ACS OMEGA

Article

Cite This: ACS Omega 2019, 4, 7829−7837

http://pubs.acs.org/journal/acsodf

Robust Superhydrophobic Cotton Fibers Prepared by Simple Dip-Coating Approach Using Chemical and Plasma-Etching Pretreatments

Phuong Nguyen-Tri,*[,†,∥] Funda Altiparmak,[†,‡] Nam Nguyen,[∥] Ludovic Tuduri,[§] Claudiane M. Ouellet-Plamondon,[∥] and Robert E. Prud'homme[†]

[†]Department of Chemistry, Université de Montréal, Montréal, QC H3C 3J7, Canada

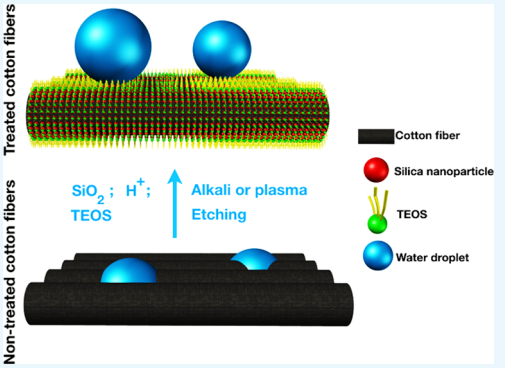
[‡]Department of Chemistry, Université de Pierre-et-Marie-Curie, Paris 75006, France

[§]Institut de Recherche Robert-Sauvé en santé et sécurité dutravail (IRSST), Montréal, QC H3A 3C2, Canada

[∥]Department of Construction Engineering, École de Technologie Supérieure, University of Quebec, Montréal, QC H3C 1K3, Canada

Supporting Information

ABSTRACT: The preparation of superhydrophobic textiles with high mechanical and chemical durability is challenging. Here, facile and fluorine-free methods, using alkali and plasma-etching treatments, followed by the addition of silica nanoparticles and tetraethyl orthosilicate (TEOS), were used to prepare superhydrophobic cotton surfaces. With different input variables and etching techniques, superhydrophobic cotton fabrics with high chemical and mechanical durability were successfully prepared, with contact angles up to 173°. A control of the surface architecture at the nanoscale in combination with a homogeneous repellent layer of TEOS in the cotton surface was achieved. The repellent properties of the as-prepared cotton remain stable under accelerated laundering and abrasion test conditions. The etching pretreatment by alkali or plasma plays a key role in obtaining superhydrophobic cotton surfaces.



1. INTRODUCTION

Superhydrophobic surfaces and coatings have received great attention from both industrial manufacturers and scientists because of a wide range of applications due to their anticorrosion,[1−3] antiwear,[4,5] antibacterial,[6−11] antifungal,[12−14] self-cleaning,[15−20] solar-reflective[21−23] and photocatalytic properties.[24−31] Superhydrophobic textiles[32,33] with self-cleaning properties have been generated by making a double structure at two different scales, characterized by the surface roughness of their microstructures and nanostructures, covered by hydrophobic substances on the top surface.[34−36]

These approaches have led to the formation of surfaces that exhibit large contact angles (greater than 150°) or low-contact-angle hysteresis (lower than 10°) for use in specific applications.[33,37] Water drops deposited on superhydrophobic surfaces are not absorbed, but they move on the surface, carrying away residual matters on their way, like dust and contaminants. Wenzel[38] and Cassie−Baxter[39] suggested that hydrophobic properties are related to the presence of a microstructure at the surface. More specifically, Cassie−Baxter's law considers that the water droplets form spheres and reside on the surface of the fibrous microstructure, remaining at the top of the asperities, forming air pockets between the water droplet and the surface.[40]

The incorporation of nanomaterials in textiles can provide new and unexpected properties such as antistaining, water repellence, wrinkle freeness, static elimination, electrical conductivity, and antibacterial characteristics without compromising their comfort and flexibility.[41] For water-repellent properties, most recent approaches are mainly based on covering the textile surface by nanoparticles[42−46] followed by a chemical treatment with water-repellent agents.[47] Rough surfaces have been obtained by introducing inorganic nanoparticles such as SiO_2,[48] TiO_2,[49] and ZnO[50] by the sol−gel methods. Fluorinated materials have been coated on textile fibers due to their low surface energy and repulsive properties to oil and water.[41,51] Cotton has often been used in the manufacture of clothing fabrics due to its characteristics including softness, comfort, flexibility, hydrophilicity with high absorption capacity, and low cost.[52] Thanks to the large number of hydroxyl groups on its surface,[53] cotton can be readily colored and modified by physical[54] and chemical methods.[55]

Received: March 12, 2019
Accepted: April 19, 2019
Published: April 30, 2019

Table 1. Treatment Conditions for Cotton Fabrics by One-Step (a) and Two-Step (b−f) Procedures

samples	pretreatment	solution A step 1	solution B step 2	contact angle (deg)
a	water/ethanol	SiO_2 (8%) + water (300 mL) + acetic acid (2 mL) TEOS (10%)		91 ± 1
b	NaOH (0.5 M)	SiO_2 (8%)	TEOS (10%)	147 ± 1
c	NaOH (0.5 M)	SiO_2 (10%)	TEOS (10%)	152 ± 1
d	NaOH (0.5 M)	SiO_2 (12%)	TEOS (10%)	160 ± 2
e	NaOH (0.5 M)	SiO_2 (12%)	TEOS (15%)[a]	173 ±2
f	plasma	SiO_2 (12%)	TEOS (15%)[a]	173 ± 2
g	plasma	SiO_2 (12%) 2 wt % of acrylic resin	TEOS (15%)[a]	167 ± 2

[a]Exceptionally, solution B was prepared in benzene instead of toluene.

