

Hydrophobic duck feathers and their simulation on textile substrates for water repellent treatment

Yuyang Liu^{1,2}, Xianqiong Chen¹ and J H Xin¹

¹ Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hong Kong, People's Republic of China

² Department of Bioproducts and Biosystems Engineering, University of Minnesota, St Paul, MN, USA

E-mail: liu751@umn.edu

Received 13 June 2008

Accepted for publication 13 October 2008

Published 7 November 2008

Online at stacks.iop.org/BB/3/046007

Abstract

Inspired by the non-wetting phenomena of duck feathers, the water repellent property of duck feathers was studied at the nanoscale. The microstructures of the duck feather were investigated by a scanning electron microscope (SEM) imaging method through a step-by-step magnifying procedure. The SEM results show that duck feathers have a multi-scale structure and that this multi-scale structure as well as the preening oil are responsible for their super hydrophobic behavior. The microstructures of the duck feather were simulated on textile substrates using the biopolymer chitosan as building blocks through a novel surface solution precipitation (SSP) method, and then the textile substrates were further modified with a silicone compound to achieve low surface energy. The resultant textiles exhibit super water repellent properties, thus providing a simple bionic way to create super hydrophobic surfaces on soft substrates using flexible material as building blocks.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Learning from nature is a very important resource of advanced materials and new technologies. Scientists and engineers are increasingly turning to nature for inspiration to solve scientific and technical problems. A vivid example is the creation of super hydrophobic surfaces by mimicking the hydrophobic surfaces of lotus leaves [1]. A super hydrophobic surface usually has a very high advancing water contact angle, typically of 150° or higher, and a very low contact angle hysteresis, which is a very low sliding angle, typically below 15°. Surfaces with such properties have attracted much attention for both industrial and biological applications [2–6], such as antifogging and self-cleaning coatings, microfluidics, domestic commodities or in the biomaterials area [7]. The super hydrophobic behavior of lotus leaves, known as the lotus-leaf effect or the self-cleaning effect, is found to be a result of the hierarchical rough structure, as well as the wax layer present on the leaf surface [8]. Actually, super

hydrophobic surfaces are widely observed in nature. Duck feathers, the legs of water striders, the wings of butterflies and other natural materials show highly water repellent properties [3, 9]. Compared with lotus leaves, duck feathers are soft and flexible, and the water repellent characteristic of duck feathers is durable, thus it provides an ideal model for the fabrication of super hydrophobic surfaces on soft substrates. In this paper, we report the fabrication of super hydrophobic surfaces on textile substrates by mimicking the surface structures of duck feathers and explore their application in self-cleaning textiles.

The fabrication of the super hydrophobic surface on a textile substrate can endow the textile with self-cleaning properties, which make the textiles clean and dry on rainy days, thus the fabrication of super water repellent textiles has been an attractive subject for several decades [10]. Imparting water repellency to textiles using chemical methods to modify the surface of the fibers and leaving the fabric permeable to air and water vapor was a well-established and well-understood technology in the 1940s [10]. Hydrophobic textiles can

be achieved by treating the textile with low surface energy materials such as fluorinated or silicon compounds. Recent progress on nanotechnologies and super hydrophobic surfaces provides great opportunities to optimize the fabrication of super hydrophobic surfaces on textile substrates.

It has been confirmed that the wettability of a solid surface is governed by the combination of two factors: the surface chemical composition and the surface texture [11–13]. With more and more researchers becoming interested in this field there are a greater number of methods reported to produce such surfaces, using simpler and cheaper means to achieve high water contact angles and low hysteresis (causing roll-off). Conventionally, super hydrophobic surfaces were fabricated using two major approaches [11]. The first approach was to create a rough structure on a hydrophobic surface, and the second approach was to decrease the surface energy of a rough surface by chemically bonding low surface energy species to the surface. Scientists have created super hydrophobic surfaces by tailoring the surface topography and using techniques such as anodic oxidation [14–17], electrodeposition and chemical etching [18–20], plasma etching [21, 22], laser treatment [23, 24], electrospinning [25–27], chemical vapor deposition [28–31], sol–gel processing [32–34] and so on. Technically, the methods for the fabrication of hydrophobic surfaces on hard substrates can reasonably be applied to textiles to produce hydrophobic textiles. However, as mentioned above, either a complicated procedure or a special instrument has been used in these methods. These methods are too complicated to use for textiles. In most of these methods, inorganic nanoparticles such as SiO_2 and TiO_2 have been deposited onto the substrates to enhance the surface roughness. Although the use of nanoparticles provides an easy way to construct artificial lotus-leaf structures on textiles, there are several serious problems accompanying these nanoparticle-built surfaces. First, in most of these reports, the artificial lotus surface was fabricated using a surface coating method. Composites containing nanoparticles were applied to the textile surface through dipping–coating procedures. Although most of these inorganic nanoparticles are nontoxic, during the application of these textiles, some of these nanoparticles would be released from the fiber surface and enter human skin, causing serious health problems. Recent study shows that nanoparticles were able to passively penetrate the skin and reach the deepest layers of the stratum corneum (the outermost layer of the skin) and hair follicle and, occasionally, reach the viable epidermis. Second, even if these nanoparticles have good fastness on textile substrates, most of the nanoparticles are made from hard inorganic materials which make the resulting textile uncomfortable to wear. For example, recently we reported the fabrication of artificial lotus surfaces on cotton textiles using modified carbon nanotubes (CNTs) as building blocks [1]. The CNTs-coated cotton fabrics exhibit super hydrophobic properties and improved physical properties [35]. However, these CNTs-coated textiles are expensive due to the high cost of CNTs. At the same time, the CNTs coating will make the textile dark and stiff after treatment. The objective of this research was to develop a simple method for the fabrication of

hydrophobic surfaces on textile substrates using safe and soft materials as building blocks.

