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ARTICLE

Hexamethyldisiloxane-modified ZnO-SiO_2-coated superhydrophobic textiles for antibacterial application

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A superhydrophobic cotton textile with high antibacterial properties has been fabricated. The cotton textile was coated through the *in situ* growth of ZnO-SiO_2 nanoparticles in presence of chitosan as the template agent via a hydrothermal process at 95 °C. This process was followed by the coating of additional layers of hexadecyltrimethoxysilane (HDTMS). The obtained cotton textile showed antibacterial property against *Staphylococcus epidermis* and *Escherichia coli* with inhibition zones up to 18.26 and 8.48 mm, respectively. Scanning electron microscopy (SEM) revealed that the coating had a rough surface, which was attributed to the distribution of ZnO-SiO_2 nanorods of hexagonal shape. This rough surface creates a superhydrophobic layer that repels the bacteria, as proven by the large water contact angle of approximately 150°. Nevertheless, the HDTMS layers prolong the durability of hydrophobicity for up to 3 h.

KEYWORDS

antibacterial textile, *E. coli*, hydrophobic textile, *Staphylococcus epidermis*, ZnO-SiO_2

1 | INTRODUCTION

Hydrophobic textiles for non-translucent, water-repellent fabrics have attracted much attention from researchers in recent years. The hydrophobic surface has a water contact angle (WCA) that is greater than 90°, resulting in the prevention of water absorption. This hydrophobic property is achieved based on a natural phenomenon called the "lotus effect," where water droplets assume a nearly spherical shape on the surface of a lotus leaf because of ultrahydrophobicity. The lotus leaf surface is excellent in self-cleaning to remove impurities, which is due to the presence of nanoscale hydrophobic wax crystals on the surface of the leaf that have strong superhydrophobic properties. Dirt particles are picked up by water droplets and washed out. This idea is widely applied to medical and sports fabrics.[1] Moreover, hydrophobic textiles are also effective in inhibiting microbial growth and eliminating impurities and as fireproof materials and UV blockers.[1,2]

Hydrophobic textiles can be fabricated by incorporating an additive on the textile surface to create a rough texture without affecting the durability and softness of its fibers.[3] Research and development to obtain hydrophobic textiles with a large contact angle was reported by Wang (2011) by coating ZnO-SiO_2 on cotton fibers using octadecyltrimethoxysilane (OTS). Xua (2013) also reported the coating of ZnO-SiO_2 on poly(ethylene terephthalate (PET) fibers using a different binding agent, namely hexadecyltrimethoxysilane. Silane compounds are also used to modify the surface properties of textiles, including the hexamethyldisiloxane (HMDS), 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane (PFDTS), *n*-dodecyltrimethoxysilane (DTMs),[4] hexadecyltrimethoxysilane (HDTMS),[1] (OTS)[3,5] and poly(trimethyl siloxane) (PTS).[1]

This study was aimed at modifying a textile surface with $ZnO\text{-}SiO_2$ nanostructures that were grown directly on cotton textile fibers in the presence of a chitosan template. The durability of hydrophobicity of the coated textile was further improved with layers of HDTMS, which has the chemical structure shown in Figure 1.

2 | RESULTS AND DISCUSSION

2.1 | Fabrication of $ZnO\text{-}SiO_2$/HDTMS cotton textile

In this study, 1,2,3,4 butanetetracarboxylic acid (BTCA) with four carboxylic groups was used as a binder, which served as a cross-linking agent between the cellulose organic compound of the cotton fiber textiles and the inorganic compound $ZnO\text{-}SiO_2$ through a covalent esterification interaction.[6,7] The optimum duration of coating of the binder on the textile surface was 24 h. Also, the growth of ZnO nanorods by the hydrothermal method could be stabilized using a precursor of zinc nitrate tetrahydrate and methylene amine in the ratio 1:1.[8] The growth of ZnO on cotton textiles was done at a temperature of 95 °C for 5 h. This coating process was aimed at designing a rough surface because roughness can lower the surface energy. A convex surface is formed when the cohesive force is greater than the adhesive force.[1,3,9] The coating process with HDTMS was repeated 1–3 times in order to obtain high hydrophobicity, as indicated by a large WCA. Figure 2 shows the weight change during the coating process of textiles with $ZnO\text{-}SiO_2$ and HDTMS. The increase in weight confirmed the coating on the surface of cotton textile.

