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Fabrication of Superhydrophobic Cellulose-Based Materials through a Solution-Immersion Process

Shenghai Li, Suobo Zhang,* and Xianhong Wang

State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences, Changchun 130022, China

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An industrial waterproof reagent [(potassium methyl silicate) (PMS)] was used for fabricating a superhydrophobic surface on a cellulose-based material (cotton fabric or paper) through a solution-immersion method. This method involves a hydrogen bond assembly and a polycondensation process. The silanol, which was formed by a reaction of PMS aqueous solution with CO₂, was assembled on the cellulose molecule surface via hydrogen bond interactions. The polymethylsilsesquioxane coatings were prepared by a polycondensation reaction of the hydroxyl between cellulose and silanol. The superhydrophobic cellulose materials were characterized by FTIR spectroscopy, thermogravimetry, and surface analysis (XPS, FESEM, AFM, and contact angle measurements). Analytical characterization revealed that nanoscale roughness protuberances uniformly covered the surface, thus transforming the cellulose from superhydrophilic to superhydrophobic with a water contact angle of 157°. The superhydrophobic coatings were satisfactory with regard to both chemical and mechanical durability, and because of the transparency of the coatings the native cotton fabric displayed no changes with regard to either morphology or color. The easy availability of the materials and simplicity of this method render it convenient for mass production.

Introduction

In recent years, superhydrophobic surfaces with water contact angles (CA) higher than 150° have attracted considerable interest with respect to both academic research and industrial applications because of their self-cleaning properties.^{1–8} It has been proposed that the superhydrophobicity arises from the combination of hierarchical micro- and nanostructures of the surfaces as well as from the low surface energy of the materials.^{9–13} Hence, many approaches, such as lithographic patterning,^{14,15} laser/plasma etching,^{16,17} vertical alignment of nanotubes/nanofibers,^{18–20} sol–gel methods,^{21–23} phase separation,^{24,25} assembly,^{26–30}

glancing angle deposition,³¹ and solution-immersion methods^{32,33} have been developed for the design and fabrication of superhydrophobic surfaces. Among these approaches, the solution-immersion method has been found to be a simple and effective technique for depositing superhydrophobic coatings onto substrates. Moreover, it gives rise to advantages such as large deposition areas, uniform deposits on the objects with desired shapes, and short processing times.³⁴ However, the solution-immersion method for fabrication of superhydrophobic surfaces was usually used on rigid engineering materials and seldom used on soft material. It is especially true when considering the fabrication of superhydrophobic coatings onto soft material surfaces. Furthermore, the preparation of soft superhydrophobic materials could extend their practical applications.

Cellulose is one of the most abundant biopolymers and the basis for many industrial derivatives and products.³⁵ The creation of superhydrophobic, self-cleaning, cellulose-based materials could find potential applications in both the textile industry and packaging area, and it is also inspired by the use of an environmentally friendly renewable resource.³⁶ Therefore, the

* To whom correspondence should be addressed. E-mail: sbzhang@ciac.jl.cn

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exploration of a facile means of transforming a very hydrophilic cellulose into an extremely hydrophobic one is justified. So far, dyeing technologies,³⁷ and branched "graft-on-graft" methods³⁸ have been investigated for constructing superhydrophobic cloth and/or paper surfaces. However, these techniques are still subject to limitations including severe conditions, tedious fabrications, and expensive materials.

The coating of surfaces with covalently attached silanes is well known.^{39,40} This field of search is predominated by silicone chemistry and could benefit from the ability to generate nanostructures through the hydrophobization of surfaces.⁴¹ The coating of silica or silicon substrates with one of the simplest silanes, that is, trichloromethylsilane (TCMS), has been reported via gas phase and solvent-solution reaction routes.⁴² In our previous work, superhydrophobic cellulose materials were prepared by chemical vapor deposition of TCMS onto hydrophilic cellulose.⁴³ Seeger and co-workers⁴⁴ were the first to report on the fabrication of silicone nanofilaments onto various substrates by polymerization of equimolar amounts of liquid TCMS and water vapor. The obtained coating consisted of polymethylsilsesquioxane nanofilaments with a superhydrophobic character. Although superhydrophobic wood and cotton fabric were prepared with this method, the mechanical properties of the cotton fabric were found to decrease due to the cellulose degrading as a result of the reaction conditions. It is known that hydrogen chloride is generated when hydroxyl substrates are treated with TCMS.⁴² Hence, when cellulosic materials are treated with TCMS, an aqueous alkaline or an ammonia atmosphere must be employed to neutralize the hydrogen chloride. Otherwise, the acidic solution can cause degradation of the cellulose. Although Robbart⁴⁵ developed a new method for the treatment of cellulosic materials with TCMS that eliminated the need of a subsequent step for neutralizing hydrogen chloride, much attention should be paid to the pretreatment of the substrate, such as substantially frozen or superdry conditions.⁴⁵ In view of these tedious treatments, other available silicon materials and facile methods should be developed for the fabrication of hydrophobic cellulose materials.