In this work, the microstructures of the duck feather were investigated using the scanning electron microscope (SEM) imaging method through a step-by-step magnifying procedure, and then the microstructures of duck feathers were copied to textile fibers using the biopolymer chitosan as building blocks. Chitosan was precipitated on cotton and polyester fiber surfaces at the nanoscale to form a rough surface. The resultant fabrics were further modified with silicone and fluoride compounds to achieve low surface energy.

2. Experimental details

2.1. Materials and instruments

Cotton and polyester fabrics were purchased from China Dye Ltd, Hong Kong. Before the finishing treatment, the fabrics were scoured by a nonionic detergent to remove the wax, grease and other finishing chemicals from the fabrics. The scouring process was performed at 80 °C for 30 min. The cleaned fabrics were dried at 120 °C for 30 min. Chitosan with different molecular weights and degrees of deacetylation was purchased from Aldrich Chemical Co. Hexdecyltrimethoxysilane (HDTMS, Aldrich, 85%) and 3-glycidioxypropyltrimethoxysilane (GPTMS, Acros Organics, 97%) were used as received without further purification. The polysiloxane emulsion was prepared by mixing 8 g HDTMS, 2 g GPTMS and 1 g SDS (sodium dodecyl sulfate, Aldrich, 96%) in HCl solution (pH = 2). The mixture was kept stirring at 75 °C for 12 h. The polysiloxane emulsion was cooled to room temperature and then the pH of the emulsion was adjusted to 8 with ammonia.

The morphologies of untreated and treated textiles were investigated using field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6335 F). The wettabilities of the fabrics were evaluated using a water contact meter (Tantec, Schaumburg, IL). A drop of water (5 μl) was placed on the textile substrates; after standing for 60 s, the profile was recorded with a digital camera and the degree was recorded. Three measurements were made on each sample to obtain an average value. Temperature and moisture were constant during the experiment (23 °C and 68%, respectively). A spray test was performed according to the AATCC 22-1996 method. The AATCC spray test uses a set small quantity of water placed about 10 cm above a fabric. The fabric is set at a 45° angle to the stream of the liquid. The liquid is then allowed to gravity feed through a standardized spreader nozzle. The duration of exposure is about 30 s. At a glancing angle of 45° to the fabric, a visual rating of how well the water beads up, based on a scale of 100 points, is given to the fabrics. One hundred is the best and 70 is considered the lowest passing grade. Wash fastness was evaluated following the AATCC Test Method 61-1996 test No. 2A, using an AATCC Standard Instrumental Atlas Launder-Ometer LEF. One wash in Atlas Launder-Ometer LEF is equivalent to five home machine launderings according to the AATCC test method.

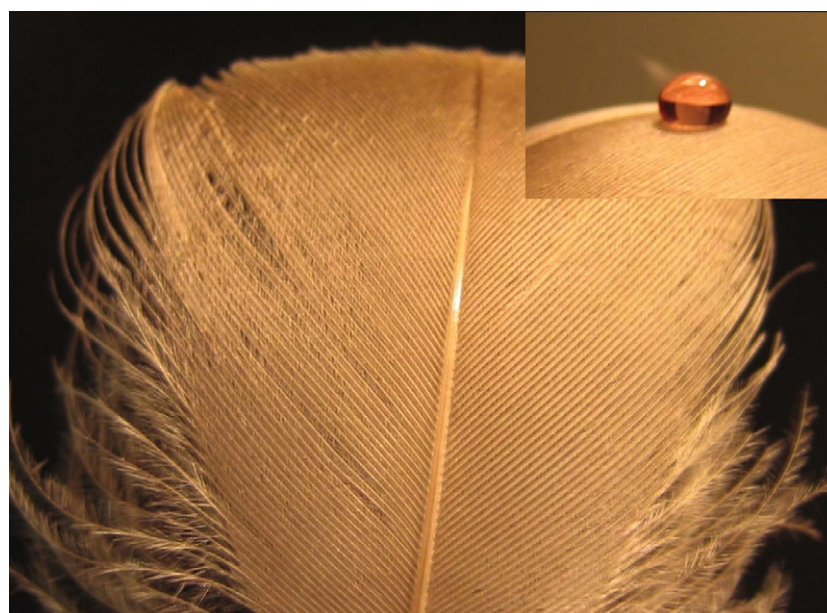


Figure 1. Optical photo of a piece of duck feather. Inset: a picture of a water droplet on a duck feather.

2.2. Preparation of chitosan solution

Stock solutions containing 0.5–2% (w/v) chitosan were prepared as follows: in a typical procedure [36], 1 g of chitosan was charged with 100 mL of 1% (v/v) aq HOAc, which was then kept stirring overnight. The chitosan solution was then filtrated with a commercial nylon stocking and was subsequently purified using a medium porous filter. The chitosan concentration in the solution was then measured by drying 1.0 g of the solution.

2.3. Treatment of fabric sample with chitosan

The fabrics were dipped in the chitosan solution for 1 min and pressed with an automatic padder (Rapid Labortex Co. Ltd, Taipei, Taiwan) at a nip pressure of 2.75 kg cm^{-2} to keep the same amount of chitosan on each of the fabrics. The wet fabrics were hung in a 10 L glass jar filled with ammonia gas. The wet fabrics were kept in the ammonia gas atmosphere for 1 min to neutralize the HOAc and then the fabrics were dried at 80°C for 5 min in a preheated oven.