The surface of cotton textiles was observed using an optical microscope with magnification ×40. As shown in Figure 3, the $ZnO\text{-}SiO_2$-coated textile without HDTMS

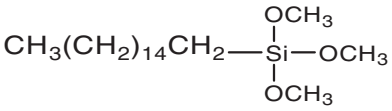

FIGURE 1 Chemical structure of hexadecyltrimethoxysilane

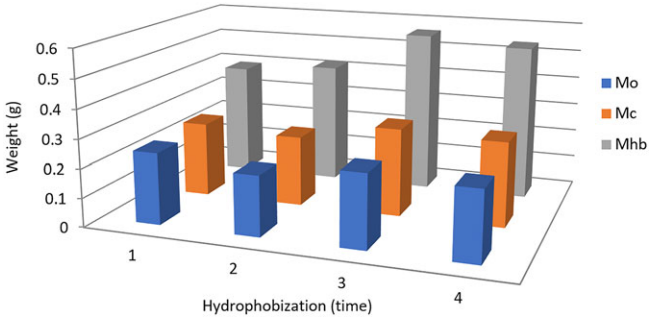

FIGURE 2 Mass conversion of cotton textile fibers. Mo is the textile before coating, Mc is the textile coated with $ZnO\text{-}SiO_2$, and Mhb is coated textile with HDTMS

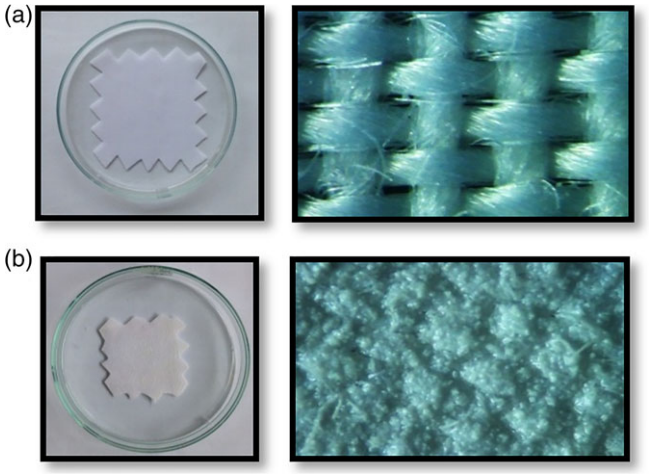

FIGURE 3 Optical photographs of cotton textile surface (a) without coating, and (b) coated with $ZnO\text{-}SiO_2$/chitosan template nanoparticles and HDTMS

appeared white, clear, and uncluttered. After HDTMS coating, the fiber surface appeared rough and shiny.

Fourier transform infrared (FTIR) spectroscopy was used to confirm the adhesion of the coating on the cotton textile surface. Figure 4 shows the FTIR spectra of the samples when the BTCA binder was applied at different concentrations of 0.5, 0.75, and 1 M. The absorption peak corresponding to C=O stretching at 1700 cm^{-1} shows a slight shift toward higher wavenumber, indicating the occurrence of esterification.

The change of chemical interaction in the coating process was indicated by the FTIR spectrum, as shown in Figure 5. The chemical interaction between BTCA binder and $ZnO\text{-}SiO_2$ chitosan template was confirmed by the reduction in the intensity of the peak at 1700 cm^{-1}, which is due to the interaction of the C=O stretching group. The coating of HDTMS on the surface was confirmed by the appearance of a peak at 1200 cm^{-1}, which is due to the S–CH group interaction.

The formation of $ZnO\text{-}SiO_2$ nanoparticles was checked using X-ray diffraction (XRD). Figure 6(a) shows the XRD pattern of $ZnO\text{-}SiO_2$ powder, which consists of peaks at $2\theta = 32°$, 34°, 36°, 47°, 56°, 63°, 68°, and 72°.