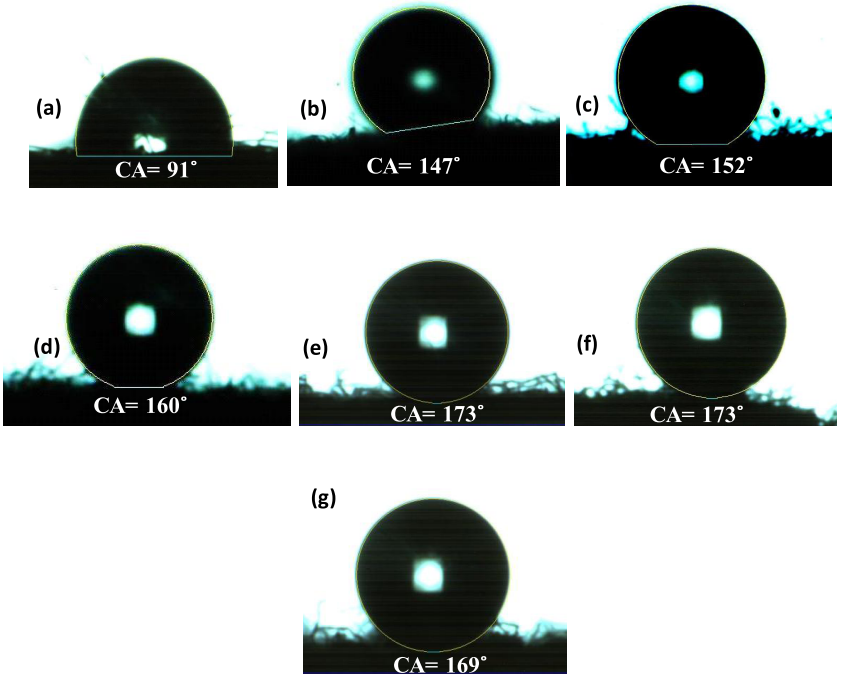


Figure 1. Contact angles of cotton fabric treated in different conditions as shown in Table 1: (a) corresponds to conditions in line a1; (b) corresponds to conditions in line b1; (c) corresponds to conditions in line c1; (d) corresponds to conditions in line d1; (e) corresponds to conditions in line e1; (f) corresponds to conditions in line f1 and (g) corresponds to conditions in line g1.

We report, here, facile and fluorine-free methods to prepare superhydrophobic cotton fabrics by a dip-coating technique using chemical and physical etching treatments of the fiber followed by the deposition of silica nanoparticles and tetraethyl orthosilicate (TEOS). By controlling the etching conditions and input variables, superhydrophobic cotton fabrics were successfully prepared with contact angle values up to 173°. These fabrics display excellent resistance to chemical and mechanical aggressors due to the covalent bonds formed between the cotton surface and TEOS. The morphology of the as-prepared superhydrophobic cottons was revealed by using mainly the scanning electron microscopy−energy-dispersive X-ray analysis (SEM−EDXA) technique. These treated cotton fabrics exhibit improved performance compared to existing ones where either durability or superhydrophobicity is lacking.

2. RESULTS AND DISCUSSION

2.1. Wettability. Table 1 describes the conditions of the preparation of the samples reported in this article, whereas Figure 1 shows the corresponding water contact angles (WCA) measurements. First, SiO_2 (8 wt %) and TEOS (10 wt %) one-step dip-coating treatment was applied to a fabric that had not been subjected to a chemical or plasma-etching pretreatment (but they were washed with water and ethanol). As shown in Table 1, line a, and Figure 1a, this process gives a low WCA of 91°.

Upon chemical pretreatment with NaOH, followed by dip-coating in solution A with 8 wt % SiO_2 and in solution B with 10 wt % of TEOS, Table 1, line b and Figure 1b, there is a jump of the WCA to 147°, indicating that etching is required to retain sufficient SiO_2 and TEOS on the fiber to improve the hydrophobicity. Similar processes with slightly higher amounts of SiO_2 (10 and 12 wt %) (Table 1, lines c and d, and Figure 1c,d) lead to a slight improvement in WCA of 152 and 160°, respectively.

Another experiment, Table 1, line e and Figure 1e, was developed keeping the SiO_2 concentration at 12 wt % but increasing the TEOS concentration to 15 wt %; this content further improves the values of WCA to a high value of 173°. A second set of experiments was developed by etching the fabric by plasma treatment, instead of chemicals. When keeping the SiO_2 and TEOS concentrations at the same value as in Figure 1e, Table 1, line f and Figure 1f, a similar value of WCA of 173° is obtained, indicating that the chemical and plasma treatments are equally effective.

DOI: 10.1021/acsomega.9b00688
ACS Omega 2019, 4, 7829−7837

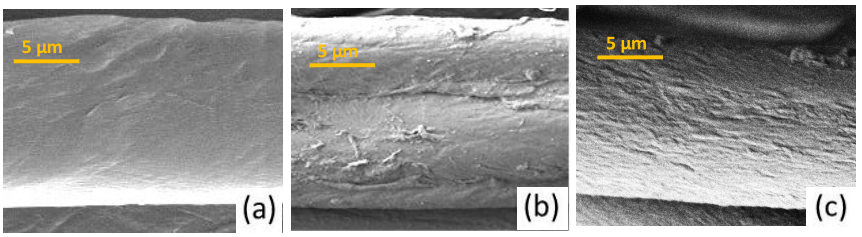


Figure 2. SEM images of (a) untreated cotton, (b) chemically treated cotton, and (c) plasma-treated cotton.

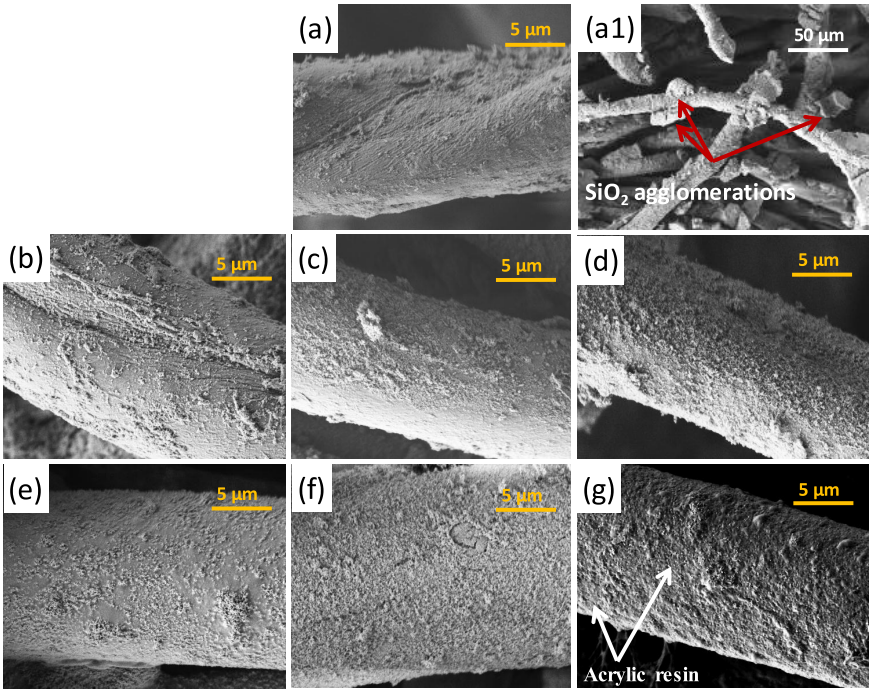


Figure 3. SEM images of treated cotton by the one-step (a) and two-step (b–g) procedures. Details of the treatment conditions are shown in Table 1, i.e., pictures (a–g) correspond to lines a–g of Table 1. Figure (a1) show an example of SiO_2 agglomeration of cotton fiber treated by the one-step approach.

Finally, etching again by plasma, keeping the SiO_2 and TEOS concentrations at 12 and 15 wt %, respectively, as in the previous case, but adding this time 2 wt % of an acrylic resin to solution A, Table 1, line g and Figure 1g, a small decrease of the contact angle from 173 to 167° is observed.

