

Fabrication of Superhydrophobic Surface on a Cellulose-based Material *via* Chemical Modification

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Superhydrophobicity is an interesting surface property underlying several fascinating natural phenomena, such as the self-cleaning ability of lotus leaves and the striding ability of spiders, which have attracted much interest in the industry and academia. A superhydrophobic surface is that on which the water contact angle (WCA) is higher than 150° and the water sliding angle is lower than 10° , hence, water droplets can easily slide/run off the surface. This principle of high water repellence of a superhydrophobic surface can be extended to practical applications, for example, to develop coatings for automobile windows, tiles, buildings, and clothes.¹⁻⁴

Superhydrophobicity of lotus leaves results from combined micro-/nanoscale structure on a surface and coating the surface with a low surface energy material. Micro-/nanoscale of surface roughness have been fabricated using a number of approaches, such as lithography,⁵ etching,⁶ immersion processing,⁷ sol-gel methods,⁸ and chemical vapor deposition.⁹ Functional fabrics, such as winter clothes as well as water-repellent, and biodegradable clothing, are gaining increased popularity. Typically, cotton fibers are interwoven with cellulose fibers, which contain numerous surface hydroxyl groups, so that the resulting cotton fabric is superhydrophilic and highly wettable. The superhydrophobic cotton fabric have been developed and applied to separate oil and water mixture.¹⁰⁻¹⁴

Cellulose is the most abundant occurring biopolymer. The esterification of cellulose is popular surface modification method that affords cellulose derivatives with increased hydrophobicity.¹⁵⁻¹⁷ Transesterification reactions have been employed to improve the water repellency of cellulose fiber (cotton), but even the most hydrophobic cotton derivative shows a low WCA of 80° . Popular chemical reactions used to obtain superhydrophobic cotton fabric include reaction with chloroacetyl chloride in a THF/pyridine,¹⁸ acetylation with acetic anhydride,¹⁹ esterification with trifluoroacetic anhydride,²⁰ and surface modification with a perfluoro-long alkyl chain.^{21,22}

The above mentioned approaches have been used by many research groups to convert a highly wettable cotton surface into a superhydrophobic surface.

Recently, membranes that show both superhydrophobicity and superoleophilicity have attracted attention for use in various academic field and industrial applications, particularly

for cleaning oil spills in the sea. Numerous methods, including an electrospinning process,²³⁻²⁶ chemical etching,²⁷⁻³⁰ solution immersion process,³¹ wet chemical approach,³² plasma processing,^{33,34} and electrochemical deposition³⁵ have been used to fabricate many superhydrophobic and superoleophilic surfaces, for the development of functional membranes that aid in oil-water separation. To fabricate a superhydrophobic surface, nanomaterials such as nanosilica, ZnO, or polymers are deposited on cotton fabric to obtain a high surface roughness with low surface energy material. Xu *et al.* used the nanosized silica particles and *n*-dodecyltrimethoxysilane (DTMS) as the low surface energy material.³⁶ Deng fabricated superhydrophobic cotton *via* the polymerization of fluorinated acrylate,³⁷ to obtain a hierarchical structure with low surface energy. Coating of fluorinated alkyl silane on the deposited nanosilica is a very popular method to create a superhydrophobic cotton surface. A superhydrophobic surface was created on a cellulose base material *via* a solution immersion process (potassium methyl silicate, PMS). The use of PMS rendered the superhydrophobic surface stable under mild basic and acidic conditions, but the WCA showed a sharp decrease when the material was immersed in a strongly basic solution.³⁸ However, most of the reported methods are time-consuming and require the use of harmful chemicals; further, the obtained superhydrophobic surface is often chemically unstable.

Herein, we report the fabrication of a superhydrophobic cotton surface *via* a simple, single step chemical reaction without the use of nanomaterials. The chemically modified cotton fabric showed high water repellency, facilitated the efficient separation of oil from an oil-water mixture, and showed durability under both acidic and basic conditions. Moreover, the modified fabric retained its original surface structure and physical properties except for its hydrophobicity.

Experiment

Instrumentation. The surface morphology of the cotton samples was observed by using a field-emission scanning electron microscope (FE-SEM, Hitachi S4300, Hitachi Inc.). The surface elemental composition was determined by utilizing Fourier transform infrared spectroscopy (FTIR, Spectrum 100, Perkin Elmer). The WCAs were measured

with 5 μL water droplets at room temperature by using a contact angle analyzer (Phoenix 300, Surface Electro Optics). The WCA values were obtained as averages of the results of three measurements.