2.4. Treatment of the fabrics with polysiloxane emulsion

The fabrics were dipped in the emulsion for 1 min, and pressed with an automatic padder (Rapid Labortex Co. Ltd, Taipei, Taiwan) at a nip pressure of 2.75 kg cm^{-2} to keep the same amount of emulsion on each of the fabrics. The wet fabrics were dried at 80°C for 5 min and then cured at 150°C for 1 min. The final fabric samples were rinsed with water several times to remove the surfactant SDS. The fabrics were dried at 80°C for 5 min and then cured at 150°C for 1 min.

3. Results and discussion

The water repellent behavior of duck feathers (figure 1(a)) has been highly attractive to people for several centuries. Ducks

(*Anatidae*) and most water birds have remarkable non-wetting feathers that enable them to dive quickly in water and not to be wetted by water. Until the work of Wenzel [37] and Cassie and Baxter [38] on the wettability of porous surfaces, ducks and other water birds were generally regarded as having attained perfection in water repellency, and it was usually taken for granted that these birds use preening oil with repelling properties far superior to any known to man. However, studies on the water repellency of preening oil on smooth surfaces have revealed that this is not the case. There exist nowadays many man-made oils and resins which are superior in this respect. Even a material with the lowest surface energy gives a water contact angle of only around 120° [39].

The microscopic structure of feathers appears to conform closely to the requirements for optimal water repellency. Figure 1 shows an optical picture of a piece of duck feather, indicating that duck feathers are highly ordered and have hierarchical branched structures. To show the microstructures of duck feathers, small pieces of duck feathers were cut from the back of domesticated ducks and observed by SEM. The feathers were cut into small pieces and fixed on aluminum stubs with double sided adhesive tape. In order to observe the microstructures clearly, the ordered structures of the feather were cracked with tweezers. Figure 2(a) shows that duck feathers are composed of branches with different dimensions, including micro-sized backbones, trunks and barbules. Figure 2(b) shows the image of a branch of the duck feather, indicating that the branch is composed of fine tomenta. The fine tomenta were further magnified and shown in figures 2(c) and (d), indicating that these micro-sized tomenta have nanosized grooves and protuberances. The SEM images in figure 2 reveal that duck feathers have multi-scale textures and those multi-scale textures are helpful for highly water repellent properties. According to the principles of superhydrophobicity [11–13], increasing of the surface roughness of a solid surface results in increasing of the water contact angle, which is usually

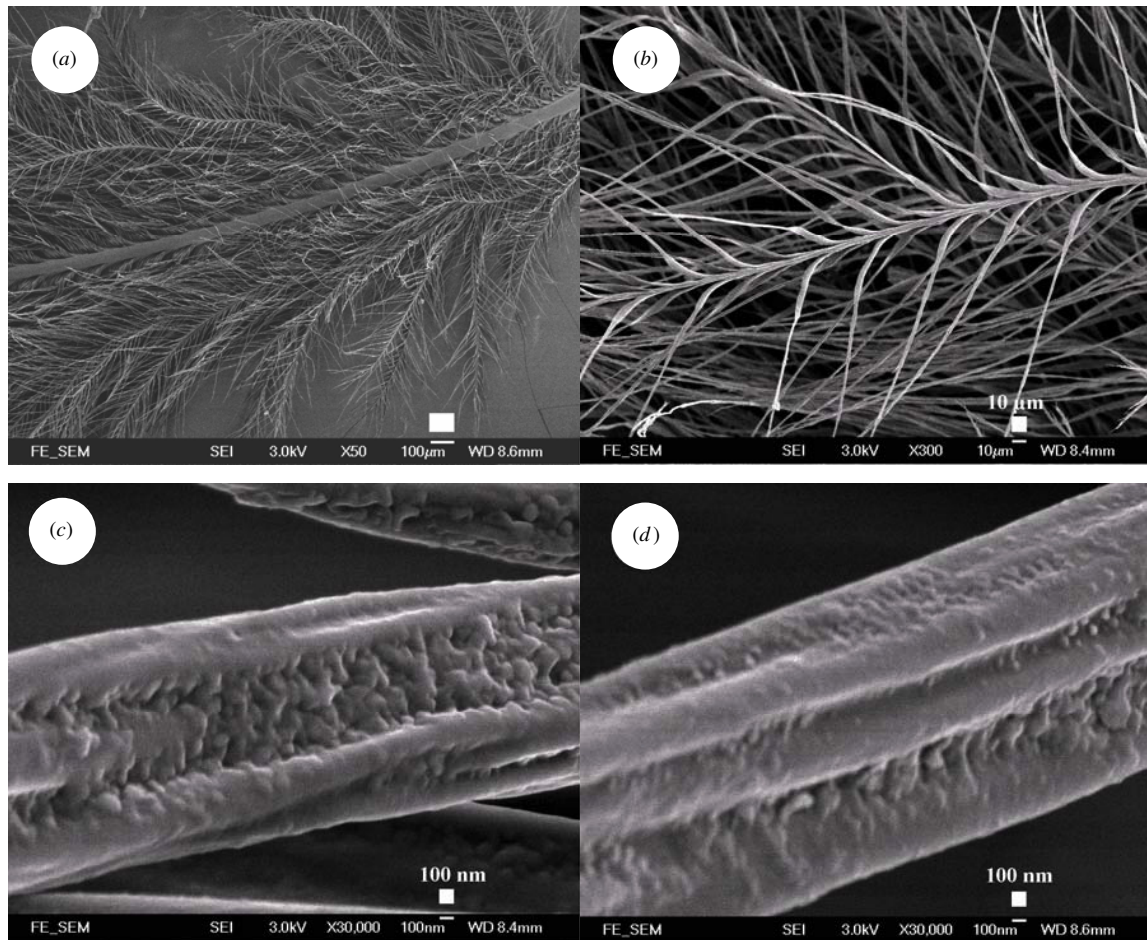


Figure 2. Multi-scale structures of duck feathers: (a) bar = 100 μm ; (b) bar = 10 μm ; (c), (d): bar = 100 nm.