These exceptionally high values of WCA, particularly under conditions 1e and 1f, can be attributed to the fact that the pretreatment of the fiber surface by etching with NaOH solution or plasma creates a rough microstructure. Then, a homogeneous distribution of nanoparticles at the submicrometer level, covered by a thin layer of TEOS, leads to the super repellent properties of the cotton fibers.

2.2. Surface Morphology and Self-Cleaning Properties. To better understand the superhydrophobicity behavior observed in the previous section, high-resolution SEM images were obtained from the fiber surface. Figure 2 shows examples of the SEM images of untreated and treated cotton fibers by different methods. It can be seen that untreated fibers are smooth (Figure 2a). However, the etching pretreatment with sodium hydroxide leads to an increase of the rugosity of the cotton fibers (Figure 2b) due to the extraction of low-molecular-weight materials and lignin present in them. A similar rough cotton surface is observed after plasma treatment (Figure 2c) due to the electron bombardment, also leading to the removal of impurities and low-molecular-weight species.

The SEM images after the deposition of SiO_2 nanoparticles and repellent TEOS are shown in Figure 3. A SEM image of cotton treated by the one-step procedure is used as a reference (Figure 3a). It can be seen that this process leads to a large number of aggregates of SiO_2 on the cotton surface. These aggregates, with dimensions of the order of several microns, are more clearly observed at the lower-magnification image (red arrows). Figure 3b presents the SEM image of cotton treated with 8 wt % SiO_2 nanoparticles as described in Table 1, line b. The increase of the nanoparticles content in solution A leads to a higher density of nanoparticles on the cotton surface (Figure 3c–e). The pretreatment with plasma (Figure 3f), followed by nanoparticles and TEOS depositions, also leads to aggregates having similar density to those obtained with chemical treatment (Figure 3e). In all cases, there is a homogeneous distribution of nanoparticles on the fiber surface. The addition of acrylic leads to homogeneous nanoparticles on the cotton fiber surface, and the acrylic resin can be observed from the SEM image (Figure 3g). The chemical or plasma pretreatments create a rough surface and, presumably, functional groups to enhance the reaction between cotton surface and SiO_2 nanoparticles.

DOI: 10.1021/acsomega.9b00688
ACS Omega 2019, 4, 7829–7837

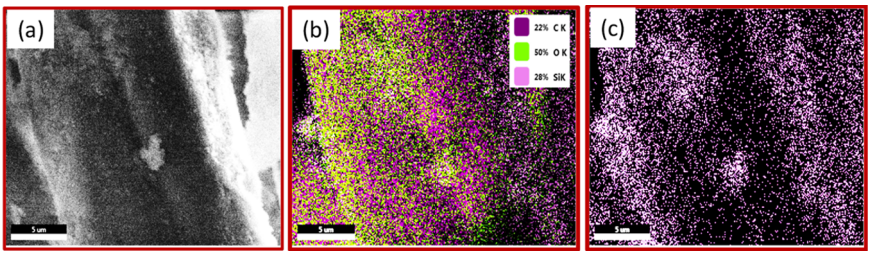


Figure 4. NaOH-treated cotton fabric (sample e, Table 1): (a) SEM image, (b) elemental analysis image, and (c) silicium mapping of a cotton fiber surface.

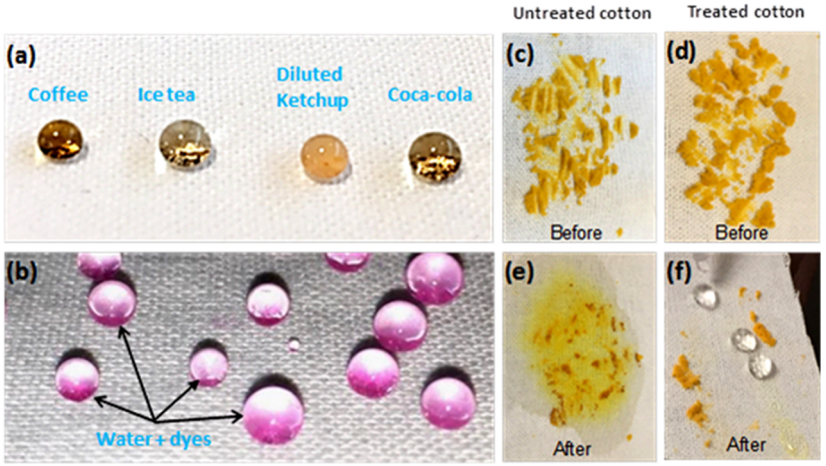


Figure 5. Photos of different liquids deposited on a NaOH-treated cotton surface (sample e, Table 1): (a) coffee, tea, diluted ketchup, and Coca-Cola; (b) water + dye (5 wt %); (c–f) photos of a natural colorant of turmeric nanopowder deposited on an untreated cotton and alkali-treated cotton (d). Before adding water drops in (c) and (d), the colorant is seen sitting on the fabric; after adding water drops, in (d), it is carried inside the fabric, whereas, in (f), it is washed away from the surface by the nonabsorbing water.

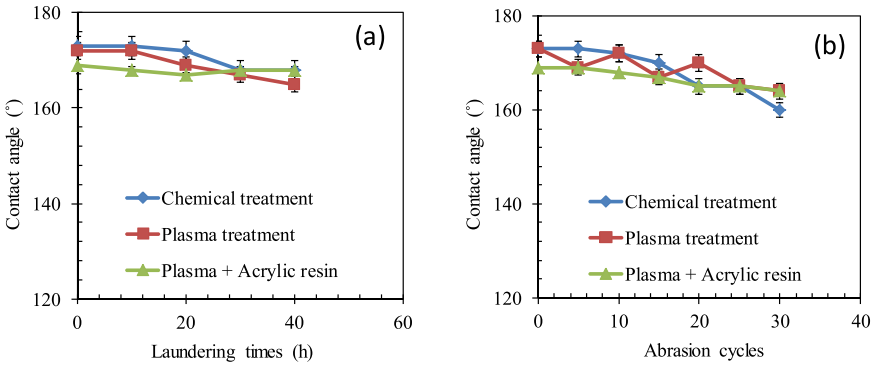


Figure 6. (a) Contact angle as a function of laundering times (2 wt % detergent, hot water) and (b) abrasion cycles after different methods of treatments: chemical treatment (sample e, Table 1); plasma treatment (sample f, Table 1); and plasma treatment + acrylic resin coating (sample g, Table 1).

