Facile transformation of hydrophilic cellulose into superhydrophobic cellulose†

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Received (in Cambridge, UK) 6th August 2007, Accepted 11th September 2007
First published as an Advance Article on the web 21st September 2007
DOI: 10.1039/b712056g

Superhydrophobic cellulose-based materials coupled with transparent, stable and nanoscale polymethylsiloxane coating have been successfully achieved by a simple process *via* chemical vapor deposition, followed by hydrolyzation and polymerization.

Superhydrophobic surfaces with water contact angles (WCA) higher than 150° have attracted considerable interest for both academic research and industrial applications in recent years, due to their self-cleaning properties.[1] It has been proposed that the superhydrophobicity arises from the combination of the hierarchical micro- and nano-structures of surfaces and the usage of the low surface energy of the materials.[2] Hence, many approaches have been developed based on this principle for the design and fabrication of superhydrophobic surfaces.[3] The chemical vapor deposition (CVD) approach is regarded as a simple and effective method to prepare supported catalysts,[4] or to mimic precise biological structure,[5] but it is seldom used to deposit superhydrophobic coatings onto substrates.[6] Although progress has been made for the fabrication of superhydrophobic surfaces, success is limited in regards to the formation of superhydrophobic surfaces on rigid substrates because deforming the substrate will destroy the superhydrophobic property. Especially, as considering the fabrication of superhydrophobic coatings onto soft material surfaces, in addition to self-cleaning properties, transparency and durability also need to be considered. Furthermore, the preparation of soft superhydrophobic materials could extend their practical application.

Cellulose is one of the most abundant biopolymers and a basis for many industrial derivatives and products.[7] The creation of superhydrophobic, self-cleaning, cellulose-fibre-based materials will have potential applications in the textile industry and packaging area, and it is also inspired by the usage of environmental friendly renewable resources.[8] Therefore, exploration for a facile method to transform a very hydrophilic substrate into an extremely hydrophobic one is important. So far, dyeing technology,[9] and branched "graft-on-graft"methods[10] have been explored for constructing superhydrophobic cloth and/or paper surfaces. However, they are still subject to severe conditions, tedious fabrication, and expensive materials limitations.

The coating of surfaces with silanes is well known. The field is predominated by silicone chemistry and could benefit from the ability to generate nanostructures in the hydrophobization of surfaces.[11] Seeger *et al.*[12] first reported the fabrication of silicone nanofilaments onto various substrates by polymerization of equimolar amounts of liquid trichloromethylsilane (TCMS) and water vapor. The obtained coating consists of polymethylsilsesquioxane nanofilaments with superhydrophobic character. Herein, we present a new facile approach with low temperature CVD for transformation of normal hydrophilic cellulose-based materials into superhydrophobic ones with covalently nanoscale polymethylsiloxane, which will be convenient for mass production.

The method employed is described as follows: first, a sheet of cotton fabric is cleaned by ultrasonic washing in ethanol and water, respectively, and then dried at 120 °C in a vacuum oven for 1 h. Second, the cotton fabric is placed in a sealed chamber for a set time, into which a saturated atmosphere of TCMS at 50 °C is introduced. The TCMS is absorbed onto the cotton fibers' surface and penetrated into the fibers, due to the porous property of the fibers and a reaction between the halide and hydroxyl group. The efficient reaction enhances the content of covalently bound silicone to the fibers' surfaces. Next, the cotton fabric is withdrawn from the chamber and immersed into an aqueous solution of pyridine (1 M) at room temperature to hydrolyze the remaining Si–Cl bonds. The cotton fabric is washed with water carefully to remove the excess reagents. Finally, the cotton fabric is treated in an oven at 150 °C for 10 min. Subsequent polymerization of Si–OH results in a nano-scaled silicone[13] coating tightly attached to the surface.

The surface wettability of the as-prepared substrates has been assessed by a series of WCA measurements. The WCA of the starting cotton fabric is 0°, due to the superhydrophilic nature of the cotton. As anticipated, the introduction of the tailored silicone coating onto the substrate results in the transformation of superhydrophilic to superhydrophobic character, with a WCA of 157° obtained under optimal conditions. An examination of the effect of the reaction time on the surface wettability shows that the WCA of the resulting material increased with increase in reaction time up to 5 min under comparable conditions (Fig. 1(a)). Interestingly, a WCA up to 124° has been observed for the resulting material in only 1 min, and a superhydrophobic fabric with WCA of $>155°$ is obtained after 5 min. No apparent changes of WCA are observed with extension of reaction time to 20 min.

