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# Superhydrophobic and Ultraviolet-Blocking Cotton Textiles

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*Supporting Information*

**ABSTRACT:** Cotton textile was coated with ZnO@$SiO_2$ nanorods in order to obtain superhydrophobic and ultraviolet (UV)-blocking properties. The coating process was conducted in mild conditions, which involved the low-temperature preparation of ZnO seeds, hydrothermal growth of ZnO nanorods, bioinspired layer-by-layer deposition of a $SiO_2$ shell on the surface of ZnO nanorods, and hydrophobic modification of ZnO@$SiO_2$ nanorods with octadecyltrimethoxysilane. Despite the highly curved morphology of cotton fibers, the ZnO@$SiO_2$ nanorods coated the textile densely and uniformly. The treated cotton textile was found to have a large UV protection factor (UPF = 101.51) together with UV-durable superhydrophobicity, as determined by contact-angle measurement under long-term UV irradiation. The good UV-blocking property can be ascribed to the high UV absorbance and scattering properties of ZnO nanorods, and the UV-durable superhydrophobicity is a result of suppression of the photoactivity of ZnO nanorods by a $SiO_2$ shell.

**KEYWORDS:** ultraviolet blocking, superhydrophobicity, ZnO@$SiO_2$ core−shell nanorod, cotton textile, surface modification

## 1. INTRODUCTION

Demands for a comfortable and healthy life make it desirable to render textile products multifunctional. In recent years, increasing concern over excessive terrestrial ultraviolet (UV) radiation received from the sun as a result of environmental pollution has pushed intensive studies on UV-blocking textiles.[1−3] The "green" lifestyle also asks for textile that can be self-cleaning,[4,5] for instance, mimicking the superhydrophobic lotus leaf in nature,[6,7] in order to save on the use of detergent and labor. There are also many other functions added to textiles, such as being water-repellent,[8] antimicrobial,[9] flame-retardant,[10] temperature-sensitive,[11] antistatic,[12] low-resistant,[13] and so on. Generally, these functions can be added to textiles via surface modification and therefore without a detrimental influence on the mechanical properties of textile fabrics.

Inorganic white pigments, such as $TiO_2$ and ZnO, have been widely used in the field of UV blocking, including application to the surface of textile fabrics to provide UV protection.[4,14−16] Especially for ZnO, its direct-band-gap semiconductor characteristic makes it behave as an excellent UV-blocking material covering the whole spectrum of UV-R (both UVA and UVB fall into the regions of 315−400 and 280−315 nm, respectively, of the solar spectra). Wang et al. modified cotton textiles with ZnO nanorods and dumbbell-shaped ZnO crystallites[17] and found that they had the potential to block a 68-nm-wider range of UV-R than a $TiO_2$ thin film.[16] There were also some works reported of the water-repellent functions on ZnO nanorod modified cotton textiles due to its special air-trapping surface morphology.[18] That seems reasonable to combine the UV-blocking and water-repellent functions on ZnO nanorod modified cotton textiles, in which case the ZnO nanorod film was not only a UV absorber but also superhydrophobic. However, in such a case, the photoactivity of ZnO must be carefully suppressed, which will cause the ZnO nanorod film to lose superhydrophobicity under UV light or sunlight.[19,20]

We have recently reported the preparation of a conformal silica shell on the surface of a ZnO nanorod by a bioinspired layer-by-layer (LbL) deposition method. This $SiO_2$ shell can effectively block the photoactivity of the ZnO nanorod via confinement of the photogenerated electron−hole pairs because its valence and conduction band edges lie far lower and higher in energy than those of ZnO. Therefore, even placed under intense UV irradiation for long term, the superhydrophobic ZnO@$SiO_2$ nanorod array still retained excellent superhydrophobicity.[21] Herein, we extended this idea to the surface modification of cotton textiles, with the expectation of obtaining durably superhydrophobic and UV-blocking multifunctional fabrics. Because cotton textile is a kind of flexible and flammable substrate, we developed a mild chemical process to prepare the superhydrophobic ZnO@$SiO_2$ nanorod array. As expected, the ZnO@$SiO_2$ nanorod coated cotton textile exhibited an excellent UV-blocking property with a UV protection factor (UPF) value of 50+ and durable superhydrophobicity even under intense UV irradiation.