Herein, we present a facile approach consisting in a solution-immersion process for the transformation of normal hydrophilic cellulose-based materials into superhydrophobic ones with covalently attached nanoscale polymethylsilsesquioxane. A commercially available waterproof reagent [potassium methyl silicate (PMS)] was used for fabricating these superhydrophobic surfaces. By using PMS, it was possible to eliminate the acidic byproduct and retain the mechanical properties of the cellulose materials. This renders PMS a more preferable reagent for fabricating superhydrophobic surfaces as compared to organic silicon halides.

Experimental Section

Materials. Filter paper and cotton were purchased from Shanghai Kechuang Chemicals Co., Ltd., and cotton fabric was obtained from a general store. Potassium methyl silicate aqueous solution (10

wt %) was supplied by Jilin Huiyuan Organosilicon Co., Ltd. and was used as received.

Preparation of Superhydrophobic Cellulose Materials by a Solution-Immersion Process. The first step in the fabrication of superhydrophobic cellulose materials involved the assembly of a precursor silanol film on the cellulose surface. The silanol solution was prepared by reacting the potassium methyl silicate (PMS) aqueous solution with CO₂ at room temperature. Typically, 2.1 g of cotton fabric (or filter paper) was soaked in 300 mL of deionized water, and 4.2 g of PMS aqueous solution was added under stirring so that the PMS content was 20 wt % relative to the cellulose material. The pH value of the mixture so formed was 12.5. Subsequently, CO₂ was bubbled through the mixture for approximately 5 min until the pH value was lowered to within the range of 7.5–8.5. After the pH value had been reduced, the methyl silicate formed silanol and slowly condensed, giving rise to oligomeric and polymeric siloxane. After preparation of the silanol solution, the cotton fabric (or filter paper) was allowed to soak in the solution for 1 min. To generate a dense coating, the cotton fabric sample was then removed from the solution, washed with water three times, and dried in a vacuum oven at 120 °C for 30 min.

Preparation of Hollow Silica Replicas. Hollow silica replicas of the as-prepared superhydrophobic cotton fabric were prepared by a heat treatment in air at 500 °C for 6 h (heating rate 10 °C/min).

Modified Fiber Characterization. FT-IR spectra were recorded on a Bruker Vertex-70 instrument with 128 scans per sample. Surface chemical characterizations were carried out by X-ray photoelectron spectroscopy (XPS) on a Thermo ESCALAB 280 system with Al/K α radiation as the X-ray source. Thermogravimetric analysis (TGA) results were obtained in air with a Perkin-Elmer TGA-2 thermogravimetric analyzer equipped with a platinum cell. Samples were heated at a constant rate of 10 °C/min from 25 to 900 °C under an air flow of 20 mL/min. The morphology of the sample was characterized by an XL30 ESEM FEG field emission scanning electron microscope (FE-SEM, FEI Company with an operating voltage of 20 kV) as well as by atomic force microscopy (AFM, Seiko Instruments Industry, Co. Ltd. SPA300HV with an SPI 3800 controller). Contact angles were obtained by Drop Shape Analysis DSA10 (Krüss GmbH, Germany) at ambient temperature, and the values were averages from measurements on at least five different positions for each sample.