used to evaluate the wettability of solid surfaces. According to Cassie's law for surface wettability, the surface on duck feathers can be regarded as heterogeneous surfaces composed of solid and air. The apparent contact angle θ_1 of the feathers is described by

$$\cos \theta_1 = f_1 \cos \theta_w - f_2,$$

where f_1 is the area fraction of tomenta with nanosized grooves and protuberances, f_2 is the area fraction of air on the feather surface, and θ_w is the contact angle of preening oil. According to Gao and Jiang's work on the legs of water striders [40], we can deduce from the equation that the air fraction between the feather and the water surface corresponds to $f_2 \approx 85\text{--}96.86\%$. Available air is trapped in spaces in the fine tomenta and nanosized grooves and protuberances to form a cushion at the feather–water interface that prevents the feather from being wetted [41].

Chitosan, a linear (β -1,4)-linked biopolysaccharide, is an *N*-deacetylated derivative polyelectrolyte of chitin, which is the structural element in the exoskeleton of crustaceans (crabs, shrimp, etc) and the second-most abundant natural polysaccharide after cellulose, with excellent biodegradability, biocompatibility and nontoxicity. Chitosan is a cationic polyelectrolyte, which makes chitosan soluble in acidic aqueous solution and insoluble in neutral and basic aqueous

solution. The selective solubility of chitosan in acidic aqueous solution provides a simple way to prepare chitosan solid materials with controlled structures. Nanoporous film [36] and nanofibers [42] were fabricated by precipitating chitosan from acidic solution to basic media. Based on the reversible solubility of chitosan in acidic and basic solutions, chitosan polymer brush has been fabricated on the surface of carbon nanotubes [43]. Based on the same procedures, chitosan was applied to textile fibers to improve the surface roughness of fibers. The procedures were schematically shown in figure 3. As shown in figure 3(a), the diluted chitosan solution was applied to textile substrates using a common dipping–coating method. After being treated with the chitosan solution, a thin solution film would be formed on the surface of textile fibers (figure 3(b)). The wet textiles were put into a container filled with ammonia gas. Ammonia was absorbed by the wet chitosan film immediately, changing the pH value of the film from acidic to basic range, resulting in the precipitation of chitosan from the solution and forming nanostructured precipitates on the surface of textile fibers (figure 3(c)). These nanoscaled precipitates will form a proper surface roughness on microscaled fibers. The textiles were dried at 80 $^{\circ}\text{C}$ for 5 min. To achieve low surface energy, the textiles were further treated with silicone compound using the common dipping–padding–drying method.

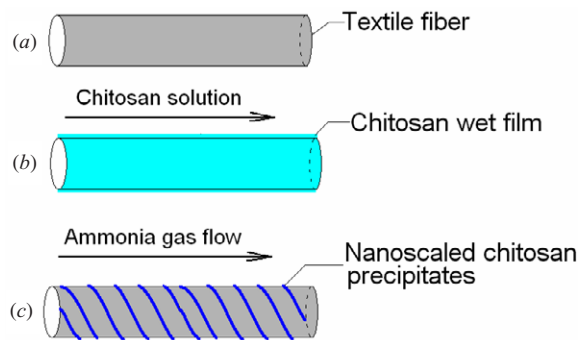


Figure 3. Procedures for fabricating nanoscaled roughness on textile fibers through the surface solution precipitation method.

Figure 4 shows the SEM images of cotton fabrics before and after treatment. Figures 4(a) and (b) present the SEM pictures of the untreated cotton fibers, indicating that the surface of the fibers is smooth with natural veins. Figures 4(c) and (d) show the SEM images of chitosan treated cotton fibers, indicating that after being treated with chitosan, nanosized chitosan precipitates have been formed on the surface of cotton fibers. Because of the good film-forming ability of

chitosan, these nanofiber-like precipitates have been fixed to the surface of cotton fibers. These nanofiber-like precipitates form a proper surface roughness on the microscaled cotton fiber. This micro-nanoscaled binary structure of the treated cotton fibers is very similar to that of duck feathers. Using the same procedures, polyester fabrics were treated with chitosan solutions. Figure 5 shows the SEM images of polyester fibers before and after treatment. Figure 5(a) shows the SEM picture of the untreated polyester fibers. It shows that the diameter of the polyester is about 15 μm and the surface of the polyester is quite smooth. Figures 5(b)–(d) present the SEM images of the chitosan-treated polyester fibers. They indicate that after being treated with the chitosan solution, nanoflower-like chitosan precipitates have been formed on the surface of polyester fibers. Compared with the structure of chitosan precipitates on the cotton surface, the structure of chitosan on polyester is quite different. From figures 5(c) and (d), one can see that the chitosan precipitates on polyester fibers have flower-like structures. This is because the chemical structures of chitosan are very similar to those of cellulose, and chitosan almost has the same physical properties (e.g., coefficient of thermal expansion) as cellulose. When the chitosan solution was dried on the cotton substrate, the dried chitosan was combined with cotton compactly. However,

