2–8 wt % silane modifiers OTES, DTES or iso-OTES. The silane-coupling agent MPTES was also doped to the silica hydrosol to improve washing durability of hydrophobicity of fabric sample and the concentration of MPTES was varied from 0 to 2.0 wt %. The electrochemically assisted deposition process was carried out using copper electrode (C.E.) and platinum electrode (P.E.) at 15.0 V for 10 min. After electrochemically assisted deposition process, the fabric sample was quickly removed from the functionalized silica hydrosol and rinsed with deionized water. Then the fabric sample was dried at 60°C and baked at 150°C for 3 min in a curing oven (Mini Thermo 350, Thermo Co.). The schematic illustration of fabrication of hydrophobic surface on cellulose substrate from silica hydrosol doped with silane agents by electrochemically assisted deposition technique was presented in Scheme 1. The silane agents included hydrophobic silane modifiers and silane-coupling agent.

### Contact Angle Measurement

The water contact angle measurement was performed using the Krüss DSA100 Drop Shape Analysis System (Krüss GmbH, Germany) at the room temperature. The water contact angle values were determined after 20 s when the deionized water drop of 8  $\mu$ L began to still on fabric sample. All the water contact angle values were averaged from three measurements at different positions of the same fabric sample.

### Washing Durability Property

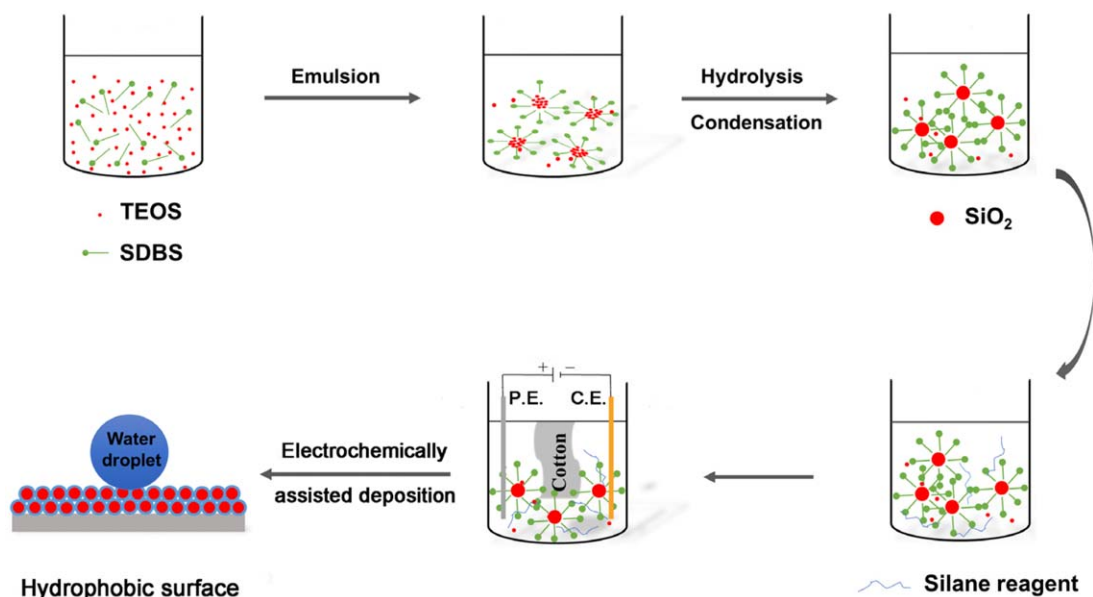
The washing durability of hydrophobicity of functionalized fabric sample was evaluated according to the standard of ISO 105-C10 : 2006 (E). The washing process was carried out using 3 g/L soap at 40°C for 30 min with the SW-12A laundering machine (Wuxi Textile Instrument Co., China).

### Scanning Electron Microscope Measurement

The surface morphologies of functionalized fabric samples were observed using the SU-1510 scanning electron microscope (JEOL, Tokyo, Japan) under 5000 $\times$  magnifications. Before testing, the fabric samples should be dried and then deposited with gold coating in a sputtering unit at a current of 10 mA.