## 2. EXPERIMENTAL SECTION

**2.1. Materials and Instrumentation.** Cotton textiles, cleaned by ultrasonic washing in ethanol and water before use, were purchased from a local fabric store. Zinc acetate hydrate, zinc nitrate hydrate, and hexamethylenediamine (HMT) were obtained from Beijing Chemical Reagent Co. Sodium silicate was obtained from Tianjin Chemical Reagent Co. Polyethylenimine (PEI; branched, MW ∼25 000) was obtained from Aldrich. Poly(sodium-*p*-styrenesulfonate) (PSS; MW 70 000) and octadecyltrimethoxysilane (OTS) were obtained from Acros. All of these chemicals were used without further purification. Deionized water (∼18 MΩ cm) was used in all experiments.

Surface morphologies of cotton textile, either modified or not with ZnO and ZnO@$SiO_2$ nanorod arrays, were observed with a field-emission scanning electron microscope (Philips XL 30) equipped with

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an energy-dispersive X-ray (EDX) spectrometer. Transmittance spectra and UPFs were measured with a Varian Cary 500 UV—vis—near-IR spectrophotometer. Static contact-angle (CA) and sliding-angle measurements were carried out with a drop-shape analysis system (Krüss DSA100) at room temperature.

**2.2. Preparation of a ZnO@SiO$_2$ Nanorod Array on Cotton Textiles.** The preparation of a ZnO@SiO$_2$ nanorod array on cotton textiles was similar to our previously reported method with a slight modification.[21] Typically, the preparation involved three steps: (1) preparation of a ZnO seed layer on a cotton textile, (2) hydrothermal preparation of a ZnO nanorod array, and (3) LbL deposition of a silica/polyelectrolyte shell.

For the growth of a ZnO seed layer, the cotton textile was dipped in ZnO nanocrystals, prepared by a sol—gel method reported by Meulenkamp[22] for 12 h, and then placed into a Teflon-lined autoclave, which contained an aqueous solution of zinc acetate hydrate (15 mM). The autoclave was sealed and heated at 95 °C for 48 h. A dissolution—recrystallization processing of ZnO nanocrystals occurred during this hydrothermal process. The cotton textile coated with a ZnO seed layer was then dried in air at 80 °C for 10 min and irradiated under UV light for 10 min to remove residual organic materials.

A ZnO nanorod array was prepared by a simple hydrothermal process.[21] The seeded cotton textile was placed in a Teflon-lined autoclave, which contained an aqueous solution of zinc nitrate hydrate (25 mM) and HMT (25 mM), followed by sealing and remaining at 95 °C for 5 h. The cotton textile with a ZnO nanorod array was then rinsed with deionized water and dried.

A SiO$_2$ shell was prepared on a ZnO nanorod array as illustrated in our previous work.[21] Aqueous solutions of PSS (1 mg mL$^{-1}$), PEI (1 mg mL$^{-1}$), and sodium silicate (40 mM) were prepared in a 0.05 mol L$^{-1}$ Tris solution, respectively. The pH values of these solutions were adjusted to 7.5 with a diluted hydrochloric or ammonium solution. The cotton textile with a ZnO nanorod array was first dipped in a PSS solution for 10 min with intermediate water washing in order to render the surface of the nanorods negatively charged. Then it was alternatingly dipped in PEI and sodium silicate solutions for 10 min also with intermediate water washing. By these procedures, a PEI/silica bilayer was conformally prepared on a ZnO nanorod array.

**2.3. Hydrophobic Modification.** A ZnO@SiO$_2$ nanorod array was modified with an OTS self-assembled monolayer, as reported in our previous work.[21] First, the sample was placed into a N$_2$-filled Teflon-lined autoclave together with a drop of OTS liquid. Then the autoclave was sealed and maintained at 130 °C for 3 h. After that, the sample was removed from the autoclave, rinsed with ethanol thoroughly, and heated at 100 °C for 10 min.