Results and Discussion

Binding of Polymethylsilsesquioxane to the Cellulose Fiber Surface. To perform the hydrophobic modification of the cellulose fiber surface, a commercially available waterproof reagent, that is, PMS, was utilized. PMS is known to remain freely soluble in highly alkaline aqueous solutions (pH > 12).⁴⁶ When the pH value is reduced, the methyl silicate forms silanol and slowly condenses to form oligomeric and polymeric siloxane. The pH-lowering agent may be selected among acids such as hydrochloric acid, sulfuric acid, nitric acid, or organic acids. The addition of the pH-lowering agent to the mixture should be conducted gradually, as a sudden change in the pH can cause precipitation of silicone.⁴⁷ In the present experiment, CO₂ was used as the pH-controlling agent to reduce the pH value during the preparation of the silanol solution. Potassium carbonate and potassium bicarbonate were formed as a byproduct when the pH value was in the range of 7.5–8.5.⁴⁷

A cotton fabric and a filter paper were used as the source of cellulose fibers, because they are composed of uniform cellulose fibers and present interspaces among the highly interlaced fibers. These interspaces may allow guest molecules to penetrate into their inner spaces. Thus, after formation of the silanol solution, silanol could be readily impregnated into the cellulose fibers

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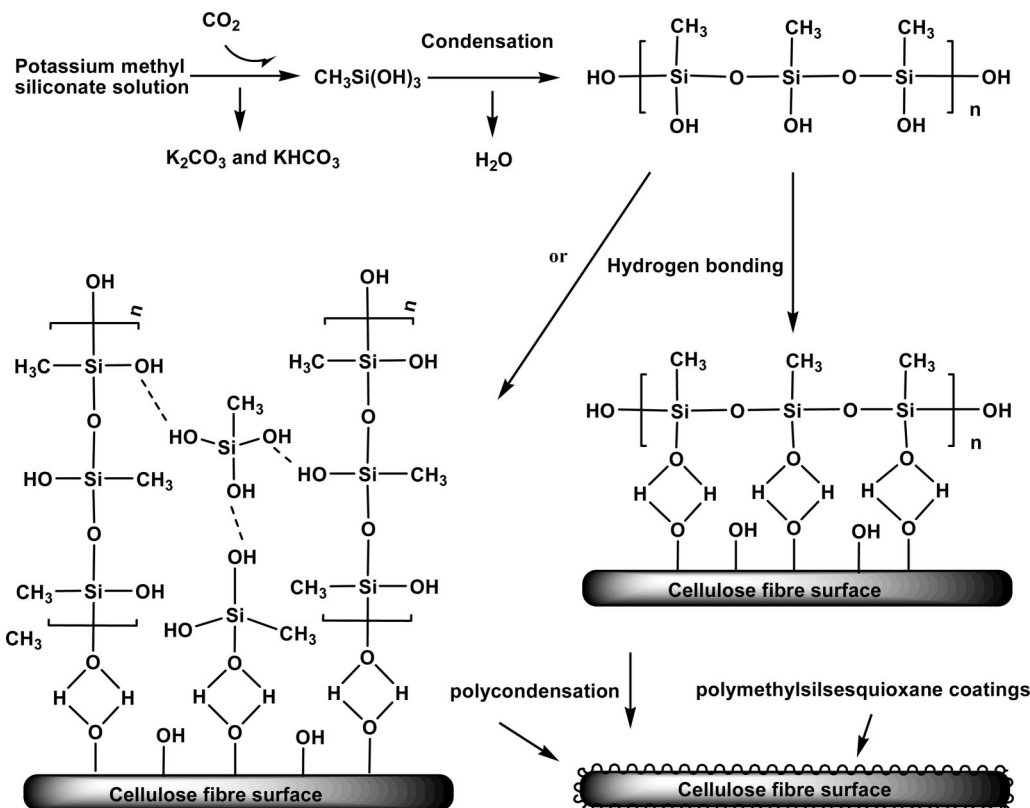


Figure 1. The formation of a superhydrophobic polymethylsilsesquioxane coating on a cellulose fiber surface.