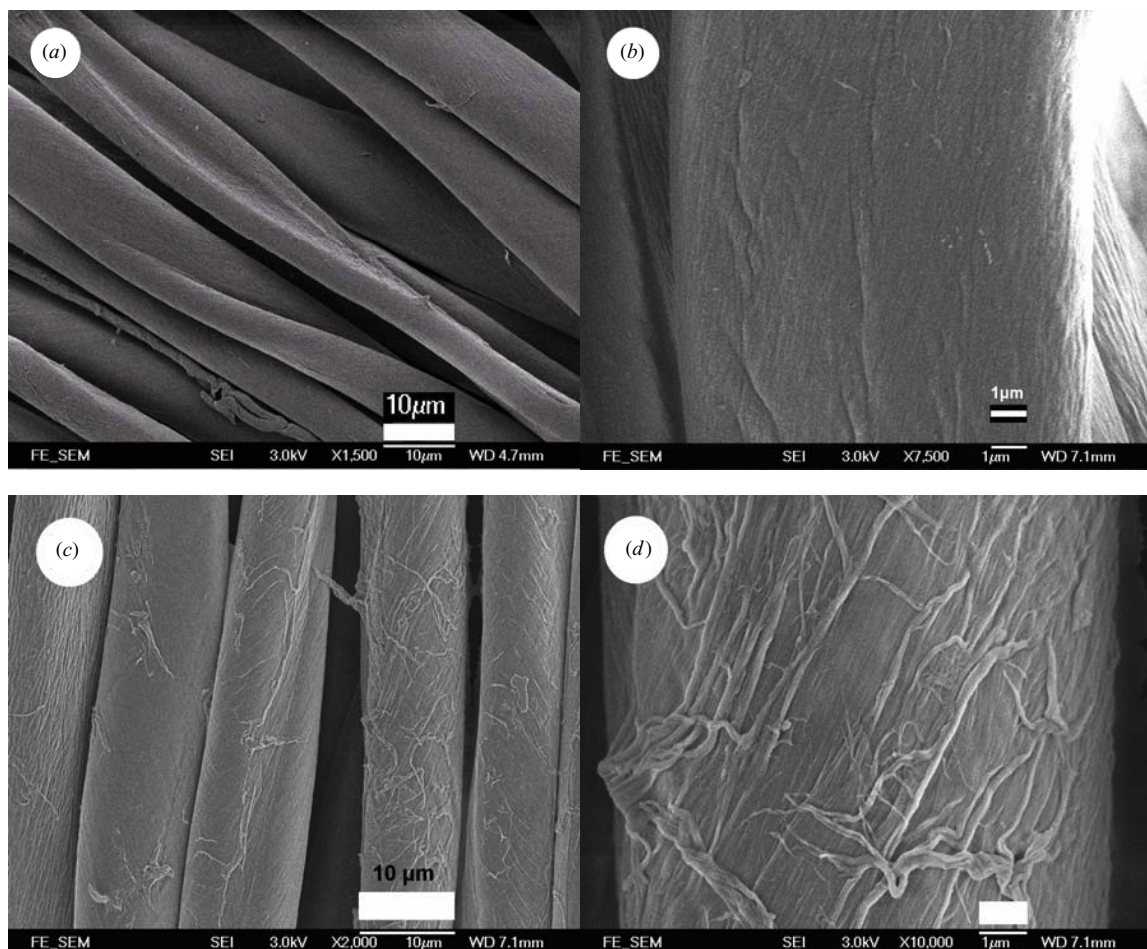


Figure 4. SEM images of untreated cotton (a and b) and chitosan-treated cotton (c and d): nanosized roughness has been formed on polyester surface.