**2.4. UV-Blocking Measurement.** According to the Australian/New Zealand Standard AS/NZS 4399:1996, UPF was measured with a Varian Cary 500 UV—vis—near-IR spectrophotometer equipped with an integrating sphere. The specimen was placed at the entrance to the sphere. Four measurements of UV transmittance were performed for each specimen with different directions. The UPF (average of four scans) was computed using the following formula: $\mathrm{UPF} = \sum_{280\,\mathrm{nm}}^{400\,\mathrm{nm}} E_\lambda S_\lambda \Delta\lambda / \sum_{280\,\mathrm{nm}}^{400\,\mathrm{nm}} E_\lambda S_\lambda T_\lambda \Delta\lambda$. In this equation, $E_\lambda$ corresponds to the relative erythemal spectral effectiveness, $S_\lambda$ is the solar spectral irradiance, $T_\lambda$ is the average spectral transmittance of a textile, and $\Delta\lambda$ is the measured wavelength interval in nanometers.

**2.5. UV-Durability Test.** Cotton textile with an OTS-modified ZnO@SiO$_2$ nanorod array was placed under a Hayashi LA-410 light source, which emits UV light in the range of 320—400 nm. The light intensity was maintained at 25.0 mW cm$^{-2}$ by adjusting the power output and the distance between the sample and the light source, which is about an order more intense than the UV intensity of normal sunlight. The water CA of the samples was measured with a drop-shape analysis system (Krüss DSA100) at five different points for each. All experiments were carried out at room temperature and ca. 30% humidity.

## 3. RESULTS AND DISCUSSION

**3.1. Coating of Cotton Textiles.** We have previously reported the preparation of a ZnO@SiO$_2$ nanorod array on hard substrates.[21] However, we could not directly replicate the reported method to the cotton textiles because the flexible and flammable nature of cotton did not allow the preparation of a high-quality ZnO seed layer via the conventional sol—gel process by which annealing at high temperature is necessary to remove the organic residual and promote crystallization of the ZnO phase.[21,23—25] Therefore, we developed herein a mild method to prepare the ZnO seed layer on cotton textile that involved dipping coating from a ZnO sol and a subsequent hydrothermal crystallization treatment. The dissolution and recrystallization of ZnO nanoparticles occurring in the hydrothermal process at low temperature (95 °C) improve the crystallization of the seed layer, which is a special advantage of soft chemistry.[26,27] This ZnO seed layer was hard to observe in our experimental conditions; however, it was found to be indispensable in the growth of a high-quality ZnO nanorod array on cotton textile.

Parts a—e of Figure 1 show typical scanning electron microscopy (SEM) images of native and treated cotton textiles. The native cotton textile presents a highly textured microscale fiber with a typical smooth surface (Figure 1a,b). However, after a series of hydrothermal treatments, oriented ZnO nanorods are densely and uniformly distributed over all cotton fibers (Figure 1c,d). The average length and diameter of the ZnO nanorods are ca. 2 $\mu$m and 440 nm, respectively, by statistics on over 100 nanorods. The size of these nanorods could be tuned by changing the growth time and/or the concentration of the crystallizing solution. After LbL deposition in PEI and silicate solutions, a uniform SiO$_2$ layer was coated on the surface of the ZnO nanorods, the mechanism of which was discussed in our previous work.[21] Figure 1e shows the top-view picture of a SiO$_2$-coated ZnO nanorod array on the cotton textile; the rougher SiO$_2$ particle layer can be seen clearly on the surface of the ZnO nanorod. Further analysis with EDX spectrometry proved the existence of a Si element in the LbL-treated nanorod array (Figure 1f).

An advantage of LbL deposition is that it can conveniently control the thickness of the deposited layers.[28] As reported before, one bilayer deposition could prepare a 4.17-nm-thick SiO$_2$ shell on ZnO nanorods grown on glass substrates, and the thickness of the SiO$_2$ shell can simply be tuned with deposition cycles.[21] Similarly, in the present work, the thickness of the SiO$_2$ shell can also be easily controlled by tuning the LbL deposition cycles, even if a flexible cotton textile substrate was used (see the Supporting Information, Figure S1). Moreover, as proven in our previous work, the dense SiO$_2$ layer not only coated the surface of the ZnO nanorod but also coated the bare seed layer that existed under the bottom of the ZnO@SiO$_2$ nanorod.[21] The cross-linked chains existing in the silica and the high reactivity between the Si—O bonds in silica and the surface hydroxyl groups on the ZnO seed layer result in a firm binding of the ZnO nanorods at the bottom and their connection on the ZnO seed layer. This may improve the mechanical properties of the nanorod array and thus may help applications of this coated textile.