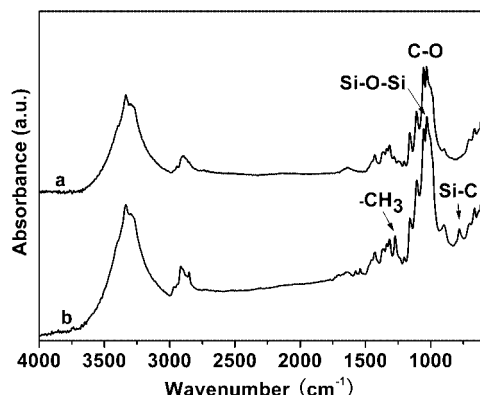


Figure 2. FT-IR spectra of the superhydrophobic cotton fabric surface for (a) the native cotton fabric and (b) the modified cotton fabric.

through the interspaces. The $-\text{Si}-\text{OH}$ groups of the hydrolyzed silane were initially assembled on the fiber surfaces via hydrogen bonds with cellulose $-\text{OH}$ groups.⁴⁸ As the reaction proceeded, water was lost and a covalent bond was formed. The reaction of the hydrolyzed silanes with the surface $-\text{OH}$ groups ultimately resulted in the condensation of a siloxane polymer that encapsulated the cellulose fibers thus giving rise to a coating (as shown in Figure 1). The polymethylsilsesquioxane thereby became covalently bound to the surface of the cellulose fibers via a polycondensation reaction under heat treatment.

Surface Element Characterization. The polymethylsilsesquioxane coating on the cotton fabric was confirmed by FT-IR (Figure 2) and X-ray photoelectron spectroscopy (XPS) (Figure 3) analyses. The FT-IR spectra displayed two absorption peaks

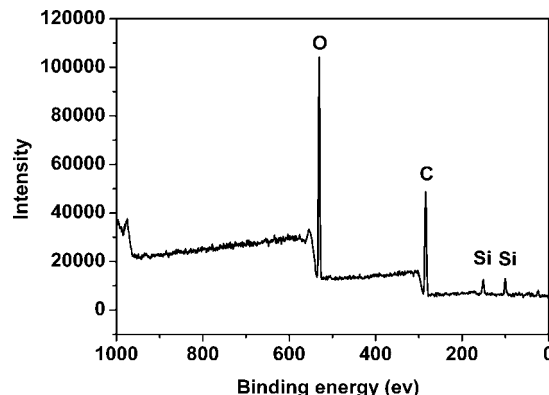


Figure 3. XPS spectra of the surface of the superhydrophobic cotton fabric.

located at 780 and 1273 cm^{-1} , which were assigned to stretching vibrations of the $\text{Si}-\text{C}$ bonds and to $-\text{CH}_3$ deformation vibrations of the siloxane components, respectively. The typical absorption peaks of the $\text{Si}-\text{O}-\text{Si}$ bonds of the siloxane components that appeared at 1130–1000 cm^{-1} were seen to overlap with that of the cellulose $\text{C}-\text{O}$ bonds. In the XPS spectrum of the as-prepared cotton fabric, the appearance of two typical peaks with binding energies of 150 and 100 eV, corresponding to Si 2s and Si 2p, respectively, indicated the presence of silicon at the surface. The Si content was estimated to be 4.7 wt % for the cotton fabric immersed in the silanol solution for 6 min.

Thermal Degradation. The thermal stability, as well as the TGA profile, of the modified fibers was in general very similar to that of the pristine substrates, as illustrated in Figure 4. The figure displays the typical single weight loss feature with a maximum decomposition temperature in the range of 270–350 $^{\circ}\text{C}$. The TGA results indicated an increase in fiber hydrophobicity after modification, as shown by the absence of the typical moisture

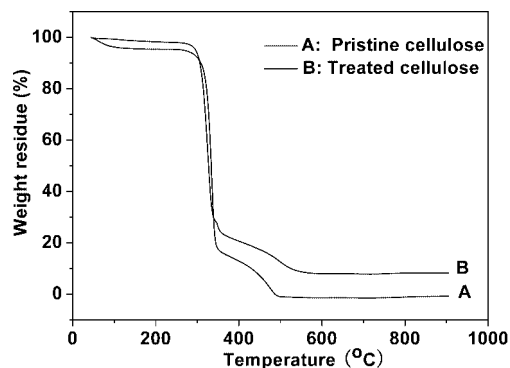


Figure 4. Thermogravimetric analysis of the cotton fabric before and after hydrophobic coating.

loss around 100 °C. This suggested a negligible water adsorption as compared to that of the pristine fibers. The TGA profile also indicated that the superhydrophobic fiber contained approximately 10 wt % of silica at the surface.