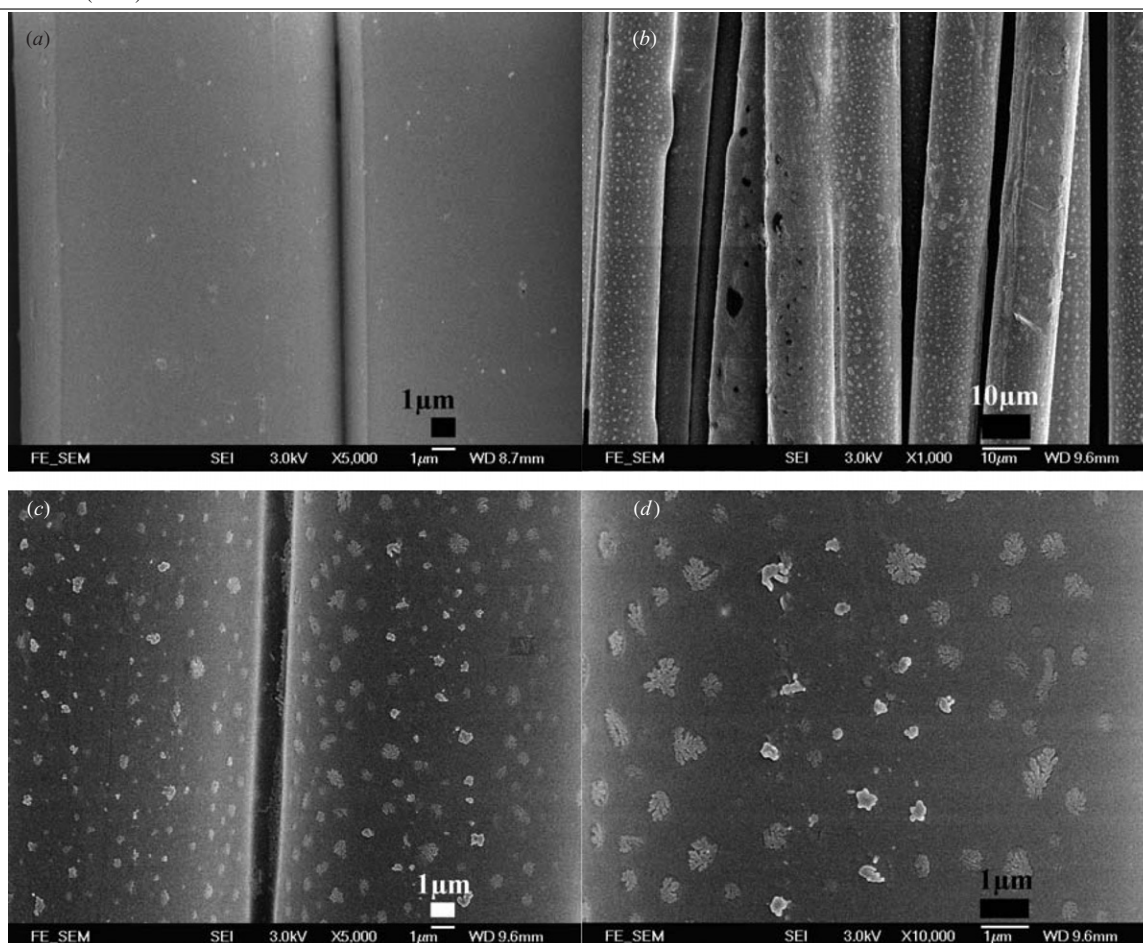


Figure 5. SEM images of untreated (a) polyester and chitosan-treated polyester (b, c and d): nanosized roughness has been formed on the polyester surface.

when the chitosan solution was dried on polyester substrates, because the chemical structure and the physical properties (e.g., coefficient of thermal expansion) of chitosan are quite different to those of polyester, the dried chitosan shrank on the polyester fibers, forming a flower-like structure on their surface. These flower-like chitosan precipitates form a nanoscaled surface roughness on the microscaled polyester fiber. These micro-nano binary structures will be very useful for fabricating a hydrophobic surface on polyester.

After being treated with chitosan, a proper nanoscaled surface roughness has been formed on both cotton and polyester fibers. The resultant textiles were further treated with polysiloxane emulsions to obtain low surface energy. Both the cotton and polyester fabrics show super water repellent properties with a water contact angle (WCA) of around 150° . Figure 6 shows a picture of a water bead on the treated cotton (figure 6(a)) and polyester (figure 6(b)) fabric, revealing that water drops are converging together forming 'drying water beads' on the fabrics. Given a little slope angle ($15\text{--}20^\circ$), these water beads will slip away easily from the textile substrates. Compared with super hydrophobic textiles built from hard material such as carbon nanotubes, these chitosan-modified textiles are cheap and environmentally friendly. At the same time, the treatment of textiles with chitosan can also endow the textiles with durable antibacterial properties [44].

The water repellent properties of pristine cotton (a), chitosan-treated cotton (b), polysiloxane-treated cotton (c), chitosan- and polysiloxane-treated cotton (d), pristine polyester (a'), chitosan-treated polyester (b'), polysiloxane-treated polyester (c'), and chitosan- and polysiloxane-treated polyester (d') are summarized in table 1. The results presented in table 1 confirmed that the surface wettability of textile substrates is governed by both the surface energy and the surface structure of the textile fibers. Sample (a) is the untreated cotton fabrics. It is well known that cotton is a porous material with good water absorption abilities. When water droplet was put onto the surface of untreated cotton fabrics, the water droplet was absorbed immediately by the cotton substrate. Sample (b) is the chitosan-treated cotton fabrics, indicating that after being treated with chitosan the water contact angle increased greatly. The super hydrophilic cotton fabrics have been changed into hydrophobic with a WCA of 130° . This is because chitosan is more hydrophobic than cotton and the nanoscaled precipitates on the cotton surface create a rough surface on cotton fibers. When a water droplet was put on cotton, due to the presence of these nanosized precipitates, lots of air was trapped in the cavities between the precipitates, and water droplets on such a surface only contact with the tips of the nanosized chitosan precipitates. The nanosized precipitates as well as the air in the cavities

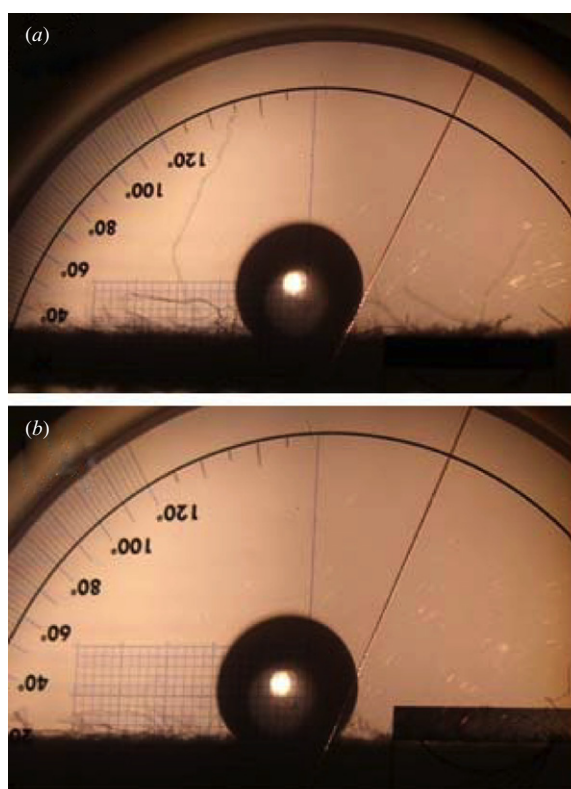


Figure 6. Profile of a water bead on the treated cotton (a) and polyester (b) fabric.