The semiquantitative elemental analysis of a plasma-treated cotton is shown in Figure 4. This figure first shows by SEM (Figure 4a) a relatively homogeneous distribution of silicium nanoparticles on the cotton fiber surfaces, as it was found in Figure 3a. Figure 4b, and confirmed by elemental analysis, shows the presence of nanoparticles on the whole fiber surface, mainly distributed at the submicrometer scale. A separate mapping image for silicium (Figure 4c) provides a direct observation of the distribution of this element on the treated cotton surface; SiO_2 nanoparticles are found on the whole cotton surface, and they are well distributed without aggregation. In other words, the concentration of nanoparticles used is suitable to form a homogeneous layer of SiO_2 on the surface of cotton.

The repellent behavior of treated cotton fabric to different liquids that have lower values of surface tension than pure water,[56−58] including coffee, ice tea, diluted ketchup, Coca-Cola, and dyed water, was also investigated. Figure 5a,b shows the photos of different liquids sitting on the treated cotton surface. They have a spherical form and have not penetrated the treated cotton structure, meaning that the cotton exhibits a superhydrophobility not only for water but also for these liquids. The self-cleaning properties of the cotton were verified with a natural colorant (turmeric nanopowder): 2 g of turmeric powder was deposited on 2 cm^2 nontreated (Figure 5c) and

DOI: 10.1021/acsomega.9b00688
ACS Omega 2019, 4, 7829−7837

alkali-treated cotton surfaces (Figure 5d). They were then wetted by 2 mL of distilled water drops for 30 s. In the case of untreated cotton, the water drops are rapidly absorbed by the cotton fabric, carrying the colorant inside the fabric structure (Figure 5e). However, in the case of the alkali-treated cotton, the water droplets were not absorbed by the fabric, and they carry the colorant away from the cotton surface as can be seen in Figure 5f.

2.3. Mechanical and Laundering Durability. For reuse purposes, treated cottons should be resistant to laundering conditions. The laundering of the treated cottons was carried out in hot water (60 °C) with and without detergent (2%). The subsequent measurements of contact angles as a function of laundering times of cotton treated with different methods are shown in Figure 6a. This figure shows that the contact angle decreases slightly after 40 h of treatment from 173° (±1) to 165° and from 172° (±1) to 167° with dip-coating and plasma-treatment methods, respectively, indicating the stability of the treatment. The sample pretreated with plasma, followed by an acrylic resin treatment, shows a stable WCA after 40 h of laundering.

The mechanical durability of the superhydrophobic coating on the fiber surface was investigated with an abrasion test, as described in the experimental section: the variation of the contact angle was followed during the abrasion cycles ranging from 1 to 40 (Figure 6b). The cotton shows a reduction of 10% of WCA after 30 abrasion cycles in the case of alkali-treated (blue curve, Figure 6b) and plasma-treated cotton fabrics (red curve, Figure 6b). The pretreatment of the cotton with plasma, followed by the addition of acrylic resin (sample g, Table 1), leads to a slightly lower WCA, but the cotton exhibits higher resistance to abrasion compared to those without resin because their WCA value remains unchanged after applying 30 abrasion cycles (green curve, Figure 6b).

2.4. Discussion. The contact state of a liquid droplet on a textured surface can be described by Wenzel[38] and Cassie–Baxter[59] theories. In the first case, it is considered that the structure can be wet by the liquid droplets due to their deep penetration of the textured surface. In contrast, the Cassie–Baxter model[59] supposes that there are air pockets between the deposited liquids and the material surface, leading to a reduction of contact area and an increase in contact angle.

Figure 7 shows the high-resolution SEM images of the surface of cotton fibers pretreated with alkali (Figure 7a) and plasma (Figure 7b), followed by the addition of dip-coated silica nanoparticles and TEOS layers. It can be seen that both pretreatment methods lead to the formation of rugosity surface with a large quantity of cavities (holes) (Figure 7). These holes were found on the whole sample surface, with various dimensions ranging from several ten to a hundred nanometer (red arrows). This structure supports the contacting liquid droplets in the Cassie–Baxter approach.

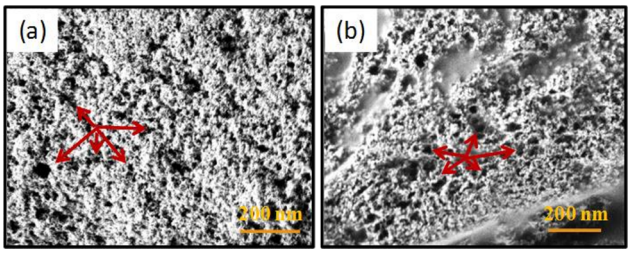


Figure 7. High-resolution SEM images at the surface of cotton fibers treated by (a) NaOH (sample e, Table 1) and (b) plasma (sample f, Table 1). Red arrows show the presence of air pockets on the surface of treated cotton fiber.

In nature, lotus leaves are repellent to liquids because they possess a double hierarchical structure with bumps called papillae, covered by hydrophobic tubes at a scale of 100 nm.[60] In the literature, similar artificial superhydrophobic textures are usually obtained in two steps: the first step involves an etching process by chemical or physical methods, followed by the addition of layered hydrophobic compounds.

In this work, two different approaches were used to obtain superhydrophobic surfaces. In the first step (step 1, Figure 8), the cotton fibers were etched by chemical or physical means. It is well known that the cotton fibers are mainly composed of cellulose, hemicelluloses, lignin, and some impurities.[61,62] The alkali pretreatment partially removes lignin and impurities on the fiber surface[63] and, thus, enhances the surface rugosity (Figure 2b). The plasma etching leads to the removal of impurities from the fiber surface, resulting in a rough surface, as shown in Figure 2c. In the second step (step 2, Figure 8), a homogeneous deposition of silica nanoparticles by dip-coating, followed by the addition of a layer of superhydrophobic agent (TEOS), leads to a rough surface and water-repellent properties by creating covalent bonds between the silane groups of TEOS and the hydroxyl groups of the silica nanoparticles (Figure 8).

Moreover, the used cotton fabric is formed by a large number of knitted fibers with dimensions of 10–20 μm (Figure 3a–g), which are comparable with bumps on a lotus leaf at the scale of 10–20 μm.[60] The choice of homogeneous and small nanoparticles (7 nm) and suitable dip-coating conditions (concentration of nanoparticles and immersion time) leads to a homogeneous distribution of nanoparticles with a double hierarchical scale of textures, as proven by SEM images (Figure 3e,f). This structure enhances the contact angle of liquid droplets as schematically shown in Figure 9. In other words, the liquid droplets exhibit higher apparent contact angles on a double hierarchical structure compared with surfaces with a single scale texture[56] (nontreated or treated only with nanoparticles). This is because air is trapped at a double length scale in a hierarchical structure, whereas it is trapped only at one length scale in the surfaces with a single texture.[56]

3. CONCLUSIONS

Superhydrophobic cotton fabrics with contact angles up to 173° were successfully prepared using 7 nm silica nanoparticles and a silane-based water-repellent agent, TEOS, in combination with two etching pretreatment methods dealing with alkali and plasma approaches. This exceptionally high value of contact angle can be explained by several reasons: (i) the alkali and plasma pretreatments lead to a homogeneous rough surface that enhances the hydrophobicity of the cotton fibers and (ii) the use of ultrasmall 7 nm silica nanoparticles leads to the creation of a double hierarchical scale on the cotton surface, which confines the contact liquid droplet on the surface without penetration to the cellulose substrate. The two etching methods used are equally effective.