Characterization of the Surface Morphology. The surface morphology and roughness were investigated by both FE-SEM and AFM. Figure 5a–c shows typical top views of the native cotton fabric as well as the modified cotton fabric. The native cotton fabric presented a highly textured microscale fiber with a typically smooth surface (Figure 5a). However, a thin layer of nanoscaled spherical protuberances was observed on the as-prepared superhydrophobic fiber surfaces (Figure 5b). These protuberances were possibly due to the deposition of the polymethylsilsesquioxane network on the surface of the microfibrils.^{48,49} The height of the protuberances pattern was estimated to 80–200 nm, and the roughness of the fiber to around 50 nm (Figure 5d). In addition, the coating layer appeared not to lead to any deleterious effects on the morphology of the native cotton fabric (Figure 5c). Figure 5e,f demonstrates that the morphologies and the color of both the cotton fabric and the filter paper remained unchanged after treatment with PMS. This indicates that the coating layer was transparent. The optical image of water droplets on the surface of a coated colored cotton fabric provided a direct demonstration of the transparency of the superhydrophobic coating.

Existing “graft-on-graft” methods for constructing superhydrophobic paper³⁸ consist in the paper surface being clearly covered by the polymer, leading to apparent changes in the surface morphology of the filter paper. Contrastingly, our method produced polymethylsilsesquioxane layers on the individual fiber surfaces, and by controlling the reaction conditions it was possible to maintain both the morphology and the color of the native cotton fabric. This method was highly effective, simple and convenient for fabricating superhydrophobic surfaces and also resulted in a transparent, morphologically unaltered superhydrophobic product for further use. Such polymethylsilsesquioxane coatings are believed to have promising applications in the fabrication of superhydrophobic biomacromolecular materials and as environmentally friendly water-repellent substitutes for commonly used fluorine compounds.^{50,51}

In an effort to obtain precise information concerning the nanocoating, the as-prepared superhydrophobic cotton fabric was calcined in air at 500 °C to remove the native cotton

fiber.⁵² The FE-SEM image of the resulting residue material after calcination displayed the nanocoating as a hollow “textilelike” silica, an exact replication of the cotton fiber (Figure 6a). The thickness of the coated layer was determined to be 180 nm (Figure 6b). The true thickness was probably thicker, as shrinkage always occurs to the overall dimension of a coating during calcination. The observation suggested that the polymethylsilsesquioxane was completely coated on the surface of single fibers, thus preventing water from coming into contact with hydroxyl groups on the fiber surface, and resulting in a superhydrophobic cotton fabric surface. This suggestion is in good agreement with the results from the CA measurements.

Contact Angles. The contact angles of the native cotton fabric and filter paper were 0° due to the superhydrophilic nature of the cellulose (Figure 7a). As anticipated, the introduction of the tailored silicone coating onto the substrate transformed it from superhydrophilic to superhydrophobic. The high CA values, that is, 158° for the modified cotton fabric and 157° for the modified filter paper, were obtained under optimal conditions (Figure 7b,c). These results indicated a predominant contribution of the low surface energy polymethylsilsesquioxane coating to the wettability of the surface.

When a water droplet sits on a hydrophobic cotton textile surface, the wetting behavior can be described by the equation from Cassie and Baxter⁵³

$$\cos \theta_{CB} = f_1 \cos \theta - f_2 \quad (1)$$

where θ_{CB} (155°) is the observed water CA on a rough, porous surface, θ (104°) is the intrinsic water CA on the smooth polymethylsilsesquioxane surface, f_1 is the liquid/solid contact area divided by the projected area, and f_2 is the liquid/vapor contact area divided by the projected area. Equation 1 has been recently modified to account for the local surface roughness on the wetted area as follows.^{54,55}

$$\cos \theta_{CB} = r_f f \cos \theta + f - 1 \quad (2)$$

where f is the fraction of the projected area of the solid surface in contact with water ($f_2 = 1 - f$) and r_f is the surface roughness of the wetted area. When polymethylsilsesquioxane particles are chemically incorporated onto the cotton fiber surface in our study, r_f is further increased in comparison with a smooth wetted area. Once r_f reaches a certain level, air may become trapped between silica particles underneath a water droplet, which would further enhance the surface hydrophobicity. The superhydrophobicity of the as-prepared materials can thus be attributed to the association of the fraction of air in the interspaces and the use of a low-surface-energy coating. Furthermore, the contribution of the woven structures on the hydrophobicity of the surface cannot be ruled out.⁵⁴