Table 1. Water repellent properties of fabric samples.

Cotton	WCA	Spray	PET	WCA	Spray
a	Absorbed	0	a'	Spread	0
b	130	50	b'	102	50
c	118	70	c'	100	80
d	152	100	d'	148	90

Cotton samples: (a) cotton, (b) chitosan-treated cotton, (c) polysiloxane-treated cotton and (d) chitosan- and polysiloxane-treated cotton. Polyester samples: (a') polyester, (b') chitosan-treated polyester, (c') polysiloxane-treated polyester and (d') chitosan- and polysiloxane-treated polyester.

between the precipitates form a barrier between the water drop and cotton substrates, thus the treated cotton shows improved hydrophobicity. However, because the surface energy of chitosan is not low enough to repel water from cotton, after the water droplet had been on the chitosan-treated cotton for 5 min, the water drop was absorbed by the cotton completely. The spray test results also show that although the chitosan-treated cotton shows a WCA of 130° it can be wetted by pressured water. Sample (c) is the polysiloxane-treated cotton fabrics, showing that after being treated with the low surface energy material polysiloxane, the super hydrophilic cotton fabrics have been changed into hydrophobic with a WCA of about 118° . From the SEM pictures in figure 4, one can find that the diameter of the cotton fiber is about $10\text{ }\mu\text{m}$ and these arrayed cotton fibers form a microscaled roughness. After being treated with polysiloxane, the cotton fiber was covered

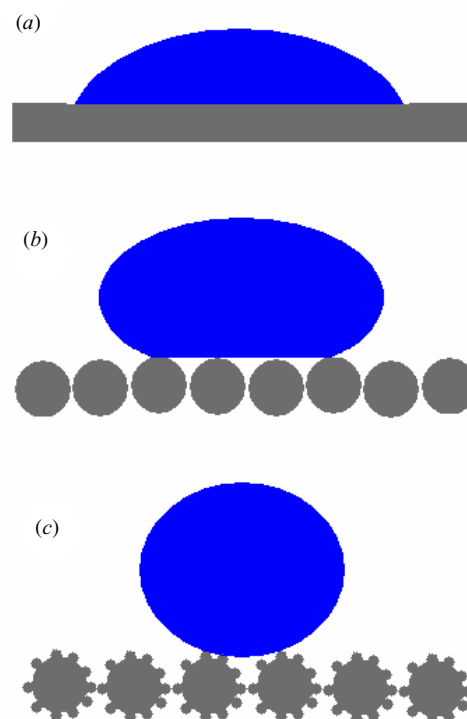


Figure 7. Possible state for water drop on different fabrics: (a) untreated fabric, (b) polysiloxane-treated fabrics and (c) chitosan- and polysiloxane-treated fabrics.

with low surface energy coating. As a result, the polysiloxane-treated cotton exhibits good water repellent properties. In this case, water droplets contact with the side of the micro-sized fibers. Compared with sample (b), sample (c) shows low WCA but long-term water repellent properties and high spray test grade. Sample (d) is the chitosan- and polysiloxane-treated cotton fabric developed in this paper. In this case, the cotton fibers have both multi-scaled surface roughness and low surface energies, and thus the chitosan- and polysiloxane-treated cotton fabrics show super water repellent properties with high water contact angles ($>150^\circ$) and high spray test grade. Sample (a') is the untreated polyester fabric. When the water droplet was put onto the surface of untreated polyester fabrics the water droplet just spread on the polyester forming a water film because polyester is more hydrophobic than cotton. Sample (b') is the chitosan-treated polyester fabric, indicating that after being treated with chitosan the polyester fabrics show an improved hydrophobic property with a water contact angle of about 102° . Sample (c') is the polysiloxane-treated polyester fabric. Because the surface of polyester is smoother than that of cotton fibers, the polysiloxane-treated cotton is more hydrophobic than the polysiloxane-treated polyester fabric. Sample (d') is the chitosan- and polysiloxane-treated polyester fabric. Because the chitosan- and polysiloxane-treated polyester fabrics have both multi-scaled surface roughness and low surface energies, they exhibit super water repellent properties with high water contact angles. A possible state for a water drop on different fabrics is presented in figure 7. The drop either follows the structures on the solid (Wenzel situation) or sits at the top on the posts (Cassie state).

4. Conclusions

Inspired by the novel water repellent phenomena of duck feathers, artificial duck feather structures were fabricated on textile substrates using a simple solution precipitation method. The microstructures of duck feathers were investigated using the SEM imaging method. The SEM pictures show that duck feathers have multi-scaled structures in their texture. The multi-scaled structures on duck feathers provide proper surface roughness for water repellent characteristics. The duck uses preening oil to create a low energy surface on its feathers. As a result, the duck feather exhibits super water repellent properties. The multi-scaled structures of duck feathers were fabricated on textile substrates to create hydrophobic textiles. The soft biopolymer chitosan was employed as building blocks to produce nanosized roughness on cotton and polyester fibers and then the textiles were further treated with polysiloxane emulsion to achieve low surface energy. The resultant textiles show super water repellent properties with comfortable handle. The method developed in this paper provides a simple way to fabricate a super water repellent surface on soft substrates using soft material as building blocks.

Acknowledgment

This work was supported by the Hong Kong Polytechnic University.