Our finding shows that the amount of silica nanoparticles and TEOS are key parameters that directly affect the superhydrophobility behavior of the treated cottons and, thus, display a high resistance to both laundering and abrasion

DOI: 10.1021/acsomega.9b00688
ACS Omega 2019, 4, 7829–7837

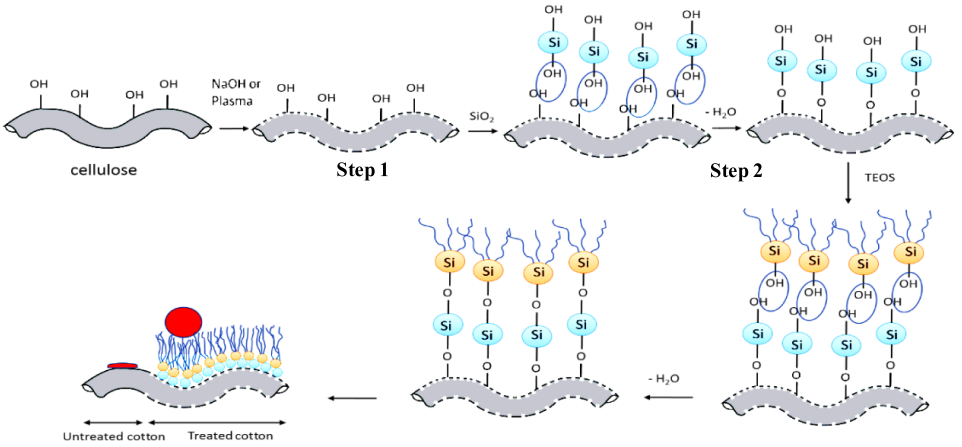


Figure 8. Schematic illustration of the preparation of superhydrophobic cotton fabric by alkali or plasma pretreatments.

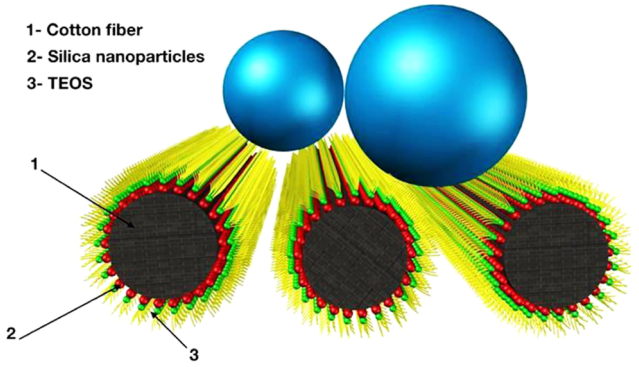


Figure 9. Schematic illustration of liquid droplets deposited on superhydrophobic cotton.

tests. The contact angle remains stable after 30 cycles of abrasion and 40 h of washing in hot water with a detergent. These cotton fabrics exhibit potential applications in various fields such as oil/water filtration and functional protective clothing with self-cleaning and repellent properties to contaminants such as chemicals or aqueous pesticides.

4. EXPERIMENTAL METHODS

4.1. Materials. Tetraethyl orthosilicate (TEOS, 98%), silica nanoparticles (7 nm in diameter), absolute ethanol, sodium hydroxide, toluene, acetic acid, and acetone of analytical grade were purchased from Sigma-Aldrich. They were used as received without further purification. A white commercial cotton fabric was kindly provided by a local tissue store (Montreal, Canada). Acrylic emulsions (Primal AC-261), having a solid content of 50 wt %, and texanol (2,2,4-trimethyl-1,3-pentanediol monoisobutyrate) as a coalescing agent were obtained from the Dow Chemical Company. The pink dyes were supplied by Brother International Corp. (Canada). The natural colorant (turmeric nanopowder) was kindly provided by the Institute of Chemistry, Hanoi, VietNam.

All cotton samples were initially cleaned with deionized water to remove impurities after a period of 10 min under vacuum at 60 °C. Some of the fabrics were then immersed in a sodium hydroxide solution (0.5 M) for 10 min for etching the cotton surface by removing low-molecular-weight components and lignin. Alternatively, the cotton surface can be etched using a plasma radiation (LEICA EM ACE600) in the presence of oxygen for 20 min; a plasma power of 19 W/min was used. This leads to a rough surface and multifunctional groups, ions, and radicals.

4.2. Preparation of Superhydrophobic Textiles by Dip-Coating. The cotton fabrics, previously etched with NaOH or by plasma treatment, were dip-coated into solution A [solution A was prepared by adding silica nanoparticles (8, 10, or 12 wt %) to a mixture of distilled water (200 mL), ethanol (100 mL), and acetic acid (2 mL)] at a rate of 500 μm/s for 10 min before retraction. This process provides a uniformly thin layer of nanoparticles on both sides of the cotton fabric (step 1). Then, the cotton fabric was submersed in solution B for 24 h [solution B was prepared by adding 12 or 15 wt % TEOS to toluene with the Stöber et al. method[64]], dried, and thermally treated to create covalent bonds between the cotton and repellent agent (step 2). In some cases, an AC-261 acrylic resin (2 wt %) was added to solution B to improve the adhesion and enhance the durability of the superhydrophobic cotton surface.

4.3. Characterization. *4.3.1. Contact Angle Measurements.* Contact angle measurements were carried out on the FTA200 Dynamic Contact Angle Analyzer at room temperature using a 10 μL water droplet. All contact angles were measured in ten different areas of the cotton fabric, and the reported values are averages.

4.3.2. SEM and EDXA. Scanning electron microscopy (SEM, JEOL JSM-7400F) was used to observe the morphology of original and treated cotton fibers. Since the samples are not conductive, a gold layer of 10 nm was coated on the sample surface using a LEICA EM ACE600 sputter coater. In addition, the SEM coupled with an energy-dispersive X-ray analysis (EDXA) apparatus was used to characterize the distribution of SiO_2 nanoparticles on the fiber surfaces.

4.3.3. Laundering and Mechanical Stability. The stability of the superhydrophobic fabrics to accelerate laundering was investigated in which coated cotton samples were immersed in a mixture solution of detergent (2 wt %) and distilled water; they were then continuously stirred using a magnetic stirrer at a rate of 100 rpm while the temperature was maintained at 60 °C during treatment. The samples were removed at different periods of time (10, 20, 30, and 40 h) to measure the changes of WCA. To determine the resistance of the superhydrophobic cottons to mechanical aggressors, abrasion tests were carried

DOI: 10.1021/acsomega.9b00688
ACS Omega 2019, 4, 7829−7837

out using a homemade device in which a 5 × 5 cm^2 treated fabric was dragged between a weight of 200 g and 180 grits sandpaper. The treated cotton was then moved at a constant rate (0.25 cm/s) before evaluating the changes in contact angles generated by this test. The tests were repeated 20 times, and the reported results are averages.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00688.