### X-ray Photoelectron Spectroscopy Analysis Measurement

The surface chemical compositions of fabric samples were analyzed with the X-ray photoelectron spectroscopy (XPS,



**Scheme 1.** Fabrication of hydrophobic cellulose surface from silica hydrosol doped with silane agent by electrochemically assisted deposition technique. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

ESCALAB 250Xi, Thermo, USA) using an Al K $\alpha$  as excitation source. The analyzer was carried out in the constant analyzer energy mode at pass energy of 20 eV.

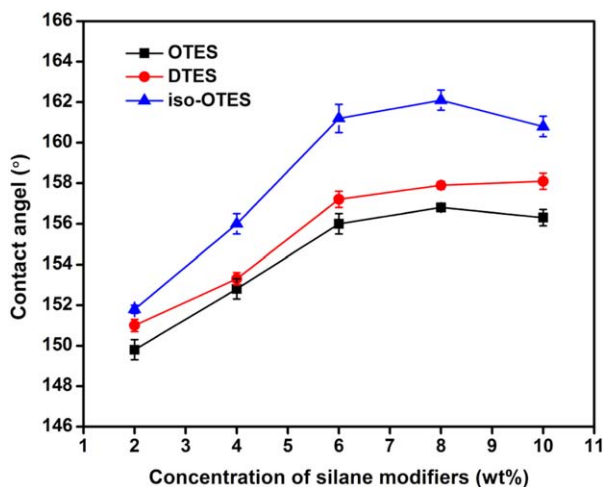
#### Thermogravimetric Analysis Measurement

Thermogravimetric analysis (TGA) of fabric sample was carried out using TGA/SDTA851E under nitrogen atmosphere. Fabric samples weighting 3–5 mg were heated from room temperature to 700°C at heating rate of 10°C/min.

## RESULTS AND DISCUSSION

### Effect of Silane Modifiers on Hydrophobicity of Fabrics

The hydrophobic modification of cellulose surface was carried out by varying the concentration of the hydrophobic silane modifiers OTES, DTES or iso-OTES from 2.0 wt % to 10 wt %.

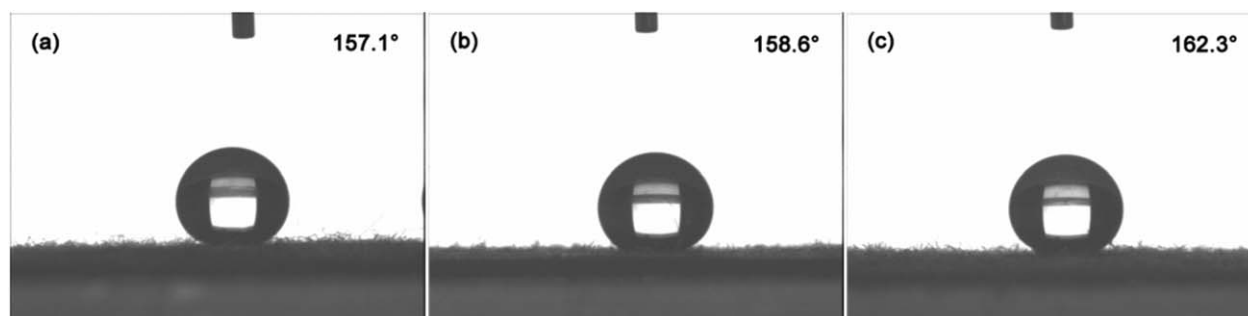


**Figure 2.** Relation curves of the concentration of silane modifiers on the hydrophobicity of deposited fabrics. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The surface wettability of fabric samples were evaluated by measuring the water contact angle of fabrics.