Chemical Stability. The chemical durability of the superhydrophobic coating was evaluated by measuring the change in CA values after treating the obtained materials with aqueous solutions of varying pH (Figure 8). It was found that the resulting superhydrophobic fabric displayed a satisfactory durability with CA values >140° after treatment with slightly acidic, neutral and mildly basic solutions for 96 h (Figure 8a). However, the corresponding CA values decreased dramatically after treatment with a strong basic solution (Figure 8b). To get a direct idea of the durability of the textile, a cotton fabric was washed with soap or laundry detergent in a regular laundry cycle. The superhy-

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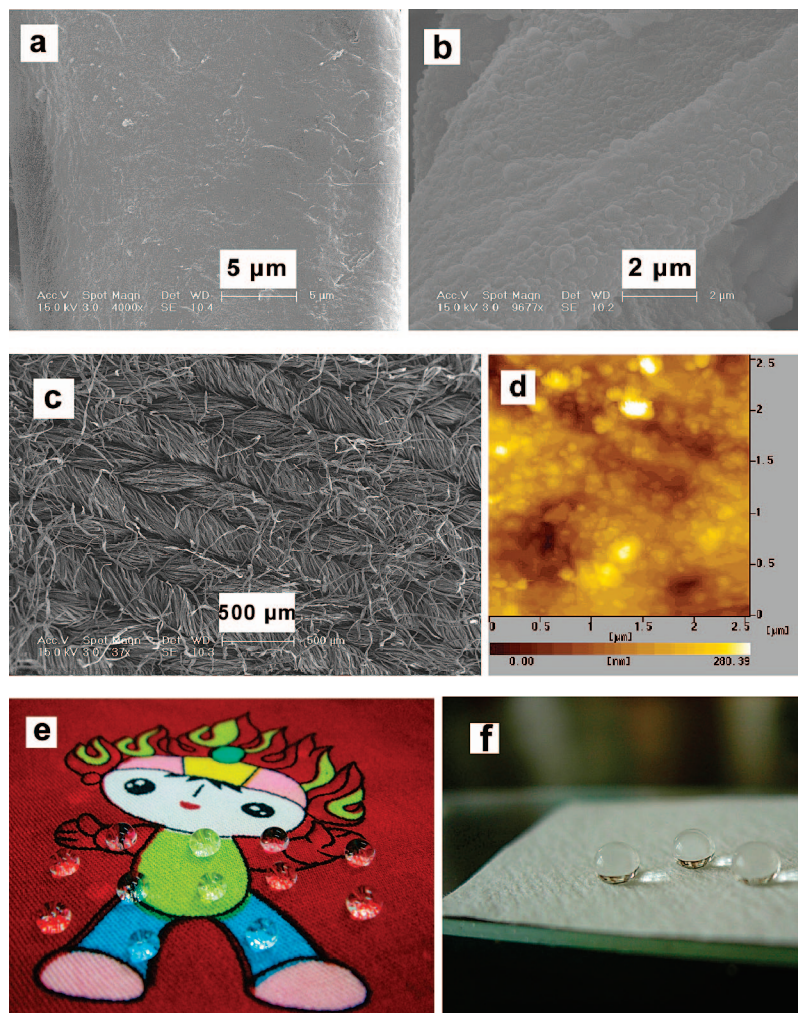


Figure 5. FE-SEM images of (a) the native cotton fiber, (b) the modified cotton fiber, and (c) the modified cotton fabric at low-magnification. (d) A three-dimensional AFM image of the modified fiber surface, (e) an image of water droplets on the surface of the modified colored cotton fabric, and (f) an image of water droplets on the surface of the modified filter paper.