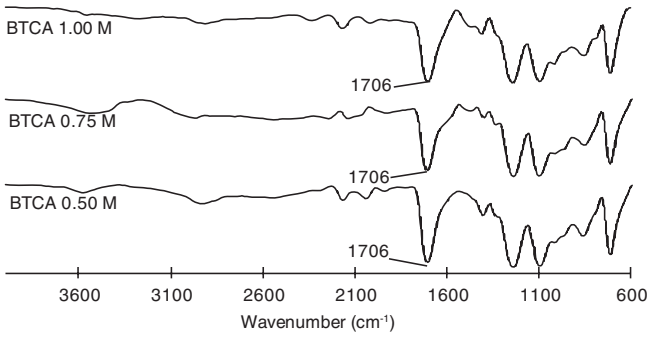

FIGURE 4 FTIR spectrum of cotton coated with (a) BTCA 0.5 M, (b) BTCA 0.75 M, and (c) BTCA 1 M

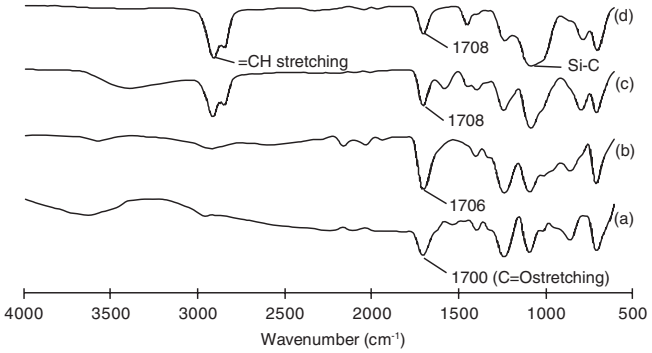

FIGURE 5 FT-IR spectrum of cotton textiles (a) without coating, (b) coated with binder BTCA, (c) coated with BTCA and ZnO-SiO_2 chitosan template, and (d) BTCA ZnO-SiO_2 template chitosan and HDTMS

The peaks at 2θ = 32°, 34°, and 36°, which correspond to *hkl* (220), (113), and (410), show the highest intensity. The XRD pattern shows that the ZnO crystal structure is in the wurtzite form with hexagonal geometry. The ZnO crystal size was 22.3 nm. Upon coating onto the cotton textile, the XRD pattern showed a semicrystalline structure. It revealed that nanoparticles of ZnO-SiO_2 were formed on the cotton textile, which were amorphous in nature. The physical appearance of the ZnO-SiO_2 nanoparticles was observed using scanning electron microscopy (SEM), as shown in Figure 7. The nanoparticles are hexagonal in shape with the particle size varying from 0.150 to 0.625 μm. When cotton fiber textiles were coated with ZnO-SiO_2, the formation of nanoparticles on the surface of cotton textile could be clearly observed (Figure 8). Before coating, the cotton fiber textile showed a smooth surface that was covered by pectin and wax compounds. These compounds will block the coating process by inhibiting the interaction of the cotton fiber textile, binder, and ZnO-SiO_2 nanoparticles. Figure 8(c) shows the morphology of cotton textile after coating with ZnO-SiO_2 nanoparticles. The surface was fully covered with hexagonal nanoparticles, creating a rough surface.

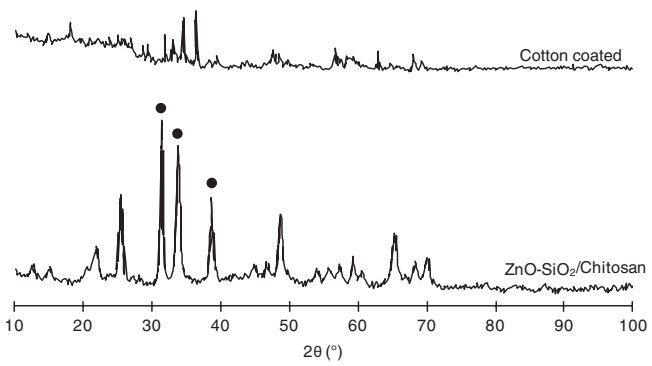

FIGURE 6 XRD patterns of (a) powder-SiO_2 ZnO chitosan template nanoparticles of cotton textile without coating, and (b) coated cotton textile with nanoparticles ZnO-SiO_2 and chitosan template