The relation curves between the concentration of hydrophobic silane modifiers and the water contact angles of fabrics were shown in Figure 2. As seen, the water contact angles of fabric samples deposited from silica hydrosol doped with hydrophobic silane modifiers were above 150.0° for a 8  $\mu$ L water drop. It was attributed to the fact that the electrochemically assisted deposition technique provided an additional driving force for sol-gel film formation, due to the catalytic effect of cathodically generated OH<sup>-</sup> ions via the reduction of oxygen or water splitting. A pH increase occurred in the micro acid silica sol near the negative electrode surface, and the condensation reactions of silane agents and sol were accelerated.<sup>15–17</sup> This caused the immediate deposition of the sol on the substrate surface. The film-forming of silica sol was promoted and the deposited fabric exhibited good hydrophobicity.

For the three hydrophobic silane modifiers, the water contact angles of fabrics increased gradually with increase in the concentration of silane modifiers up to 6 wt % and then almost remained constant thereafter. The result was because in higher than 6 wt %, the replacement of OH groups by hydrophobic groups of silane modifiers on the silica film was almost completed and no further silylation could proceed. Besides, the influence of the steric hindrance in branched alkyl groups prevented from further replacement of hydrophobic groups on the silica surface.<sup>25</sup> The water contact angle values of fabrics samples functionalized from silica hydrosol doped with 8 wt % OTES, DTES and iso-OTES were 157.1  $\pm$  0.2°, 158.6  $\pm$  0.2° and 162.3  $\pm$  0.5°, respectively. And the images of the water droplet (8  $\mu$ L) on cellulose substrate surface were presented in Figure 3. In terms of the fabric sample functionalized from silica hydrosol doped with 8 wt % iso-OTES, the larger water contact angle value was due to the introduction of the non-polar and



**Figure 3.** Images of water contact angles of fabric samples deposited from silica hydrosol modified with 8 wt % (a) OTES, (b) DTES, and (c) iso-OTES.

hydrolytically stable of  $-\text{Si}(\text{C}_8\text{H}_{17})$  groups on the cellulose substrate surface.<sup>26</sup>

#### Effect of MPTES on Washing Durability of Hydrophobicity

To improve the washing durability of hydrophobicity of functionalized fabrics, the silane-coupling agent MPTES varied from 0 to 2.0 wt % was used to dope the silica hydrosol. The water contact angles of fabric samples deposited from silica hydrosol with iso-OTES, MPTES before and after washing were shown in Figure 4.

From Figure 4, it was clear that all fabric samples (excluding the sample functionalized from silica hydrosol doped with 2.0 wt % MPTES) exhibited excellent hydrophobicity with the water contact angle above  $150^\circ$  before the washing. It implied that the addition of the silane-coupling agent MPTES containing hydrophilic group  $-\text{SH}$  could affect the hydrophobicity of the functionalized fabric sample.<sup>27</sup> All the samples exhibited different decrease of water contact angles after washing and the decrease increased with the increase of washing times.

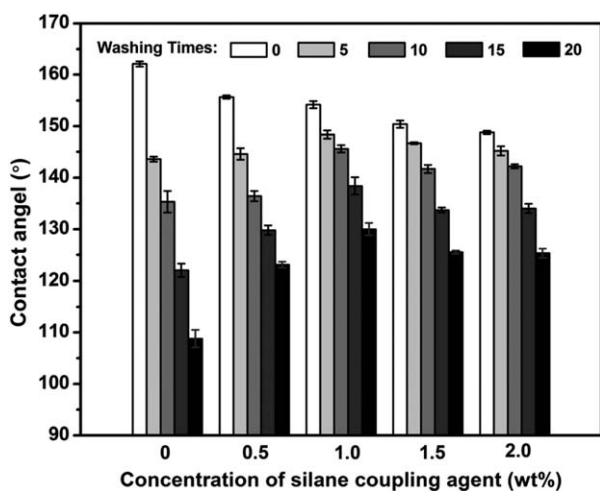
The fabric sample functionalized from silica hydrosol doped without MPTES presented an obvious decrease of hydrophobicity during washing. In contrast, all the fabric samples functionalized from silica hydrosol doped with MPTES exhibited good washing durability of hydrophobicity. Especially, for the fabric sample functionalized from silica hydrosol doped with 1.0 wt %