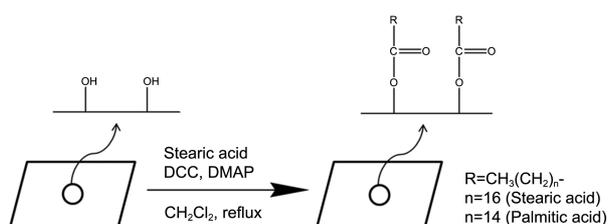
Materials

Cotton fabrics were purchased from a local (Yongin) market. Stearic acid, *N,N'*-dicyclohexylcarbodiimide (99%, DCC), dichloromethane (anhydrous) and 4-(dimethylamino)pyridine (99%, DMAP) were obtained from Sigma-Aldrich (U.S.A). All the chemicals were analytical grade and used as received.

Fabrication of Superhydrophobic Cotton Fabric. A sheet of cotton fabric ($10 \times 10 \text{ cm}^2$) was cleaned by sonification for 5 min each in ethanol and water, and then dried at $35 \text{ }^\circ\text{C}$ for 1 h. The cleaned cotton fabric was placed in a 200 mL round bottom flask, and dichloromethane (50 mL) was added under argon gas flow. Then, stearic acid (10 g, 35.2 mmol), DCC (7.9 g, 38.7 mmol), and DMAP (0.47 g, 3.87 mmol) were added to flask consecutively, and the reaction mixture was refluxed for 5 h under argon gas flow. The modified cotton sheet was washed first with ethanol (10 mL) and then with water (10 mL) to remove impurities, and dried at $70 \text{ }^\circ\text{C}$ for 1 h in oven. The treated cotton fabric was cut into appropriate size for characterization.

Results and Discussion

The formation of superhydrophobic surface on the cotton fabric involved a chemical reaction. The surface hydroxyl groups of the cotton fabric underwent esterification with stearic acid in the presence of DCC and catalytic amount of DMAP in methylene chloride (Scheme 1). X-ray photoelectron spectroscopy (XPS) measurements were employed to investigate the chemical composition of the untreated and chemically modified cotton fabrics. As seen in Figure 1, the spectrum of the modified fabric showed two peaks (C_{1s} , O_{1s}), and the ratio of the C/O was increased from 1.08 to 1.46, thus confirming the esterification of the hydroxyl groups. High-resolution analysis revealed that the C_{1s} peak comprised four peaks at 283.9, 284.6, 286.3, 287.6 which were attributed to C-H, C-C, C=O and O=C-O bonds, respectively. The presence of the O=C-O bond in the case of the superhydrophobic surface was also confirmed by FT-IR spectral analysis. The FT-IR spectra of the untreated and



Scheme 1. Process of the fabrication of superhydrophobic and superoleophilic cotton fabric.

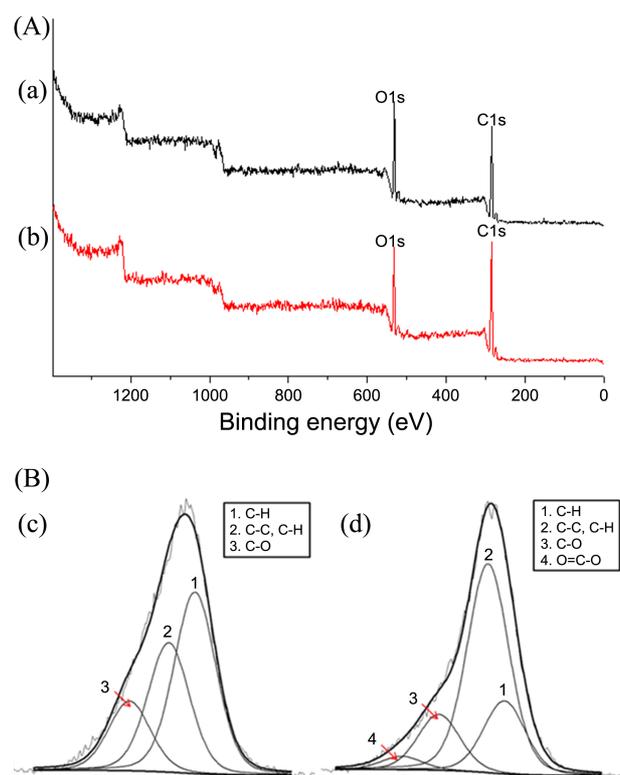


Figure 1. (A) XPS results for (a) untreated and (b) chemically treated cotton surface. (B) High-resolution C_{1s} region of (c) untreated and (d) chemically treated cotton.

treated cotton fabric in the range $600\text{--}4000 \text{ cm}^{-1}$ are presented in Figure 2(A). In the spectra of modified cotton fabric, the typical absorption peak due to the ester carbonyl was at 1750 cm^{-1} , while this peak was absent in the spectrum of the untreated fabric; this observation confirmed the successful esterification reaction and the formation of fatty ester linkages (Figure 2(B)).