**3.2. UV-Blocking Property.** The term "ultraviolet protection factor (UPF)" is widely used in the textile and clothing industry worldwide to indicate protection from UV radiation (UV-R; both UVA and UVB fall into the regions of 315—400 and

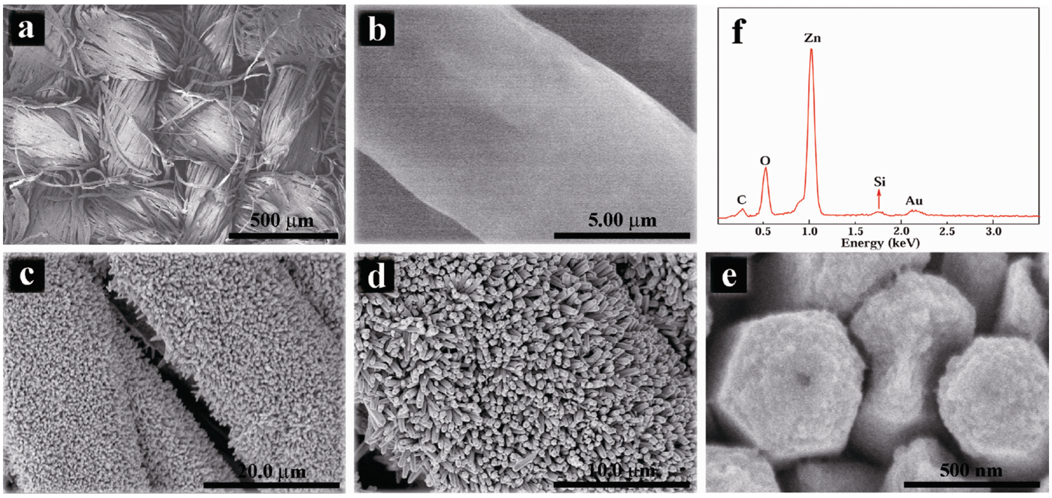

**Figure 1.** SEM images of native (a and b) and ZnO nanorod array coated (c and d) cotton textiles. (e) High-magnification SEM image of a $ZnO@SiO_2$ nanorod array grown on the surface of a cotton textile. (f) EDX spectrum of the sample corresponding to image e.

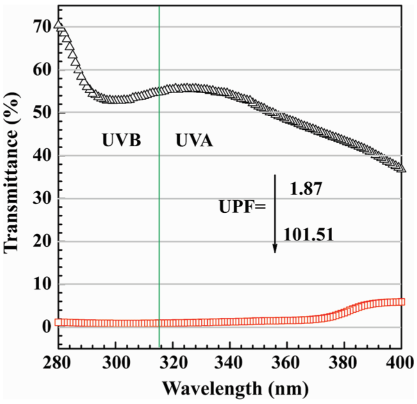

**Figure 2.** Transmittance spectra of native (triangles) and $ZnO@SiO_2$ nanorod array coated (squares) cotton textiles.

280−315 nm, respectively, of the solar spectra). A UPF rating indicates how much UV-R is blocked by a material. For example, a textile with a UPF rating of 20 would only allow $^1/_{20}$th of the hazardous UV-R falling on its surface to pass through it, and therefore UV-R exposure will be reduced by a factor of 20. The UPF ratings of less than 15, between 15 and 50, and more than 50 (50+) are generally classified as bad, good, and excellent UV-blocking properties for textiles, respectively. A low UPF (less than 15) of cotton is inadequate protection for outdoor activities. Clothing with a greater UPF should be developed to provide high levels of UV protection in a variety of conditions.

Figure 2 displays the transmittance spectra of native and treated cotton textiles and their corresponding UPF values. The native cotton textile has high transmittance for UV light ($T >$ 36.8%), and the transmittance exhibited an increasing tendency from the visible to the UV spectral region. However, for the $ZnO@SiO_2$ nanorod array treated textile, the UV transmittance obviously decreased ($T <$ 5.8%). Especially in the region of 280−375 nm, there is almost no UV light transmitting through the textile. The UPF value of native cotton textile was only 1.87, while that of the $ZnO@SiO_2$ nanorod treated one was as high as 101.51. This high UPF results in excellent protection from solar radiation. Therefore, these materials might be applied to many reinforced UPF fields, such as screens, curtains, window blinds, awnings, and outdoor shelters.