The chemical durability of the superhydrophobic coating is evaluated by measuring the change of WCA values of the obtained materials, which are treated with aqueous solutions with different pH values (Fig. 1(b)). The results show that the resulting superhydrophobic fabric still shows satisfactory durability with

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† Electronic supplementary information (ESI) available: Experimental procedures. See DOI: 10.1039/b712056g

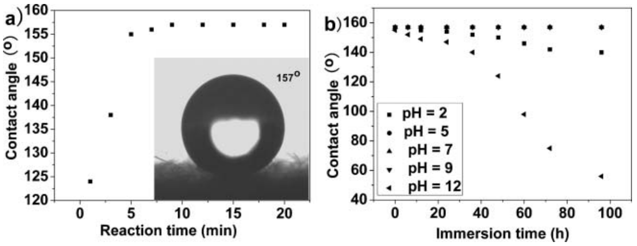

Fig. 1 (a) The relationship between contact angle and reaction time. (b) The relationship between contact angle and immersion time at different pH values on superhydrophobic cotton fabric.

WCA of >140° after being treated for 96 h with slightly acidic, neutral and mildly basic solutions. However, the corresponding WCA values decrease dramatically after being treated with strongly basic solution. To get a direct sense of the durability of the textile, a resulting cotton fabric was washed with soap or laundry detergent powder in a regular laundry cycle. The superhydrophobic character of the used material still remains after 20 washes, which indicates that the as-prepared superhydrophobic coatings have satisfactory stability, which is consistent with the general inertness of silicones contributing to high stability.[14]

The superhydrophobic coating of the cotton fabric is confirmed by FT-IR (Fig. 2(a)) and X-ray photoelectron spectroscopy (XPS) analysis (Fig. 2(b)). The FT-IR spectrum shows two absorption peaks located at 781 and 1274 cm^{-1} which can be assigned to the stretching vibrations of the Si–C bonds and –CH_3 deformation vibrations of the siloxane components, respectively. The typical absorption peaks of Si–O–Si bonds of the siloxane components appearing at 1130–1000 cm^{-1} overlap with that of C–O bonds in cellulose. In the XPS spectrum of the as-prepared cotton fabric, appearance of two typical peaks with binding energy of 150 and 100 eV, corresponding to Si 2s and Si 2p, respectively, indicate the presence of silicon at the surface. The Si content is estimated to be 13.2 wt% for the cotton fabric exposed to the TCMS vapor for 5 min.

The surface morphology and roughness are investigated by both field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM). Fig. 3(a)–(d) show typical top views of the native and treated cotton fabric. The native cotton fabric presents a highly-textured microscale fibre with a typical smooth surface (Fig. 3(a)). However, a thin layer of nanoscaled spherical protuberances are observed on the as-prepared superhydrophobic fibre surfaces (Fig. 3(b) and (h)). The height of the protuberances pattern is estimated to be 50–200 nm, and the roughness of the fibre is around 50 nm (Fig. 3(h)). The nanoscaled coating is clearly attached to the fibre.

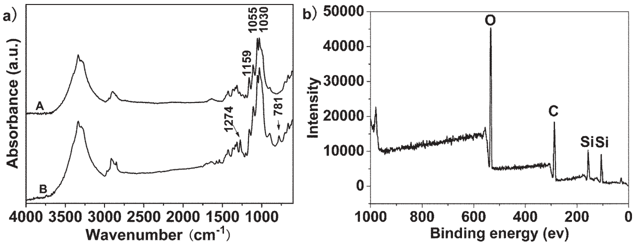

Fig. 2 (a) The FT-IR spectra of a native cotton fiber (A) and the superhydrophobic cotton fiber (B). (b) The XPS spectra analysis of the superhydrophobic cotton fiber surface.

In an effort to get precise information of the nano-coating, the as-prepared superhydrophobic cotton fabric was calcined in air at 500 °C to remove the original cotton fibre.[15] The FE-SEM image of resulting residue material shows that the nano-coating is hollow "textile-like" silica, which is an exact replication of cotton fibre after calcination in air (Fig. 3(e) and (f)). This observation indicates that the polymethylsiloxane was fully coated on the surface of single fibres, which prevents the contact of water with hydroxyl groups on the fibre surface, resulting in a superhydrophobic cotton fabric surface. This is in good agreement with the WAC measurements. The thickness of the coated layer is determined to be 165 nm. The true thickness is probably higher, as shrinkage always occurs to the overall dimensions of the coating during calcination. In addition, the coating layer appears to lead to no deleterious effects on the morphology of the original cotton fabric. Fig. 3(c) and (d) show that the fabric morphology and color show no change before and after treatment with TCMS. This indicates that the modification method has taken place truly on a single fibre surface, and the coating layer is transparent. The optical image of water droplets on the surface of a coated colored cotton

