



# Dynamically modifiable wettability comparisons of the hydrophilic and hydrophobic substrates coated with F/TiO<sub>2</sub> hybrid sol by UV irradiation

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## ABSTRACT

To prepare a functional surface with dynamically modifiable wettability on cotton and polyester fabrics by hybrid coating, the F/TiO<sub>2</sub> hybrid sol were synthesized with tetrabutyl titanate and fluoride silane coupling agent via sol–gel technology. The anatase component in F/TiO<sub>2</sub> hybrid powder was mixed with rutile component from XRD, and the crystal component was unchanged in UV light and dark store condition. The switchable wettability of the fabric was assessed by contact angle in different conditions and time. The maximum contact angles of cotton and polyester fabrics coated with F/TiO<sub>2</sub> hybrid sol were 141.8° and 136.1°, respectively, and through UV irradiation, the minimum contact angles of cotton and polyester fabrics coated with F/TiO<sub>2</sub> hybrid sol were both 0°, respectively. Within storing in dark, the contact angles nearly completely reverted. The switchable cycle of the cotton was 84 h, while the switchable cycle of the polyester was 168 h. From AFM and fabric constructions (porosity, permeability and roughness) analysis, the fiber morphology had more effect on the contact angle than the fabric constructions. The F/TiO<sub>2</sub> hybrid powder and the coated fabric floated on water for their excellent hydrophobicity, and the samples deposited at the bottom of water as the wettability of coated fabric increased via UV irradiation. The irradiated samples were placed in dark, and the samples floated on water again. The water diffusion and permeable capacities further confirmed the dynamically modifiable wettability. The water diffusivity and permeable capacity further confirmed the excellent switchable wettability of coated fabrics by F/TiO<sub>2</sub> hybrid sol through UV irradiation or storage in dark.

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## 1. Introduction

Hydrophobic and hydrophilic surfaces as special wetting phenomenon have attracted much interest in recent years for their wide use on fundamental research and practical applications [1–4]. Such surfaces are usually achieved by the combination of two different processes: by creating hierarchical micro/nanostructures on hydrophobic substrates or by chemically modifying a micro/nanostructured surface with low surface energy materials [5–8]. As research continues, the novel functional surfaces, such as switchable wettability have aroused great interest [9].

The ability to deposit surfaces with switchable wettability assumes an actively pursued research area in materials science due to its implications in disparate technological fields [10–13]. There are two approaches to obtain switchable wettability: by microstructure or surface free energy transitions with the external stimulations. The reversible wetting behavior has been extensively

researched for their potential applications in self-cleaning surfaces, intelligent microfluidic devices, lab-on-a-chip systems, and so on [5,14–16].

During the numerous switchable wettability pathways, a more powerful strategy relies on the modifiable capability of some transition-metal oxides, namely TiO<sub>2</sub>, ZnO, etc., to increase their hydrophilicity under band-gap photoexcitation, and to revert back to the initial conditions upon storage in dark [12,17–20]. TiO<sub>2</sub> or modified TiO<sub>2</sub> represent exclusive platforms on which UV-switchable wettability are triggered concertedly with the semiconductor photocatalytic activity, and many researches have been fixed on the switchable wettability base on micro-/nanostructured films grown directly onto substrates via sol–gel reaction/calcination, sputtering or chemical vapour deposition [17]. Sawada et al. [21] synthesized a fluoroalkyl end-capped vinyltrimethoxysilane oligomer by sol–gel reaction under alkaline conditions in the presence of TiO<sub>2</sub> nanoparticles in tetrahydrofuran to afford the corresponding fluorinated oligomer/TiO<sub>2</sub> nanocomposites [RF-(VM-SiO<sub>2</sub>)<sub>n</sub>-RF/TiO<sub>2</sub>]. The wettability for water switched between superhydrophobicity and superhydrophilicity by alternation of UV irradiation and dark storage on

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glass. Athanassiou's group [17] examined the wettability evolution of compact TiO<sub>2</sub> thin films made of surfactant-capped nanocrystals, which could convert from a highly hydrophobic state to a highly hydrophilic and metastable one under UV irradiation. The conversion process of hydrophilicization-hydrophobicization within the contact angle 100°–20° was carried out over several cycles of alternating 120 min pulsed UV irradiation and vacuum storage periods for 5 h.

For the dynamically modifiable wettability, most substrates are glass, silicon wafer or metal sheet, which are even and thermodynamic. The literatures about dynamically modifiable wettability on fiber substrates, such as cotton, polyester are very few. In this paper, a photoconductive F/TiO<sub>2</sub> hybrid sol was synthesized and coated on fiber substrates, including cotton and polyester. The hydrophobic–hydrophilic switchable property was represented by the contact angle under the response condition of UV irradiation or dark store.