We believe the excellent UV-blocking property of the treated cotton textile is a combined result of the good absorption and strong scattering of a $ZnO@SiO_2$ nanorod array. ZnO has a direct band gap of 3.37 eV; thus, it can strongly absorb light with an $h\nu$ energy that matches or exceeds their band gap energy, which lies in the UV range of the solar spectrum. Meanwhile, the length and diameter of $ZnO@SiO_2$ nanorods are ~2 $\mu$m and 440 nm, respectively, which are over the wavelength of UV light. Therefore, the nanorod array can scatter UV light strongly. The multiscattering between ZnO nanorods also helps in the effective absorbance of incident UV light.

**3.3. Surface Wettability.** The wettability of the cotton textile was examined by CA measurements. The native cotton sample can be completely wetted by water (Figure 3a), which is common and well-known for cotton textile. After OTS modification, the water CA of the native cotton textile increased to 132.2° (Figure 3b), and for the $ZnO@SiO_2$-coated sample, the CA value was even beyond 150° (Figure 3c) and its roll-off angle was only 9°. The small roll-off angle, together with the large CA, strongly suggests that the $ZnO@SiO_2$ nanorod coated cotton textile has good superhydrophobicity.

Because the interweaving set of fibers produces a highly porous structure and constructs a typical air−solid composite surface, when a liquid droplet sits on the cotton textile surface, the wetting behavior can be described by the Casssie−Baxter equation (eq 1)[29]

$$\cos \theta^* = f_1 \cos \theta - f_2 \qquad (1)$$

where $\theta^*$ is the apparent CA on a rough surface, $\theta$ is the intrinsic CA on the corresponding smooth surface, $f_1$ is the liquid/solid contact area divided by the projected area, and $f_2$ is the liquid/vapor contact area divided by the projected area. This equation was recently modified to account for the local surface roughness on the wetted area as follows (eq 2):[7,30]

$$\cos \theta^* = rf_1 \cos \theta - f_2 \qquad (2)$$

Here $r$ is the surface roughness factor of the wetted area ($r \geq 1$). According to the equation, a large $r$ value of the liquid/solid

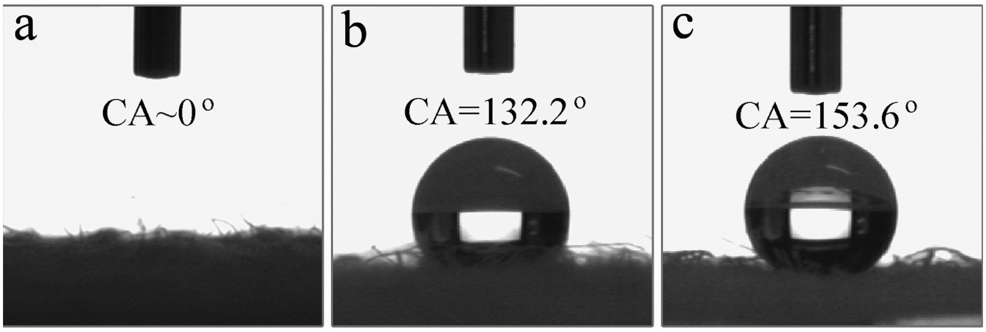

**Figure 3.** Photographs of water droplets placed on native cotton textile (a), OTS-modified cotton textile (b), and cotton textile coated with an OTS-modified ZnO@$SiO_2$ nanorod array (c).

contact area will further enhance the hydrophobic property of a composite surface. In our experiment, the coating of ZnO@$SiO_2$ nanorods greatly increased the surface roughness of the textile, which can be clearly observed in the SEM images (Figure 1), and thus enhanced its superhydrophobicity. Here we exclude the possible effect of the surface fraction of air pockets among ZnO nanorods on the increase of water CAs; the effect, if any, should be little because in our system the air pocket volume originating from ZnO@$SiO_2$ nanorods is much smaller compared to the large interspaces between woven textiles.