MPTES, the water contact angle still remained  $130.0 \pm 1.2^\circ$  after 20 washing times. The results indicated that the addition of silane-coupling agent MPTES improved the washing durability of hydrophobicity of fabric. It could be attributed to the fact that the addition of MPTES containing the  $-\text{SH}$  group played a role on the interaction between silica gel coating and cellulose surface.<sup>28,29</sup> As a result, the adhesion between cellulose substrate and silica gel coating was enhanced and the washing durability of hydrophobicity was improved. The schematic illustration of fabrication of durable hydrophobic cellulose fiber from silica hydrosol doped with hydrophobic silane modifier iso-OTES and silane-coupling agent MPTES was given in Scheme 2.

#### Morphology of Hydrophobic Fabrics

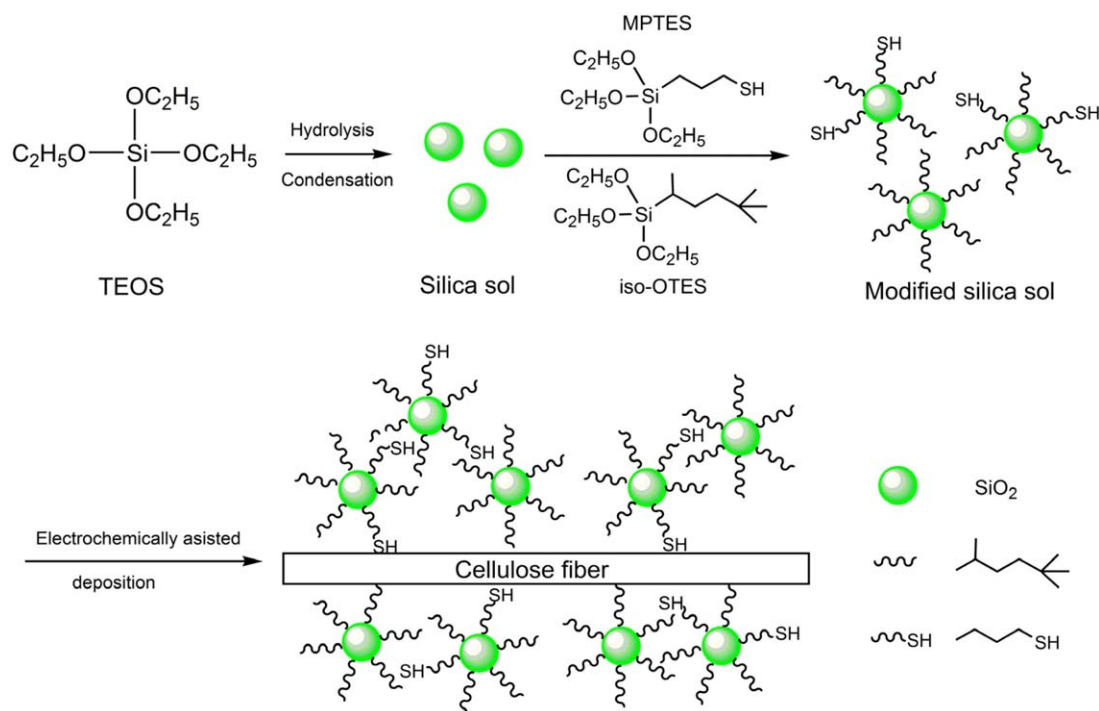
The surface morphologies of functionalized fabrics before washing and after 20 washing times were measured using SEM to characterize the durability of hydrophobicity directly. The fabric samples were functionalized from the silica hydrosol doped with only iso-OTES or iso-OTES and MPTES. As shown in Figure 5(a,c), both cellulose fiber surfaces before washing were deposited with a silica gel coating, which made surfaces rough and hydrophobic. The water contact angle values of fabric functionalized from silica hydrosol doped with only iso-OTES and doped with iso-OTES, MPTES were  $162.3 \pm 0.5^\circ$  and  $154.2 \pm 0.7^\circ$ , respectively. The fabric functionalized from silica hydrosol doped with iso-OTES and MPTES also presented good hydrophobicity even the addition of the silane-coupling agent MPTES could decrease the water contact angle of fabric sample compared to the sample functionalized from silica hydrosol doped with only iso-OTES. However, the silica gel coating deposited from the silica hydrosol with iso-OTES and MPTES was slightly dense compared to the silica gel coating deposited from the silica hydrosol with only iso-OTES.