Treatment of cotton fabric with only with SiO_2 nanoparticles (Figure S1) shows that the Si ratio is around of 16% (Figure S1b) before treating with TEOS compared to 28% after TEOS treatment (Figure 4b); this is because the TEOS contains also Si element (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Phuong.nguyen.tri@umontreal.ca. Tel.: + 514-340 5121 (7326).

ORCID

Phuong Nguyen-Tri: 0000-0001-6578-5716

Claudiane M. Ouellet-Plamondon: 0000-0003-3795-4791

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for the financial support of this work.

■ REFERENCES

(1) Zheludkevich, M. L.; Shchukin, D. G.; Yasakau, K. A.; Möhwald, H.; Ferreira, M. G. S. Anticorrosion Coatings with Self-Healing Effect Based on Nanocontainers Impregnated with Corrosion Inhibitor. *Chem. Mater.* **2007**, *19*, 402−411.

(2) Abdollahi, H.; Ershad-Langroudi, A.; Salimi, A.; Rahimi, A. Anticorrosive Coatings Prepared Using Epoxy−Silica Hybrid Nanocomposite Materials. *Ind. Eng. Chem. Res.* **2014**, *53*, 10858−10869.

(3) Xiang, T.; Han, Y.; Guo, Z.; Wang, R.; Zheng, S.; Li, S.; Li, C.; Dai, X. Fabrication of Inherent Anticorrosion Superhydrophobic Surfaces on Metals. *ACS Sustainable Chem. Eng.* **2018**, *6*, 5598−5606.

(4) Yan, L.; Xiang, Y.; Yu, J.; Wang, Y.; Cui, W. Fabrication of Antibacterial and Antiwear Hydroxyapatite Coatings via In Situ Chitosan-Mediated Pulse Electrochemical Deposition. *ACS Appl. Mater. Interfaces* **2017**, *9*, 5023−5030.

(5) Ebert, D.; Bhushan, B. Transparent, Superhydrophobic, and Wear-Resistant Coatings on Glass and Polymer Substrates Using SiO2, ZnO, and ITO Nanoparticles. *Langmuir* **2012**, *28*, 11391−11399.

(6) Rtimi, S.; Sanjines, R.; Pulgarin, C.; Kiwi, J. Quasi-Instantaneous Bacterial Inactivation on Cu−Ag Nanoparticulate 3D Catheters in the Dark and Under Light: Mechanism and Dynamics. *ACS Appl. Mater. Interfaces* **2016**, *8*, 47−55.

(7) Nardi, T.; Rtimi, S.; Pulgarin, C.; Leterrier, Y. Antibacterial surfaces based on functionally graded photocatalytic Fe_3O_4@TiO_2 core−shell nanoparticle/epoxy composites. *RSC Adv.* **2015**, *5*, 105416−105421.

(8) Rtimi, S.; Giannakis, S.; Pulgarin, C. Self-Sterilizing Sputtered Films for Applications in Hospital Facilities. *Molecules* **2017**, *22*, No. 1074.

(9) Bonnefond, A.; Gonzalez, E.; Asua, J. M.; Leiza, J. R.; Kiwi, J.; Pulgarin, C.; Rtimi, S. New evidence for hybrid acrylic/TiO2 films inducing bacterial inactivation under low intensity simulated sunlight. *Colloids Surf., B* **2015**, *135*, 1−7.

(10) Patil, A. J.; Zhao, Y.; Liu, X.; Wang, X. Durable superhydrophobic and antimicrobial cotton fabrics prepared by electrostatic assembly of polyhexamethylene biguanide and subsequent hydrophobization. *Text. Res. J.* **2018**, *88*, 1788−1799.

(11) Ellinas, K.; Kefallinou, D.; Stamatakis, K.; Gogolides, E.; Tserepi, A. Is There a Threshold in the Antibacterial Action of Superhydrophobic Surfaces? *ACS Appl. Mater. Interfaces* **2017**, *9*, 39781−39789.

(12) Hoque, J.; Akkapeddi, P.; Yadav, V.; Manjunath, G. B.; Uppu, D. S. S. M.; Konai, M. M.; Yarlagadda, V.; Sanyal, K.; Haldar, J. Broad Spectrum Antibacterial and Antifungal Polymeric Paint Materials: Synthesis, Structure−Activity Relationship, and Membrane-Active Mode of Action. *ACS Appl. Mater. Interfaces* **2015**, *7*, 1804−1815.

(13) Zhi, Z.; Su, Y.; Xi, Y.; Tian, L.; Xu, M.; Wang, Q.; Padidan, S.; Li, P.; Huang, W. Dual-Functional Polyethylene Glycol-b-polyhexanide Surface Coating with in Vitro and in Vivo Antimicrobial and Antifouling Activities. *ACS Appl. Mater. Interfaces* **2017**, *9*, 10383−10397.

(14) Hwang, G. B.; Page, K.; Patir, A.; Nair, S. P.; Allan, E.; Parkin, I. P. The Anti-Biofouling Properties of Superhydrophobic Surfaces are Short-Lived. *ACS Nano* **2018**, *12*, 6050−6058.

(15) Guldin, S.; Kohn, P.; Stefik, M.; Song, J.; Divitini, G.; Ecarla, F.; Ducati, C.; Wiesner, U.; Steiner, U. Self-Cleaning Antireflective Optical Coatings. *Nano Lett.* **2013**, *13*, 5329−5335.

(16) Stieberova, B.; Zilka, M.; Ticha, M.; Freiberg, F.; Caramazana-González, P.; McKechnie, J.; Lester, E. Application of ZnO Nanoparticles in a Self-cleaning Coating on a Metal Panel: An Assessment of Environmental Benefits. *ACS Sustainable Chem. Eng.* **2017**, *5*, 2493−2500.

(17) Xiao, L.; Deng, M.; Zeng, W.; Zhang, B.; Xu, Z.; Yi, C.; Liao, G. Novel Robust Superhydrophobic Coating with Self-Cleaning Properties in Air and Oil Based on Rare Earth Metal Oxide. *Ind. Eng. Chem. Res.* **2017**, *56*, 12354−12361.

(18) Nguyen-Tri, P.; Nguyen, T. A.; Carriere, P.; Ngo Xuan, C. Nanocomposite Coatings: Preparation, Characterization, Properties, and Applications. *Int. J. Corros.* **2018**, *2018*, 1−19.

(19) Satyabrata, M. T.; Nguyen, T. A.; Nguyen-Tri, P. *Noble Metal-Metal Oxide Hybrid Nanoparticles*; Elsevier, 2018; Vol. *1*.