## 2. Experimental

### 2.1. Materials

The poplin 100% cotton fabric weighting 141.0 g/m<sup>2</sup> and 100% polyester fabric weighting 120.1 g/m<sup>2</sup> are produced by Jiangsu Hongdou Industrial Co., Ltd. (China). The tetrabutyl titanate (TBT), ethanol and HCl are supplied by Sinopharm Chemical Reagent Co., Ltd. (China). All the chemicals are analytical reagent grade. The 1H,1H,2H,2H-perfluorooctyltrimethoxysilane is offered by Harbin Xeogia fluorine-silicon chemical Co. (China), and it is technical grade.

### 2.2. Preparation of F/TiO<sub>2</sub> hybrid sol

The F/TiO<sub>2</sub> hybrid sol was prepared by adding diluted TBT 23 g (TBT: ethanol 1:3, weight ratio) into the mixture (71.0 g) containing HCl (1 mol/L) and H<sub>2</sub>O (HCl:H<sub>2</sub>O=2:8, weight ratio) in a flask at 500 rpm with a magnetic stirring apparatus at room temperature. 6 g 1H,1H,2H,2H-perfluorooctyltrimethoxysilane solution (50 wt% in ethanol) was added into the flask. The mixture was stirred at 30 °C for 8 h with a magnetic stirring apparatus and then aged for 120 h. Before used on fabric, the F/TiO<sub>2</sub> hybrid sol was neutralized by NH<sub>3</sub>·H<sub>2</sub>O (1 mol/L) to the pH value about 6.0.

### 2.3. Fabric modification

The cotton and polyester fabrics were pre-cleaned in deionized water and then dried at 50 °C for 2 h before other treatment. The fabrics were immersed in the F/TiO<sub>2</sub> hybrid sol at room temperature for 30 min, and then dried at 60 °C for 20 min and lastly baked at 150 °C for 3 min.

### 2.4. Irradiation and dark treatments

To induce hydrophilicity, the fabrics coated with F/TiO<sub>2</sub> hybrid sol were irradiated with the UV light (light intensity 21.0 mW/cm<sup>2</sup>, distance 40.0 cm, predominantly wavelength 253.7 nm). The contact angle was measured during the irradiating process. When the contact angle was decreased to 0°, the fabrics coated with F/TiO<sub>2</sub> hybrid sol and irradiated with the UV light were placed in dark box under ambient environment (with relative humidity of 30–40%), and the contact angle was also measured.

### 2.5. XRD spectra

The X-ray diffraction (XRD) spectra of the coatings were recorded in an X-ray diffractometer system (Bruker AXS GMBH,

**Table 1**  
Standard spray test rating chart.

Rating	Evaluation
100	No sticking or wetting of upper surface
90	Slight random sticking or wetting of upper surface
80	Wetting of upper surface at spray points
70	Partial wetting of whole of upper surface
50	Complete wetting of whole of upper surface
0	Complete wetting of whole upper and lower surfaces

D8). The X-ray source was a Cu K $\alpha$  radiation ( $\lambda=0.15418$  nm), which was operated with scanning step 4°/min the 2 $\theta$  between 5° and 90°.

### 2.6. Fabric porosity

Fabric porosity was assessed by photoshop and Matlab softwares. Before importing to photoshop software, the fabrics were pictured by a DZ3 video zoom microscope (Union Co., LTD) with the transmission model under 40 magnifications. The image in photoshop was performed by selecting “Desaturate” and then clicking “threshold” (level 150). The image was exported in “jpg” format after carried out “opposition”. Then the image was imported into Matlab software and executed the related programs [22]. The Matlab software gave the fabric porosity in the output page. The mean fabric porosity was obtained by measuring 3 times for every sample.

### 2.7. Water permeability property

Permeability property presented the wettability of the fabric. Fabric sample, instead of filter paper, was placed into a funnel, and then deionized water was poured into the funnel. According to the hydrophobic property, the water was dripped into the measuring cylinder for 1 min. The larger the hydrophobic property was, the less the water was in the measuring cylinder.

### 2.8. Water repellency spray property

To determine the surface wetting resistance of the treated fabrics, AATCC 22-2010 water repellency spray test method was used to evaluate the treated fabric repellency. The treated cellulose and polyester fabrics were conditioned at 20 ± 2 °C and 65 ± 2% RH for 24 hours before testing. The treated fabrics (18 cm × 18 cm) were stretched tight in an embroidery hoop, held at a 45° angle in the test apparatus and sprayed with 250 mL of water through a specified spray head from a height of 150 mm. The standard spray test rating chart was listed in Table 1 and Fig. 1.

### 2.9. Air permeability property

The air permeability of fabric was measured by YG461E digital air permeability instrument, prepared by Ningbo Textile Instrument Factory. The differential pressure was preset 100 Pa/mm H<sub>2</sub>O, and every sample was measured 5 times.