### 3.4. UV-Durable Superhydrophobicity.

As an important photocatalytic material, ZnO shows strong oxidative power under UV excitation, with which it can completely decompose organic substances as well as the UV-induced superhydrophilic transition.[20,31] The photocatalytic activities of various ZnO materials were investigated extensively in recent decades.[32−34] Similar to $TiO_2$, two principal pathways have been proposed for the ZnO photocatalytic oxidation.[35] One is direct photocatalytic oxidation by holes in the valence band of ZnO. The other is photocatalytic oxidation by the active oxygen species, such as hydroxyl radicals, superoxides, and singlet dioxygen molecules, generated on the ZnO surface during UV irradiation. Although the exact mechanism of a UV-induced superhydrophilic process has still not been made clear, it is generally considered to be the result of surface photochemical reactions and/or photoinduced surface reconstruction.[35] Therefore, the previously reported ZnO superhydrophobic materials all showed a wettability transition from superhydrophobicity to superhydrophilicity under UV irradiation.[19,20]

A $SiO_2$ shell can effectively suppress the UV sensitivity of a ZnO nanorod array. Similar to the results reported before, the ZnO@$SiO_2$ nanorod array coated cotton textile showed nearly unchanged CA values during UV irradiation. Even after the UV irradiation time was prolonged to 2 weeks, it still exhibited durable superhydrophobicity (Figure 4). The water droplets dropped on the surface of a ZnO@$SiO_2$ nanorod array coated cotton textile kept their shape and quickly fell from the cotton (see the inset in Figure 4 and the Supporting Information). The small roll-off angle and low-stick surface make it an ideal self-cleaning material. Note that the intensity of the as-used UV light is about an order more intense than that in sunlight, suggesting that the ZnO@$SiO_2$ nanorod array modified superhydrophobic cotton textile may have potential applications in daily life. This interesting phenomenon can be well explained by the blocking effect of a $SiO_2$ shell on the photoactivity of ZnO nanorods. As we know, the valence and conduction band edges of $SiO_2$ lie far lower and higher in energy than the corresponding bands of ZnO, respectively.[36] This can effectively confine the photogenetated holes and electrons within the ZnO nanorods and thus restrain the surface photochemical reactions between photogenerated holes and the OTS monolayer modified on the surface of nanorods. As a result, the core−shell nanorod array coated cotton textile exhibited excellent UV-durable superhydrophobicity.

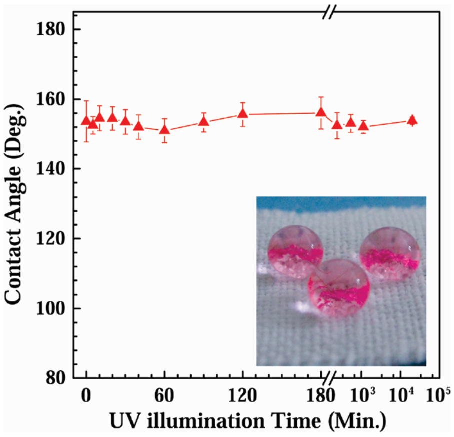

**Figure 4.** Evolution of water CA on an OTS-modified ZnO@$SiO_2$ nanorod array coated cotton textile under UV irradiation (25 mW $cm^{-1}$). The *x* axis after the break is scaled logarithmically. The inset is a macroscopic view of water droplets on the surface of a UV-irradiated sample.

Incidentally, we also examined the washing durability of a ZnO@$SiO_2$ nanorod array coated cotton textile. After continuous laundering for 24 h, the superhydrophobicity of the textile changed negligibly, suggesting a good washing durability (see the Supporting Information, Figure S2).

## 4. CONCLUSIONS

In summary, we have successfully obtained a UV-blocking and durable superhydrophobic cotton textile by introducing a ZnO@$SiO_2$ nanorod array to the woven fiber network followed by hydrophobic surface modification with OTS. Because ZnO nanorods have high absorbance and scattering for UV light and the insulating $SiO_2$ shell can effectively suppress the photoactivity of ZnO nanorods, the OTS-modified ZnO@$SiO_2$ nanorod array coated cotton textile exhibited an ultrahigh UPF value and durable superhydrophobic properties under UV irradiation, even prolonging the UV irradiation time to 2 weeks. This multifunctional cotton textile will have potential applications in various areas, such as medical, military, biological, and optoelectronic industrial fields.

## ASSOCIATED CONTENT

**Supporting Information.** Typical SEM images and EDX spectra of a ZnO@$SiO_2$ nanorod array with different deposition cycles of a $SiO_2$ shell, a photograph of a water droplet placed on the surface of an OTS-modified ZnO@$SiO_2$ nanorod array coated cotton textile after 24 h of laundering treatment, and a video of water droplets sliding off the as-prepared cotton textile. This material is available free of charge via the Internet at http://pubs.acs.org.

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