After 20 washing times, obvious changes of surface morphologies could be clearly observed in the SEM images. As shown in Figure 5(b), a large break of silica gel coating was observed on the surface of fabric sample functionalized from silica hydrosol doped with only iso-OTES after 20 washing times. The water contact angle of fabric sample was merely  $108.8 \pm 1.7^\circ$  and the vanished parallel ridges and grooves on cellulose fiber tended to appear again, denoting the seriously flaking off of functionalized silica gel coating. In SEM image of the fabric sample functionalized from silica hydrosol doped with iso-OTES and MPTES, broken coating of silica gel was observed after 20 washing times. But there also existed lots of silica gel flaking on cellulose fiber

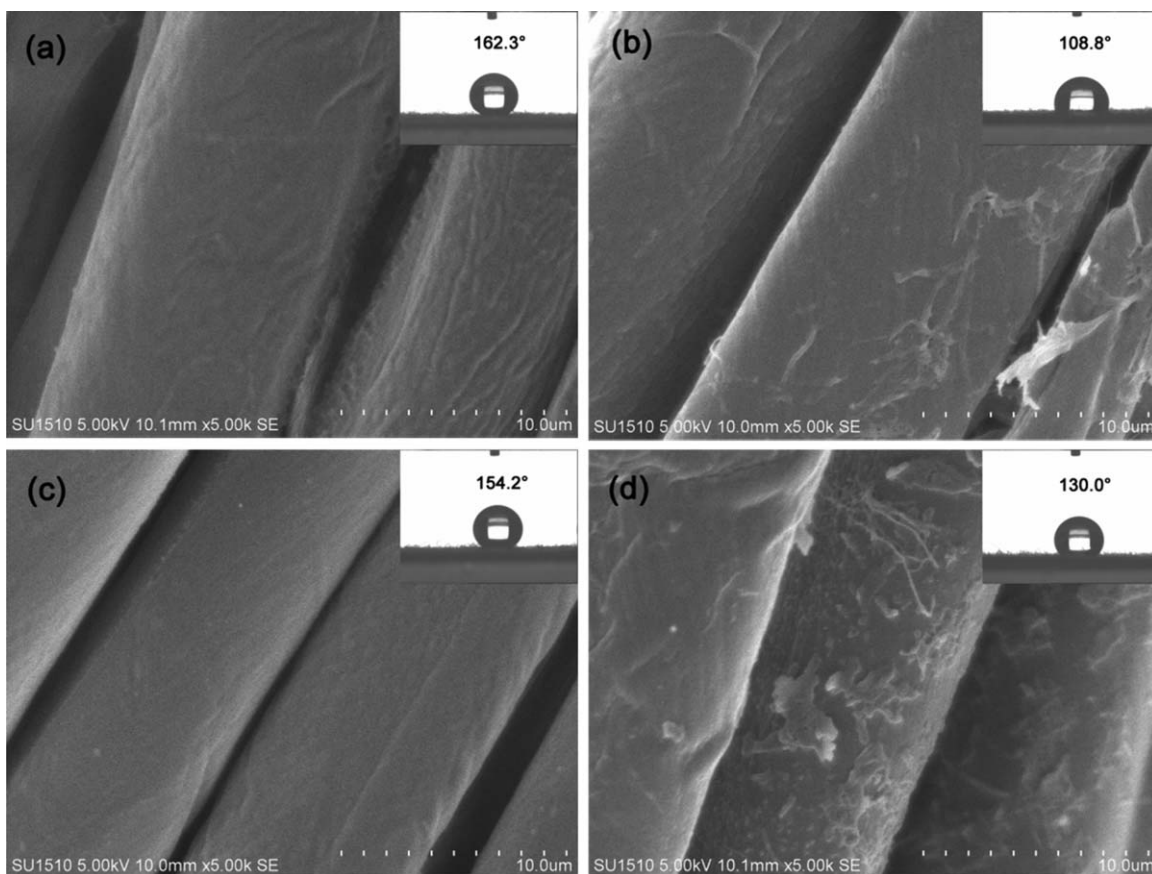


**Figure 4.** Effect of concentration of silane-coupling agent MPTES on washing durability of hydrophobicity.

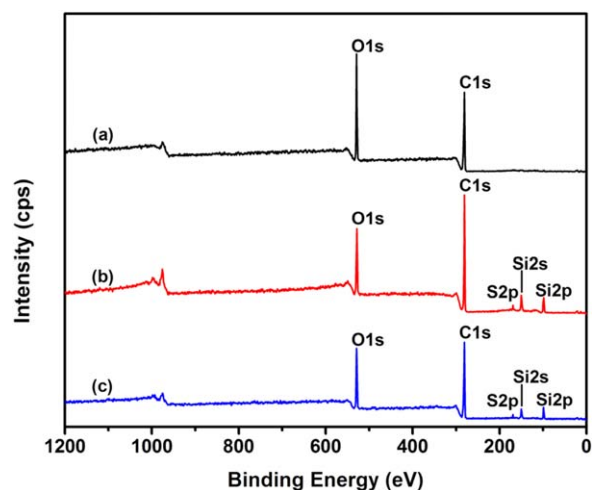




**Scheme 2.** Schematic illustration of fabrication of durable hydrophobic cellulose fiber from silica hydrosol doped with iso-OTES and MPTES. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 5.