### 2.10. Coefficient and surface roughness

The coefficient and surface roughness of a fabric were measured by a KES-FB4 Kawabata Evaluation System-Fabric (KES Kato Tech, Japan). The sample size is 20 cm × 20 cm, and the experimental conditions were at 25 °C and 40% relative humidity.

### 2.11. Washing procedure

The washing process is the resistance of fabrics to change in any of its characteristics when fabrics are subjected to washing.

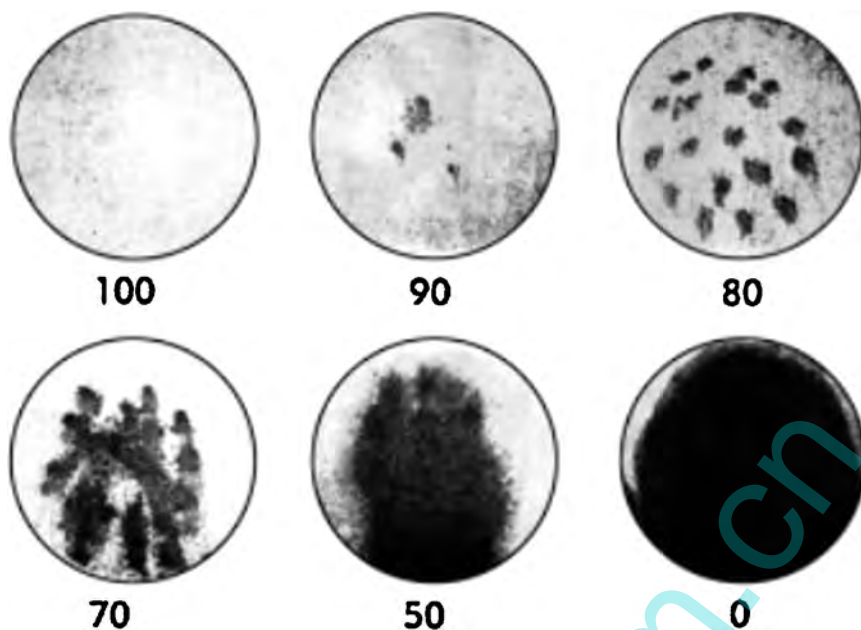


Fig. 1. Standard spray test rating chart.

The washing fastness was tested according to the standard of ISO 105-C10:2006 (E) using 3 g/L soap at 40 °C for 30 min with the 12-A washing fastness tester supplied by Wenzhou Darong Textile Instrument Co., Ltd. (China).

### 2.12. Atomic force microscopy measurement

The topography of the fabric coated with F/TiO<sub>2</sub> hybrid sol was investigated by atomic force microscopy (AFM) at 25 °C and 40% relative humidity using a CSPM4000 AFM made by Benyuan Co. Ltd. (China) operated in contact mode. The tip is slowly scanned across the surface of the coatings. The force between the atoms on the surface of the scanned material and those on the scanning tip leads the tip to deflect. This deflection is recorded by using a laser focused on the top of the cantilever and reflected onto photodetector. The photodetector signals are used to map the surface characteristics of specimens with resolutions down to the nanoscale.

## 3. Results and discussion

### 3.1. Characteristics of F/TiO<sub>2</sub> hybrid powder

From Fig. 2, the characteristic absorption peaks of the F/TiO<sub>2</sub> hybrid powder at 25.1°, 62.9° and 68.9° represented the anatase, which corresponded to the crystal indices: 101, 204 and 116, respectively, and the characteristic absorption peaks at 27.1°, 36.1° and 54.1° indicated the rutile. Both of the two components were represented, and the rutile component was more than the anatase component. The characteristic absorption peaks were nearly the same the original F/TiO<sub>2</sub> hybrid powder after irradiated in UV and/or stored in dark place, which indicated that the UV and dark treatments had less effects on the crystal types. Sawada et al. [21] reported that anatase type titanium oxide presented good dynamically modifiable wettability for water between superhydrophobicity and superhydrophilicity by alternation of UV irradiation and dark storage. As cotton and polyester substrates could not be withstand high temperature, all the powders were calcinated at 150 °C for 3 min. At this condition, it was difficult to prepare pure anatase TiO<sub>2</sub>. The anatase component was the significant substrate for photosensitization under UV light.

### 3.2. F/TiO<sub>2</sub> hybrid powder floatability in water

The wettability of F/TiO<sub>2</sub> hybrid powder in water was assessed by the powder state in water. From Fig. 3(a), nearly all the F/TiO<sub>2</sub> hybrid powder floated on water. However, the powder was sunk in water after irradiated in UV for 24 h. Sequentially, the irradiated powder was placed in dark for 48 h and then poured into the test tube. The powder was floated on water again, instead of sink at the bottom of test tube. The density of F/TiO<sub>2</sub> hybrid powder was about 4.0 g/cm<sup>3</sup> and usually deposited in water. For the crystal texture of TiO<sub>2</sub> and fluoride component, the F/TiO<sub>2</sub> hybrid powder was hydrophobic. The surface of the water curves down toward the edge of F/TiO<sub>2</sub> hybrid powder (Fig. 3(e)). The powder was thus supported by the surface tension of the water.