(20) Nguyen-Tri, P.; Ouellet Plamondon, C.; Rtimi, S. *Nanomaterials-Based Coatings: Fundamentals and Applications*; Elsevier, 2019; Vol. *1*, p 474.

(21) Atiganyanun, S.; Plumley, J. B.; Han, S. J.; Hsu, K.; Cytrynbaum, J.; Peng, T. L.; Han, S. M.; Han, S. E. Effective Radiative Cooling by Paint-Format Microsphere-Based Photonic Random Media. *ACS Photonics* **2018**, *5*, 1181−1187.

(22) Xing, Z.; Tay, S.-W.; Ng, Y. H.; Hong, L. Porous SiO_2 Hollow Spheres as a Solar Reflective Pigment for Coatings. *ACS Appl. Mater. Interfaces* **2017**, *9*, 15103−15113.

(23) Zhang, J.; Zhu, C.; Lv, J.; Zhang, W.; Feng, J. Preparation of Colorful, Infrared-Reflective, and Superhydrophobic Polymer Films with Obvious Resistance to Dust Deposition. *ACS Appl. Mater. Interfaces* **2018**, *10*, 40219−40227.

(24) Kiwi, J.; Nadtochenko, V. New Evidence for TiO_2 Photocatalysis during Bilayer Lipid Peroxidation. *J. Phys. Chem. B* **2004**, *108*, 17675−17684.

(25) Rtimi, S.; Pulgarin, C.; Nadtochenko, V. A.; Gostev, F. E.; Shelaev, I. V.; Kiwi, J. FeOx-TiO_2 Film with Different Microstructures Leading to Femtosecond Transients with Different Properties: Biological Implications under Visible Light. *Sci. Rep.* **2016**, *6*, No. 30113.

(26) Rtimi, S.; Pulgarin, C.; Robyr, M.; Aybush, A.; Shelaev, I.; Gostev, F.; Nadtochenko, V.; Kiwi, J. Insight into the catalyst/photocatalyst microstructure presenting the same composition but leading to a variance in bacterial reduction under indoor visible light. *Appl. Catal., B* **2017**, *208*, 135−147.