** SEM images of fabric samples functionalized from silica hydrosol modified with only 8 wt % iso-OTES (a) before washing and (b) after 20 washing times; fabric samples functionalized from silica hydrosol modified with 8 wt % iso-OTES and 1 wt % MPTES (c) before washing and (d) after 20 washing times.

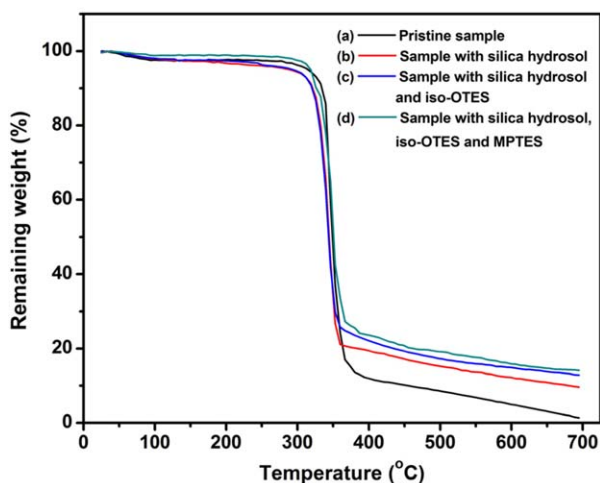


**Figure 6.** XPS spectra of (a) the pristine fabric sample, fabric sample functionalized from silica hydrosol modified with 8 wt % iso-OTES and 1 wt % MPTES (b) before washing and (c) after 20 washing times. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

compared to the fabric sample functionalized from silica hydrosol doped with only iso-OTES. The fabric sample also showed better hydrophobic property with the water contact angle remaining  $130.0 \pm 1.2^\circ$ . The results indicated that the silica gel coating of the fabric sample functionalized from silica hydrosol doped with iso-OTES and MPTES had a stronger adhesion to cellulose fiber than that of sample functionalized with only iso-OTES. It also indicated that the addition of the silane-coupling agent MPTES played a role in the improvement of washing durability of hydrophobic fabric.