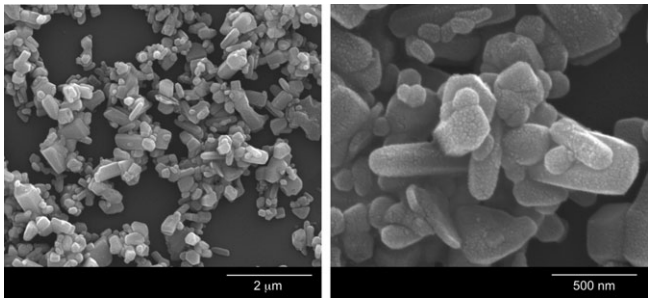

FIGURE 7 Surface morphology of ZnO-SiO_2 chitosan template

2.2 | Hydrophobicity of cotton textiles

The hydrophobicity of the surface of the textile was checked by measuring the WCA. Without hydrophobization, the ZnO-SiO_2-coated cotton textile shows a WCA of 100°, indicating that the textile is hydrophobic. Coating with HDTMS enhanced the hydrophobicity significantly.[10,11] As shown in Figure 9, the largest WCA was achieved by the ZnO-SiO_2-coated textile with two layers of HDTMS. WCA reached 150°, which indicates that the textile is superhydrophobic.[12–14] WCA was affected by the number of HDTMS coatings.

The durability of hydrophobicity was determined by the duration of time that water droplets could maintain a WCA higher than 90°. The longer the WCA could be maintained above 90°, the higher the durability. As shown in Figure 10, three coatings of HDTMS gave the highest durability. For cotton textiles without HDTMS and coated with ZnO-SiO_2 nanoparticles together with two hydrophobization cycles, a WCA higher than 90° was retained for 90 min. On the other hand, ZnO-SiO_2-coated cotton textiles with one and four hydrophobization cycles were stable for 150 min. Remarkably, ZnO-SiO_2-coated cotton textiles with three hydrophobization cycles showed superhydrophobicity with a WCA of 150°, which is superior to those of the other samples. The durability of the superhydrophobic surface could be maintained for 45 min. After 45 min, the cotton textiles become hydrophobic and remained stable for 3 h.

2.3 | Antibacterial testing

The antibacterial capability of all modified textiles was investigated against two types of bacteria, namely the Gram-positive *Staphylococcus epidermis* and the Gram-negative *Escherichia coli.* These bacteria are pathogens that can cause various diseases such as diarrhea, vomiting, and nausea.[9,15,16] The antibacterial capability of the modified textiles against *S. epidermis* and *E. coli* was measured by the zone of inhibition, as shown in Figure 11. Without any coating, the cotton textile is vulnerable for habitation of *S. epidermis* and *E. coli.* In contrast, the ZnO–SiO_2-coated cotton textile with the HDTMS layer shows an inhibition zone for *S. epidermis* and *E. coli* of 18.26 and 8.48 mm, respectively. We have thus proved that hydrophobization

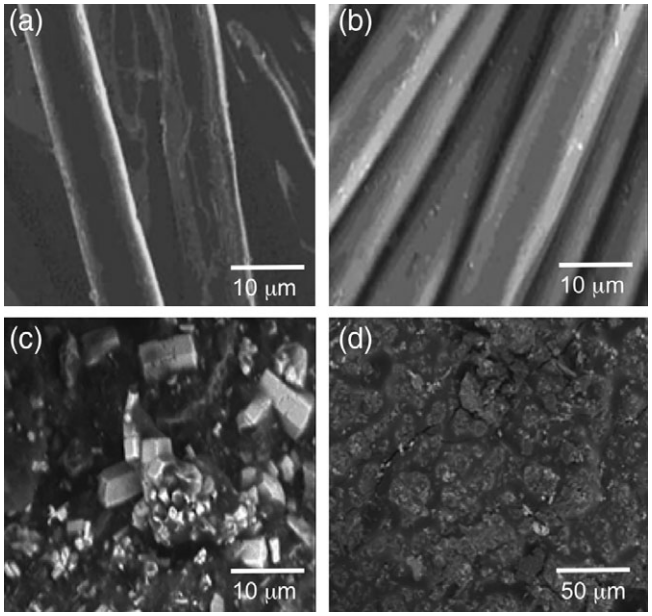

FIGURE 8 Morphology of the surface of cotton fiber textiles (a) without coating, (b) coated with BTCA, (c) coated with nanorods ZnO-SiO_2 chitosan template, and (d) coated with ZnO-SiO_2 chitosan template and HDTMS

can improve the antibacterial capability. This can be attributed to the fact that hydrophobization repels water, thus reducing the amount of water on the textile surface.[11,17] Table 1 lists the zone of inhibition of all modified textiles.