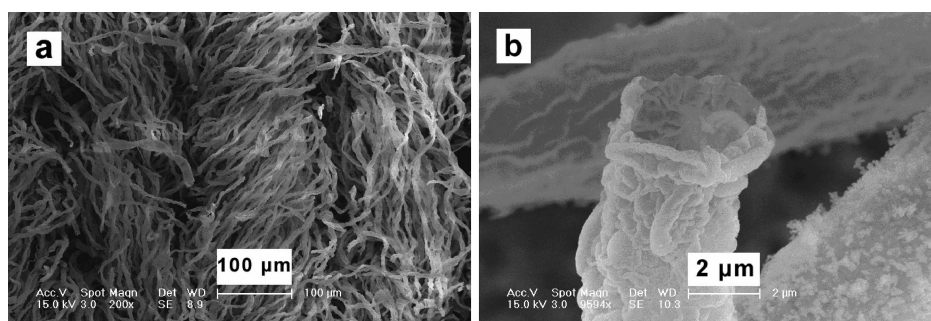


Figure 6. FE-SEM images of (a) the hollow textilelike silica at low magnification and (b) the hollow silica fiber.

drophobic character of the used material was maintained after 20 washes, thus indicating that the as-prepared superhydrophobic coatings had a satisfactory stability. The general inertness of silicones was believed to contribute to this high stability.⁵⁶

Conclusions

A commercially available, waterproof reagent (PMS) was used for fabricating superhydrophobic surfaces on cellulose-based materials through a solution-immersion method. The silanol, which was formed by a reaction of a PMS aqueous

solution with CO_2 , was assembled on the cellulose molecule surface via hydrogen bond interactions, and the superhydrophobic coatings were formed by a subsequent polycondensation reaction. This reaction process resulted in the covalent attachment of a polymethylsilsequioxane layer to the surfaces of the cellulose fibers. Uniform nanoscale roughness protuberances with inherent microscale roughness characteristics were obtained, thus bringing about a superhydrophobic

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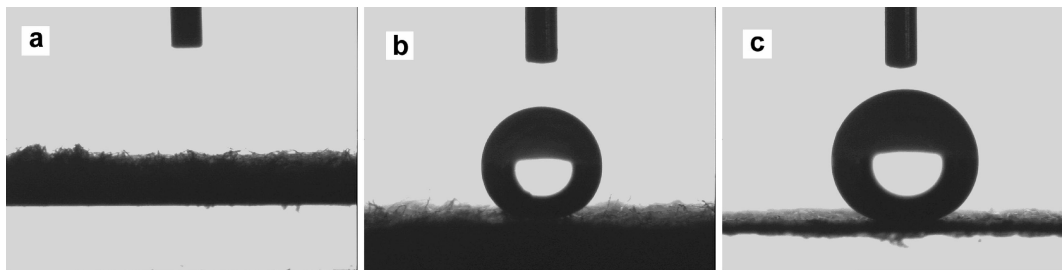


Figure 7. The contact angle of a water droplet on (a) the native cotton fabric (0°), (b) the modified cotton fabric (158°), and (c) the modified filter paper (157°).

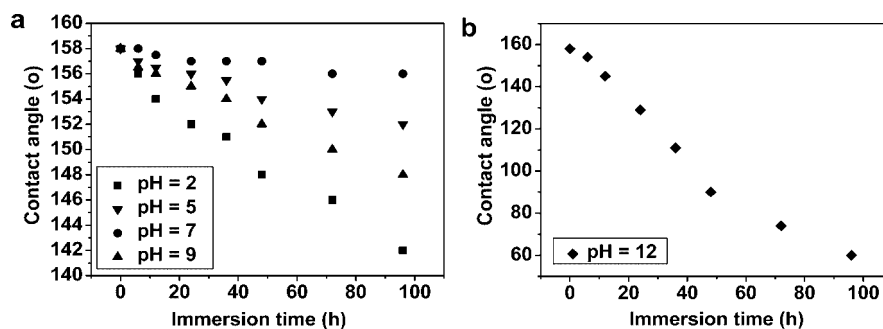


Figure 8. The relationship between contact angles and the immersion time at varying pH for the superhydrophobic cotton fabric.

character coupled with a satisfactory durability. The creation of superhydrophobic, self-cleaning, cellulose-based materials with transparent characteristics could have potential applications in the textile industry and packaging material area. The use of commercially available waterproof PMS in fabricating superhydrophobic cellulose materials could thereby eliminate acidic products and retain the mechanical properties of the as-prepared cellulose materials. The PMS thus constitutes a more preferable reagent for fabricating super-

hydrophobic cellulose materials as compared to organic silicon halides.

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