#### XPS Analysis of Fabrics

To determine the surface chemical compositions of functionalized fabrics before washing and after 20 washing times, the sam-



**Figure 7.** TGA curves of (a) the pristine fabric sample, (b) the fabric sample functionalized from silica hydrosol, (c) the fabric sample functionalized from silica hydrosol with 8 wt % iso-OTES, and (d) the fabric sample functionalized from silica hydrosol with 8 wt % iso-OTES and 1 wt % MPTES. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table I.** Chemical Composition of Fabric Samples

Samples	Chemical composition (at %)			
	C	O	Si	S
Pristine fabric	64.83	35.17	0	0
Before washing	62.27	21.83	14.81	1.09
After 20 washing times	61.93	26.79	10.37	0.91

ples were characterized by XPS measurement. In terms of the pristine fabric sample, only peaks at 283 eV and 530 eV corresponding to C and O elements were detected, as shown in Figure 6(a). In contrast, in the XPS spectra of the functionalized fabric sample before washing, the additional characteristic peaks of S2p, Si2s, and Si2p appeared at 164 eV, 150 eV and 101 eV, respectively. Moreover, there was a large increase of the C/O ratio from 1.84 to 2.85 according to Table I that could contribute to the long alkyl group in iso-OTES. The results confirmed that the silica hydrosol modified with iso-OTES and MPTES was deposited onto cellulose fibers.

As for the functionalized fabric sample after 20 washing times, the C/O ratio (2.31) and the intensities of Si2s, Si2p decreased with respect to the functionalized fabric sample before washing. It implied that part of the hydrophobic silica gel coating had been removed from the cellulose fiber surface by washing process. However, the hydrophobic silica gel coating was not removed fully after 20 washing times. This also explained the better hydrophobic property of the functionalized fabric sample after 20 washing times. It further confirmed that the fabric sample functionalized from the silica hydrosol doped with iso-OTES and MPTES performed good washing durability of hydrophobicity.

#### Thermogravimetric Analysis of Fabrics

Thermogravimetric analysis was carried out to evaluate the remaining weight of fabric samples. As presented in the Figure 7, after being heated to 700°C, the remaining weight percentage of the pristine fabric sample was 1.34%, which showed the pristine fabric sample was almost burned away. As for the fabric sample functionalized with silica hydrosol, the remaining weight was 9.62%, which implied that the silica nanoparticles were successfully deposited on the cellulose fiber surface. In terms of the fabric sample functionalized from silica hydrosol doped with iso-OTES, the remaining weight increased to 12.83%. The increase indicated that the hydrophobic silane modifier of iso-OTES with low surface energy was deposited onto cellulose fiber surface with silica nanoparticles. Compared to the fabric sample functionalized from silica hydrosol doped with only iso-OTES, the remaining weight of the fabric sample functionalized from silica hydrosol doped with iso-OTES and MPTES further increased to 14.16%. The result implied that the silane-coupling agent of MPTES was deposited onto cellulose fiber surface as well as silica nanoparticles and iso-OTES.

## CONCLUSIONS

The durable excellent hydrophobic surface on cellulose substrate was fabricated using functionalized silica hydrosol via a facile electrochemically assisted deposition technique. The silica hydrosol was prepared using emulsifier SDBS, precursor TEOS and acidic catalyzer HCl. The good hydrophobic fabric with more than water contact angle  $157.0^\circ$  was obtained with OTES, DTES or iso-OTES as the silane modifiers. The maximum water contact angle was  $162.3 \pm 0.5^\circ$  using 8 wt % iso-OTES which contained the non-polar and hydrolytically stable of  $-\text{Si}(\text{C}_8\text{H}_{17})$  groups. The addition of silane-coupling agent MPTES with the  $-\text{SH}$  group improved the washing durability of hydrophobicity of fabric. The water contact angle of fabric still remained  $130.0 \pm 1.2^\circ$  after 20 washing times using 1.0 wt % MPTES. The electrochemically assisted deposition of silica hydrosol is simple and ensures its promising application in fabricating durable hydrophobic textiles.

## ACKNOWLEDGMENTS

The authors are grateful for the financial support of National Natural Science Foundation of China (21174055).

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