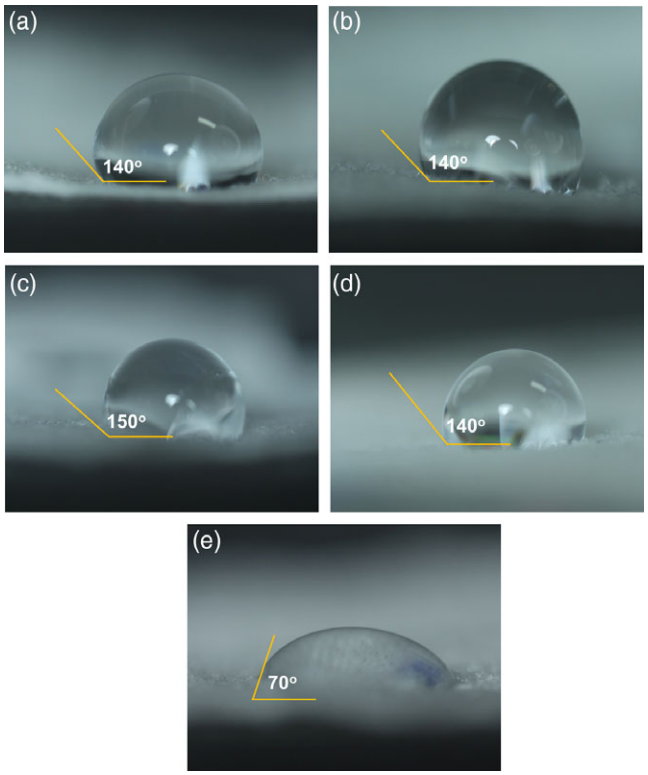

FIGURE 9 Photo of water contact angle measurements on the surface of the cotton textile coated with ZnO-SiO_2 chitosan template with different numbers of coating for hydrophobization: (a) one time, (b) two times, (c) three times, (d) four times, and (e) without hydrophobization

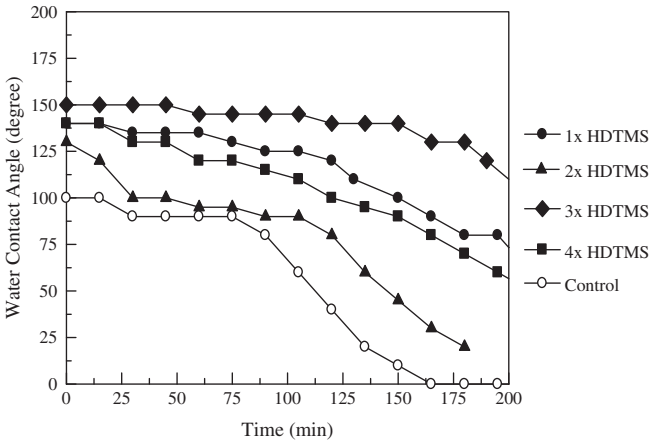

FIGURE 10 Durability of hydrophobicity of cotton textiles based on WCA after 3 h

As summary, the antibacterial capability of ZnO-SiO_2/HDTMS-modified cotton textile is related to the hydrophobicity of the surface of the cotton textile. The highly hydrophobic surface repels the transport medium of bacteria, which is water. Hence, the bacteria cannot have access to the textiles. In our study, the high hydrophobicity is a result of the synergy between the high surface roughness created by the ZnO-SiO_2 nanoparticles and the hydrophobic nature of the HDTMS coating. As can be seen, HDTMS coating on ZnO-SiO_2 created an even larger zone of inhibition against *S. epidermis* and *E. coli.*

3 | EXPERIMENTAL

3.1 | Materials

Silky cotton cloth (cotton silky), zinc oxide (ZnO, Merck), zinc nitrate tetrahydrate ($Zn[NO_3]_2ċ4H_2O$, Merck), methyleneamine ($C_6H_{12}N_4$, Merck), butane carboxilic tetraacid ($C_6H_6O_8$, Merck), chitosan ($[C_6H_{11}NO_4]n$, Merck), tetraethyl orthosilicate ($C_8H_{20}O_4Si$, Merck), and hexadecyltrimethoxysilane ($C_{19}H_{42}O_3Si$, Aldrich) were used as received without further purification.