The WCA of the untreated cotton fabric was 0° because of the abundance of surface hydroxyl groups and the resulting hydrophilicity. On the other hand, the chemically modified cotton fabric became superhydrophobic because of the esterification of the hydroxyl groups with stearic acid. Water droplets mixed with a red dye and ethylene glycol droplets were placed on the superhydrophobic cotton fabric (Figure 3(a)). The successful superhydrophilic to superhydrophobic transformation of the cotton fabric by chemical modification could be easily confirmed from the high WCA of 151° (Figure 3(b)). As opposed to conventional methods such as nanoparticle deposition, chemical vapor deposition, and chemical grafting, we did not induce roughness on the cellulose fibers (Figure 4). The resulting micro-/nano-cellulose fiber bundle and esterification of cellulose fibers with a long-chain fatty acid afforded both superhydrophobicity and superoleophilicity to the cotton fabric.

The water droplet stayed on the superhydrophobic cotton fabric for 1 h and then decreased in size because of slow evaporation, but there was no decrease in the WCA (Figure 5).

When corn oil was dropped on the modified cotton fabric,

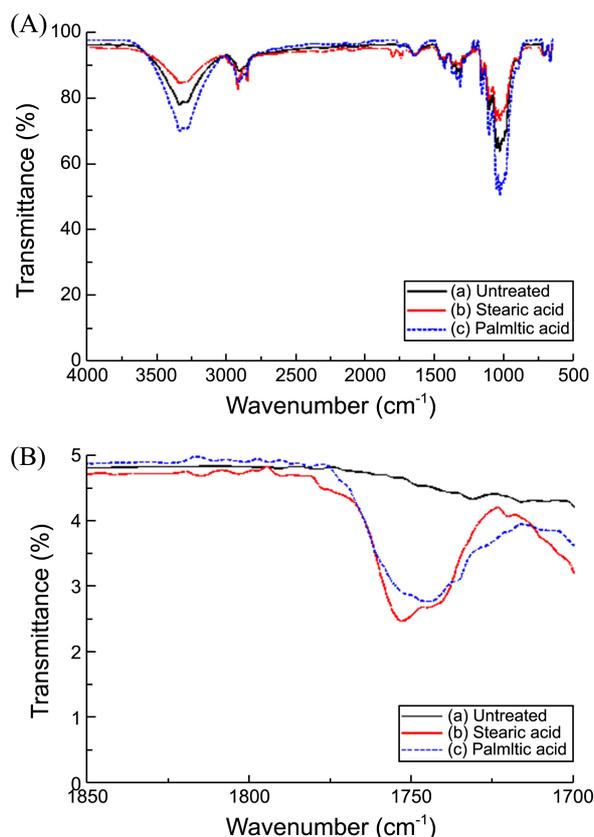


Figure 2. (A) FT-IR spectra of untreated (a) and superhydrophobic cotton fabric (b), and (c). (B) Enlargement of the peak at 1700 cm^{-1} .

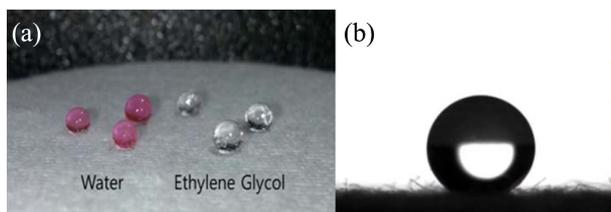


Figure 3. (a) Water droplets (red dye contained) and ethylene glycol droplets on superhydrophobic cotton fabric, (b) water contact angle (151°).

the oil droplets spread easily on the surface. The contact angle of corn oil droplet was impossible to measure. These results showed that the modified cotton fabric showed both superhydrophobicity and superoleophilicity.

Figure 6 shows the use of the cotton fabric in the oil-water separation process. 7 mL each of corn oil and water containing a blue dye for better distinction from the oil were mixed, and the emulsion was shaken vigorously for 1 min to ensure through mixing of the liquids. The resulting mixture was poured on the modified fabric at room temperature, under air atmosphere. The corn oil in the mixture immediately infiltrated into the fabric, and was collected in the beaker, while the water remained on the fabric and was collected in the bottle. Complete separation of the corn oil from water was achieved in 90 second, with quantitative recovery of both oil and water.