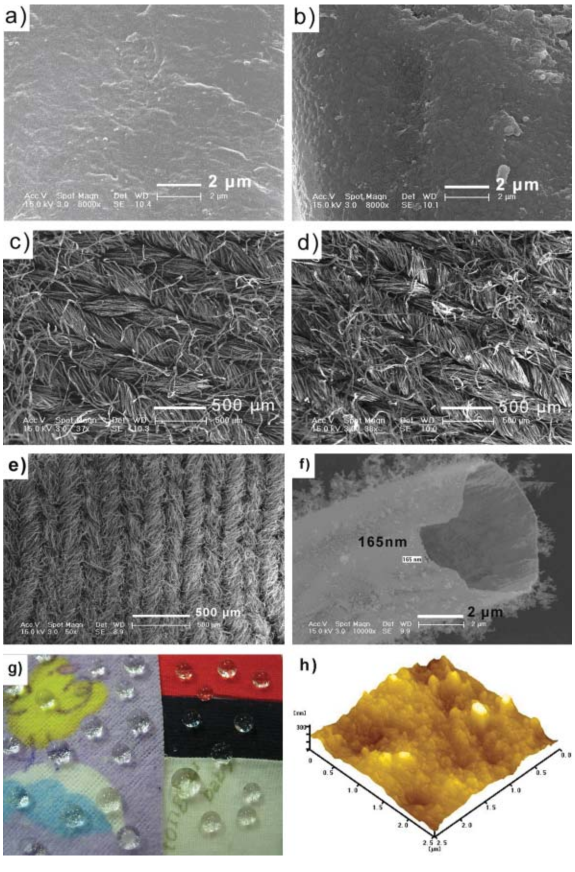

Fig. 3 FE-SEM images of: (a) native cotton fibre, (b) TCMS modified cotton fibre, (c) low-magnification native cotton fabric, (d) low-magnification modified fabric, (e) low-magnification hollow "textile-like" silica, (f) single hollow silica wire. (g) Image of water droplets on the surface of a modified colored cotton fabric. (h) 3D AFM image of the modified fibre surface.

fabric (Fig. 3(g)) gives a direct demonstration that the superhydrophobic coating is transparent. Although the preparation of superhydrophobic surfaces has been extensively studied, only a few methods have been reported for preparation of transparent films so far.[16]

In contrast to "graft-on-graft" methods for constructing superhydrophobic paper,[10] where the paper surface is clearly covered by the polymer, and the surface morphology of the filter paper has changed apparently, our methods produced a polymethylsiloxane layer on individual fibre surfaces with no changes on morphology and color of the original cotton fabric. This method is highly effective, simple and convenient to operate for constructing superhydrophobic surfaces, and also results in a transparent, stable, morphology retained superhydrophobic product for further use. The polymethylsiloxane coating may have promising applications in daily used materials, and be used as an environmental friendly water-repellent substitute for commonly used fluorine compounds.[17]

Taking account of the satisfactory superhydrophobic character and durability of the resulting materials, a thorough understanding of the superhydrophobicity of the as-prepared surface can be obtained from the Cassie–Baxter equation:[18]

$$\cos \theta_r = f_1 \cos \theta - f_2 \quad (1)$$

Here, θ_r (155°) and θ (104°) are the WCA on a rough fabric surface and on a smooth silicone surface, respectively; and f_1 and f_2 are the fractions of solid surface and air in contact with liquid, respectively ($f_1 + f_2 = 1$). According to this equation, the f_2 value of the rough fabric surface with nano silicone is estimated to be 0.87, which indicates that the achievement of superhydrophobicity is a main result of the air trapped in the rough surface of protuberances and cavities on such woven fabric. The superhydrophobicity of as-prepared materials may be attributed to the association of the fraction of air in the interspaces and usage of low surface energy coating. In addition, the contribution of the woven structures on the hydrophobicity of the surface can not be ruled out.[19] Furthermore, the designed and well-performed covalent reaction of surface hydroxyl group with TCMS, without the presence of water in our study, also benefits the enhanced hydrophobicity and durability, which is well consistent with the observations of McCarthy *et al.*[20]

In conclusion, a facile way to transform very hydrophilic cellulose surfaces into an extremely superhydrophobic ones has been developed based on the reaction of hydroxyl groups and TCMS by chemical vapor deposition technique. The process resulted in a polymethylsiloxane layer covalently attached to the surface with uniform nanoscaled roughness protuberances with an inherent microscale roughness which brought about the superhydrophobic character coupled with satisfactory durability. The creation of superhydrophobic, self-cleaning, cellulose-fibre-based materials and transparency could have potential applications in the textile industry and package material area. As expected, the approach is versatile and can be conducted on a variety of organic and inorganic substrates with hydroxyl group functionalized surfaces, and especially for PVA, paper or other biomass-based substrates.

This research was financially supported by the National Basic Research Program of China (2003CB615704) and the National Science Foundation of China (No. 20474061). We are grateful to Mr Jilin Zhang and Mr. Junpeng Gao for their help with the contact angle measurements.

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