DOI: 10.1021/acsomega.9b00688
ACS Omega 2019, 4, 7829−7837

(27) Milošević, I.; Rtimi, S.; Jayaprakash, A.; van Driel, B.; Greenwood, B.; Aimable, A.; Senna, M.; Bowen, P. Synthesis and characterization of fluorinated anatase nanoparticles and subsequent N-doping for efficient visible light activated photocatalysis. *Colloids Surf., B* **2018**, *171*, 445−450.
(28) Zhang, X.; Jin, M.; Liu, Z.; Tryk, D. A.; Nishimoto, S.; Murakami, T.; Fujishima, A. Superhydrophobic TiO2 Surfaces: Preparation, Photocatalytic Wettability Conversion, and Superhydrophobic−Superhydrophilic Patterning. *J. Phys. Chem. C* **2007**, *111*, 14521−14529.
(29) Nguyen Tri, P.; Nguyen, T. A.; Nguyen, T. H.; Carriere, P. Antibacterial Behavior of Hybrid Nanoparticles. In *Noble Metal-Metal Oxide Hybrid Nanoparticles*; Woodhead Publishing, 2019; pp 141−155.
(30) Nguyen Tri, P.; Ouellet-Plamondon, C.; Rtimi, S.; Assadi, A. A.; Nguyen, T. A. Methods for Synthesis of Hybrid Nanoparticles. In *Noble Metal-Metal Oxide Hybrid Nanoparticles*; Woodhead Publishing, 2019; pp 51−63.
(31) Tri, P. N.; Rtimi, S.; Nguyen, T. A.; Vu, M. T. Physics, Electrochemistry, Photochemistry, and Photoelectrochemistry of Hybrid Nanoparticles. In *Noble Metal-Metal Oxide Hybrid Nanoparticles*; Woodhead Publishing, 2019; pp 95−123.
(32) Zhou, X.; Zhang, Z.; Xu, X.; Guo, F.; Zhu, X.; Men, X.; Ge, B. Robust and Durable Superhydrophobic Cotton Fabrics for Oil/Water Separation. *ACS Appl. Mater. Interfaces* **2013**, *5*, 7208−7214.
(33) Xu, L.; Zhang, X.; Shen, Y.; Ding, Y.; Wang, L.; Sheng, Y. Durable Superhydrophobic Cotton Textiles with Ultraviolet-blocking Property and Photocatalysis Based on Flower-Like Copper Sulfide. *Ind. Eng. Chem. Res.* **2018**, *57*, 6714−6725.
(34) Su, X.; Li, H.; Lai, X.; Zhang, L.; Liao, X.; Wang, J.; Chen, Z.; He, J.; Zeng, X. Dual-Functional Superhydrophobic Textiles with Asymmetric Roll-Down/Pinned States for Water Droplet Transportation and Oil−Water Separation. *ACS Appl. Mater. Interfaces* **2018**, *10*, 4213−4221.
(35) Wang, L.; Zhang, X.; Li, B.; Sun, P.; Yang, J.; Xu, H.; Liu, Y. Superhydrophobic and Ultraviolet-Blocking Cotton Textiles. *ACS Appl. Mater. Interfaces* **2011**, *3*, 1277−1281.
(36) Zhang, C.; Li, P.; Cao, B. Fabrication of Superhydrophobic−Superoleophilic Fabrics by an Etching and Dip-Coating Two-Step Method for Oil−Water Separation. *Ind. Eng. Chem. Res.* **2016**, *55*, 5030−5035.
(37) Tuteja, A.; Choi, W.; Ma, M.; Mabry, J. M.; Mazzella, S. A.; Rutledge, G. C.; McKinley, G. H.; Cohen, R. E. Designing superoleophobic surfaces. *Science* **2007**, *318*, 1618−1622.
(38) Wenzel, R. N. Resistance of Solid Surfaces to Wetting by Water. *Ind. Eng. Chem.* **1936**, *28*, 988−994.
(39) Cassie, A. B. D.; Baxter, S. Wettability of Porous Surfaces. *Trans. Faraday Soc.* **1944**, *40*, 546−551.
(40) Wang, S.; Jiang, L. Definition of Superhydrophobic States. *Adv. Mater.* **2007**, *19*, 3423−3424.
(41) Yetisen, A. K.; Qu, H.; Manbachi, A.; Butt, H.; Dokmeci, M. R.; Hinestroza, J. P.; Skorobogatiy, M.; Khademhosseini, A.; Yun, S. H. Nanotechnology in Textiles. *ACS Nano* **2016**, *10*, 3042−3068.
(42) Xue, C.-H.; Deng, L.-Y.; Jia, S.-T.; Wei, P.-B. Fabrication of superhydrophobic aromatic cotton fabrics. *RSC Adv.* **2016**, *6*, 107364−107369.
(43) Huang, J. Y.; Li, S. H.; Ge, M. Z.; Wang, L. N.; Xing, T. L.; Chen, G. Q.; Liu, X. F.; Al-Deyab, S. S.; Zhang, K. Q.; Chen, T.; Lai, Y. K. Robust superhydrophobic TiO_2@fabrics for UV shielding, self-cleaning and oil−water separation. *J. Mater. Chem. A* **2015**, *3*, 2825−2832.
(44) Cao, C.; Ge, M.; Huang, J.; Li, S.; Deng, S.; Zhang, S.; Chen, Z.; Zhang, K.; Al-Deyab, S. S.; Lai, Y. Robust fluorine-free superhydrophobic PDMS−ormosil@fabrics for highly effective self-cleaning and efficient oil−water separation. *J. Mater. Chem. A* **2016**, *4*, 12179−12187.
(45) Li, S.; Huang, J.; Chen, Z.; Chen, G.; Lai, Y. A review on special wettability textiles: theoretical models, fabrication technologies and multifunctional applications. *J. Mater. Chem. A* **2017**, *5*, 31−55.
(46) Zhu, T.; Li, S.; Huang, J.; Mihailiasa, M.; Lai, Y. Rational design of multi-layered superhydrophobic coating on cotton fabrics for UV shielding, self-cleaning and oil-water separation. *Mater. Des.* **2017**, *134*, 342−351.
(47) Nguyen-Tri, P.; Tran, H. N.; Plamondon, C. O.; Tuduri, L.; Vo, D.-V. N.; Nanda, S.; Mishra, A.; Chao, H.-P.; Bajpai, A. K. Recent progress in the preparation, properties and applications of superhydrophobic nano-based coatings and surfaces: A review. *Prog. Org. Coat.* **2019**, *132*, 235−256.
(48) Pinto, T. V.; Costa, P.; Sousa, C. M.; Sousa, C. A. D.; Pereira, C.; Silva, C. J. S. M.; Pereira, M. F. R.; Coelho, P. J.; Freire, C. Screen-Printed Photochromic Textiles through New Inks Based on SiO2@naphthopyran Nanoparticles. *ACS Appl. Mater. Interfaces* **2016**, *8*, 28935−28945.
(49) Windler, L.; Lorenz, C.; Von Goetz, N.; Hungerbühler, K.; Amberg, M.; Heuberger, M.; Nowack, B. Release of Titanium Dioxide from Textiles during Washing. *Environ. Sci. Technol.* **2012**, *46*, 8181−8188.
(50) Hatamie, A.; Khan, A.; Golabi, M.; Turner, A. P. F.; Beni, V.; Mak, W. C.; Sadollahkhani, A.; Alnoor, H.; Zargar, B.; Bano, S.; Nur, O.; Willander, M. Zinc Oxide Nanostructure-Modified Textile and Its Application to Biosensing, Photocatalysis, and as Antibacterial Material. *Langmuir* **2015**, *31*, 10913−10921.
(51) Scarratt, L. R. J.; Hoatson, B. S.; Wood, E. S.; Hawkett, B. S.; Neto, C. Durable Superhydrophobic Surfaces via Spontaneous Wrinkling of Teflon AF. *ACS Appl. Mater. Interfaces* **2016**, *8*, 6743−6750.
(52) Zhukovskyi, M.; Sanchez-Botero, L.; McDonald, M. P.; Hinestroza, J.; Kuno, M. Nanowire-Functionalized Cotton Textiles. *ACS Appl. Mater. Interfaces* **2014**, *6*, 2262−2269.
(53) Makarem, M.; Lee, C. M.; Sawada, D.; O'Neill, H. M.; Kim, S. H. Distinguishing Surface versus Bulk Hydroxyl Groups of Cellulose Nanocrystals Using Vibrational Sum Frequency Generation Spectroscopy. *J. Phys. Chem. Lett.* **2018**, *9*, 70−75.
(54) Molina, R.; Teixidó, J. M.; Kan, C.-W.; Jovančić, P. Hydrophobic Coatings on Cotton Obtained by in Situ Plasma Polymerization of a Fluorinated Monomer in Ethanol Solutions. *ACS Appl. Mater. Interfaces* **2017**, *9*, 5513−5521.
(55) Wang, B.; Ruan, X.; Chen, L.; Chen, J.; Yang, Y. Heterogeneous Chemical Modification of Cotton Cellulose with Vinyl Sulfone Dyes in Non-Nucleophilic Organic Solvents. *Ind. Eng. Chem. Res.* **2014**, *53*, 15802−15810.
(56) Kota, A. K.; Kwon, G.; Tuteja, A. The Design and Applications of Superomniphobic Surfaces. *NPG Asia Mater.* **2014**, *6*, No. e109.
(57) Pan, S.; Kota, A. K.; Mabry, J. M.; Tuteja, A. Superomniphobic Surfaces for Effective Chemical Shielding. *J. Am. Chem. Soc.* **2013**, *135*, 578−581.
(58) Zou, H.; Lin, S.; Tu, Y.; Liu, G.; Hu, J.; Li, F.; Miao, L.; Zhang, G.; Luo, H.; Liu, F.; Hou, C.; Hu, M. Simple approach towards fabrication of highly durable and robust superhydrophobic cotton fabric from functional diblock copolymer. *J. Mater. Chem. A* **2013**, *1*, 11246−11260.
(59) Cassie, A. B. D.; Baxter, S. Wettability of porous surfaces. *Trans. Faraday Soc.* **1944**, *40*, No. 546.
(60) Quéré, D. Wetting and Roughness. *Annu. Rev. Mater. Res.* **2008**, *38*, 71−99.
(61) Kang, S.; Xiao, L.; Meng, L.; Zhang, X.; Sun, R. Isolation and structural characterization of lignin from cotton stalk treated in an ammonia hydrothermal system. *Int. J. Mol. Sci.* **2012**, *13*, 15209−15226.
(62) Oliver, W. C.; Pharr, G. M. Measurement of hardness and elastic modulus by instrumented indentation: Advances in understanding and refinements to methodology. *J. Mater. Res.* **2004**, *19*, 3−20.
(63) Cherian, B. M.; Pothan, L. A.; Nguyen-Chung, T.; Mennig, G.; Kottaisamy, M.; Thomas, S. A Novel Method for the Synthesis of Cellulose Nanofibril Whiskers from Banana Fibers and Characterization. *J. Agric. Food Chem.* **2008**, *56*, 5617−5627.

DOI: 10.1021/acsomega.9b00688
ACS Omega 2019, 4, 7829−7837

(64) Stöber, W.; Fink, A.; Bohn, E. Controlled growth of monodisperse silica spheres in the micron size range. *J. Colloid Interface Sci.* **1968**, *26*, 62−69.

DOI: 10.1021/acsomega.9b00688
ACS Omega 2019, 4, 7829−7837