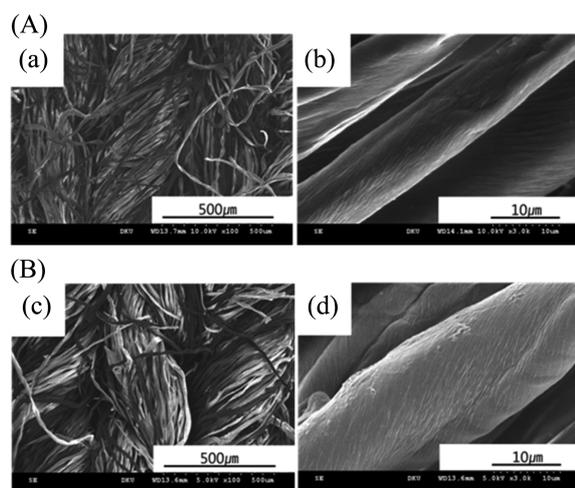


Figure 4. (A) FE-SEM image of (a) untreated cotton and (b) magnified image of a single fiber. (B) FE-SEM image of (c) chemically treated cotton and (d) magnified image of a single fiber.

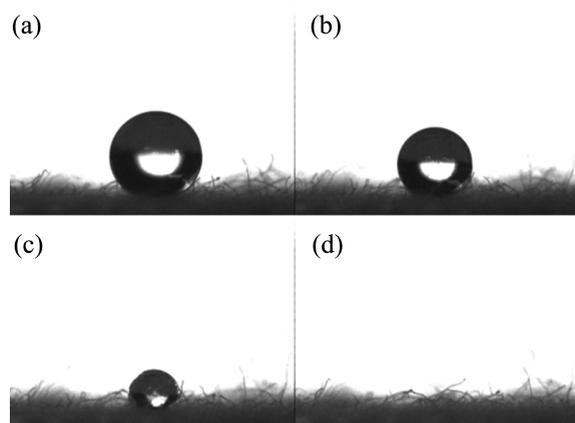


Figure 5. Decrease in the volume of water at (a) 0 min, (b) 20 min, (c) 40 min, and (d) 60 min.

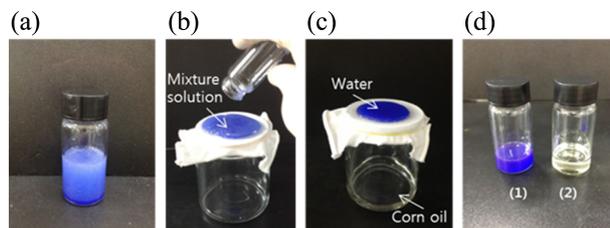


Figure 6. Separation of corn-oil and water mixture using the superhydrophobic cotton fabric (a) Mixture solution; (b), (c) image after pouring the mixture solution of corn oil and water; (d) photograph after separation: (1) water, (2) corn oil.

The chemical stability of the modified surface was evaluated by measuring the change in the WCA after immersing the fabric in aqueous solutions of different pH levels, for various lengths of time (Figure 7). The WCA showed a very small decrease (it was more than 146°) even after 5 days of immersion in acidic, neutral, and basic solutions, thus confirming the high chemical stability and stable superhydropho-

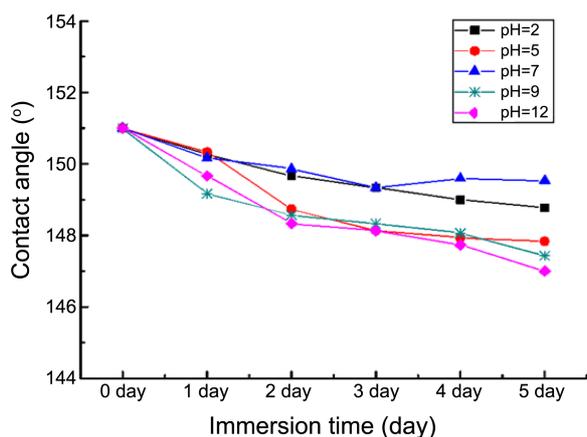


Figure 7. Variation in water contact angles on the treated cotton fabric at various pH conditions.

bicity of the surface.

In conclusion, we have demonstrated a simple, one-step chemical method for preparing cotton fabrics showing both superoleophilicity and superhydrophobicity. The hydroxyl groups on the cellulose surface could be readily esterified with a long-chain fatty acids (stearic acid, palmitic acid, etc.). The chemically treated cotton fabric showed long-term stability under strong acidic or basic condition, very high water repellency, and superoleophilicity, even when no nanostructure was formed on its surface. Such functional fabrics may find widespread application in various industrial fields, especially for oil-water separation.

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