References

- [1] Liu Y Y, Tang J, Wang R H, Lu H F, Li L, Kong Y Y, Qi K H and Xin J H 2007 *J. Mater. Chem.* **17** 1701–78
- [2] Lee Y, Park S-H, Kim K-B and Lee J-K 2007 *Adv. Mater.* **19** 2330–5
- [3] Sun T, Feng L, Gao X and Jiang L 2005 *Acc. Chem. Res.* **38** 644–52
- [4] Zhu Y, Zhang J, Zheng Y, Huang Z, Feng L and Jiang L 2006 *Adv. Funct. Mater.* **16** 568
- [5] Zhao N, Weng L, Zhang X, Xie Q, Zhang X and Xu J 2006 *Chem. Phys. Chem.* **7** 824
- [6] Wang S, Feng L and Jiang L 2006 *Adv. Mater.* **18** 767
- [7] Blossey R 2003 *Nat. Mater.* **2** 301–6
- [8] Barthlott W and Neinhuis C 1997 *Planta* **202** 1–8
- [9] Feng X and Jiang L 2006 *Adv. Mater.* **18** 3063–78
- [10] Gao L and McCarthy T J 2006 *Langmuir* **22** 5998
- [11] Roach P, Shirtcliffe N J and Newton M I 2008 *Soft Matter* **4** 224
- [12] Quere D and Reyssat M 2008 *Phil. Trans. R. Soc. A* **366** 1539–56
- [13] Nosonovsky M and Bhushan B 2008 *Adv. Funct. Mater.* **18** 843–55
- [14] Tsujii K, Yamamoto T, Onda T and Shibuichi S 1997 *Angew. Chem., Int. Ed.* **36** 1011
- [15] Shibuichi S, Yamamoto T, Onda T and Tsujii K 1998 *J. Colloid Interface Sci.* **208** 287
- [16] Narita M, Kasuga T and Kiyotani A 2000 *J. Japan Inst. Light Met.* **50** 594
- [17] Thieme M, Frenzel R, Schmidt S, Simon F, Hennig A, Worch H, Lunkwitz K and Scharnweber D 2001 *Adv. Eng. Mater.* **3** 691
- [18] Shirtcliffe N J, McHale G, Newton M I and Perry C C 2005 *Langmuir* **21** 937
- [19] Zhang X, Shi F, Yu X, Liu H, Fu Y, Wang Z Q, Jiang L and Li X Y 2004 *J. Am. Chem. Soc.* **126** 3064
- [20] Shi F, Wang Z and Zhang X 2005 *Adv. Mater.* **17** 1005
- [21] Ogawa K, Soga M, Takada Y and Nakayama I 1993 *Japan. J. Appl. Phys.* **2** 32 L614
- [22] Olde Riekerink B M, Terlingen J G A, Engbers G H M and Feijen J 1999 *Langmuir* **15** 4847
- [23] Khorasani M T, Mirzadeh H and Kermani Z 2005 *Appl. Surf. Sci.* **242** 339
- [24] Khorasani M T and Mirzadeh H 2004 *J. Appl. Polym. Sci.* **91** 2042
- [25] Jiang L, Zhao Y and Zhai J 2004 *Angew. Chem., Int. Ed.* **43** 4338
- [26] Acatay K, Simsek E, Ow-Yang C and Menciloglu Y Z 2004 *Angew. Chem., Int. Ed.* **43** 5210
- [27] Ma M, Hill R M, Lowery J L, Fridrikh S V and Rutledge G C 2005 *Langmuir* **21** 5549
- [28] Lau K S, Bico J, Teo K B, Chhowalla M, Amaratunga G A, Milne W I, McKinley G H and Gleason K K 2003 *Nano Lett.* **3** 1701
- [29] Liu H, Feng L, Zhai J, Jiang L and Zhu D 2004 *Langmuir* **20** 5659
- [30] Wu Y, Bekke M, Inoue Y, Sugimura H, Kitaguchi H, Liu C and Takai O 2004 *Thin Solid Films* **457** 122
- [31] Huang L, Lau S P, Yang H Y, Leong E S, Yu S F and Praver S 2005 *J. Phys. Chem. B* **109** 7746
- [32] Tadanaga K, Kitamuro K, Matsuda A and Minami T 2003 *J. Sol-Gel Sci. Technol.* **26** 705
- [33] Nakajima A, Fujishima A, Hashimoto K and Watanabe T 1999 *Adv. Mater.* **11** 1365
- [34] Shirtcliffe N J, McHale G, Newton M I and Perry C C 2003 *Langmuir* **19** 5626
- [35] Liu Y Y, Wang X W, Qi K H and Xin J H 2008 *J. Mater. Chem.* **18** 3454–60
- [36] Liu Y Y, Tang J, Chen X Q and Xin J H 2005 *Carbohydr. Res.* **340** 2816–20
- [37] Wenzel R N 1936 *Ind. Eng. Chem.* **28** 988
- [38] Cassie A B D and Baxter S 1944 *Trans. Faraday Soc.* **40** 546
- [39] Nishino T, Meguro M, Nakamae K, Matsushita M and Ueda Y 1999 *Langmuir* **15** 4321
- [40] Gao X F and Jiang L 2004 *Nature* **432** 36
- [41] Bormashenko E, Bormashenko Y, Stein T, Whyman G and Bormashenko E 2007 *J. Colloid Interface Sci.* **311** 212–16
- [42] Liu Y Y, Chen X Q, Chen W, Yang K and Xin J H 2005 *Chem. Lett.* **34** 1640
- [43] Liu Y Y, Tang J, Chen X Q and Xin J H 2005 *Carbon* **43** 3178
- [44] Gao Y and Cranston R 2008 *Text. Res. J.* **78** 60