3.2 | Coating of cotton textile with BTCA

Cotton textiles were cleaned by washing with a detergent (2 g/L). Then, it was dried in an oven at 80 °C for 15 min. The cleaned cotton textile was dewaxed by soaking in 3.7×10^{-3} M Na_2CO_3 and washed until neutral. The cotton was then heated at 100 °C for 5 min, followed by rinsing with distilled water and drying again at 80 °C for 15 min. The dewaxed textile was dipped in BTCA for 24 h at room temperature. Finally, textile was dried in an oven at 80 °C for 15 min.

3.3 | Growth of ZnO-SiO_2 nanoparticles using chitosan as template on the cotton textile

The BTCA-treated cotton textiles were spin-coated with a solution of suspensions of ZnO-SiO_2 and chitosan as

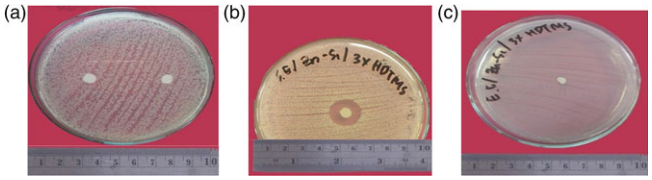

FIGURE 11 Zone of inhibition of textiles: (a) uncoated, (b) coated with ZnO-SiO_2/chitosan and HDTMS to *S. epidermis* inhibition, and (c) coated with ZnO-SiO_2/chitosan to *E. coli* inhibition

TABLE 1 Zone of inhibition of the modified textile against *S. epidermis* and *E. coli*

	Zone of inhibition (mm)	
Textile	***S. epidermis***	***E. coli***
SiO_2/chitosan	7.00	6.90
ZnO/chitosan	7.80	7.50
ZnO-SiO_2/chitosan	13.54	7.96
ZnO-SiO_2/chitosan and HDTMS	18.26	8.48
HDTMS	2.20	1.42

template agent in distilled water. The textiles were then dried in an oven at a temperature 80 °C for 15 min.

3.4 | Hydrophobization of cotton textiles

The cotton textiles coated with ZnO-SiO_2 were dipped in an HDTMS solution and then heated at 120 °C for 3 h in a autoclave.

3.5 | Antibacterial testing

Textile samples were cut into disks of diameter of 0.6 mm. Next, these disks were placed in a Petri dish containing nutrient agar (NA) pre-inoculated with *S. epidermidis* and *E. coli.* The plates with the samples were then incubated for 24 . The zone of inhibition around the cotton textiles was measured.

3.6 | Characterization

All cotton textile samples were characterized using SEM (Hitachi S-3400 N), XRD (Xpert-Pro), optical microscopy, and FT-IR (Thermo Scientific: Nicolet iS 10).

3.7 | Hydrophobicity testing of cotton textiles

The textile samples were placed on a flat glass surface and dripped with distilled water. A camera was placed at 10 cm from the samples to capture their photographs. The WCA was then measured.

4 | CONCLUSION

Superhydrophobic cotton textiles could be fabricated by the *in situ* growth of ZnO-SiO_2 nanoparticles followed by HDTMS coating. The coated textiles showed a WCA of 150°. The HDTMS coating prolonged the hydrophobicity for 3 h. SEM revealed that the ZnO-SiO_2 nanoparticles were well distributed on the surface of the cotton textile, creating high surface roughness, thus inducing high hydrophobicity. Hydrophobization by HDTMS further enhanced the hydrophobicity of the textile. The coated cotton textiles showed antibacterial capability against *S. epidermis* and *E. coli* with an inhibition zone of 18.26 and 8.48 mm, respectively. In summary, a superhydrophobic textile with high durability has been fabricated for antibacterial purposes.

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