The F/TiO<sub>2</sub> hybrid powder was irradiated in UV light, and the Ti<sup>4+</sup> was changed into Ti<sup>3+</sup> [9,23]. Abundant –OH was generated on the surface of TiO<sub>2</sub> particle. The hydroxyl increased the wettability of the F/TiO<sub>2</sub> hybrid powder, and the interface between powder and H<sub>2</sub>O was unstable. The powder was easily wet and entered into water (Fig. 3(f)). The surface tension disappeared when the powder

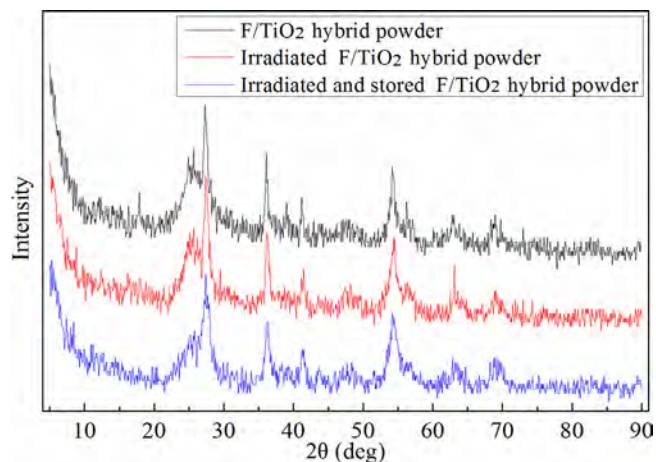
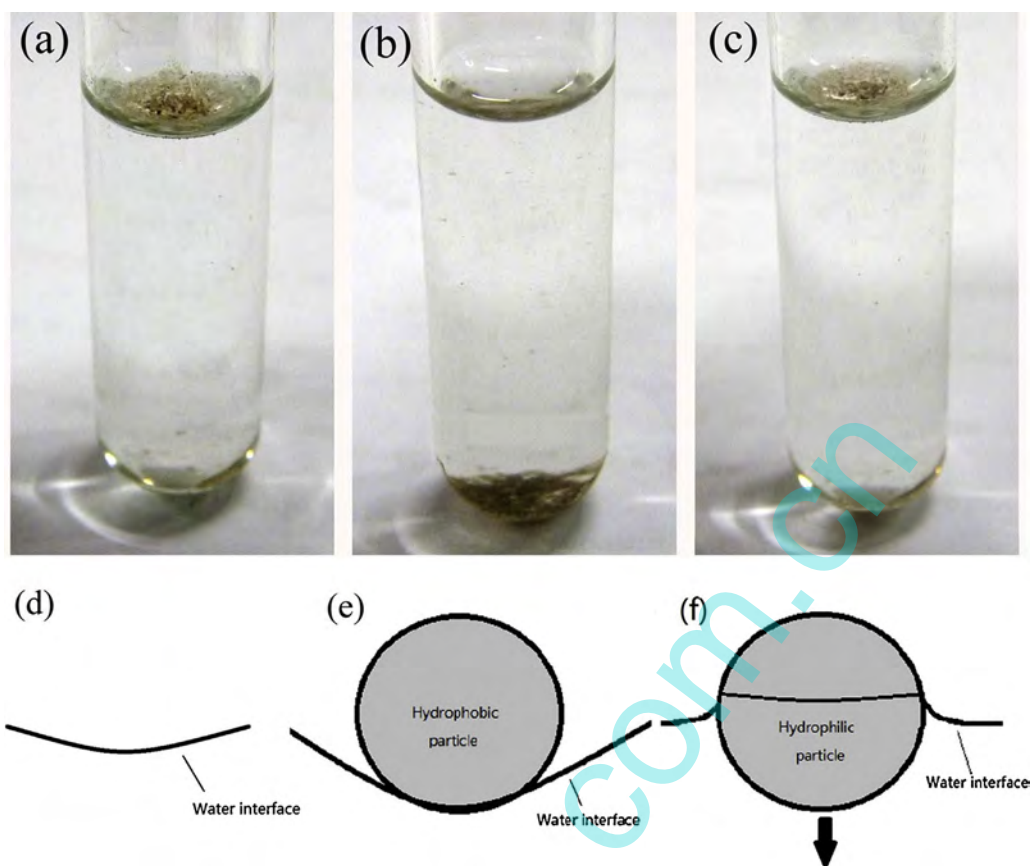


Fig. 2. XRD spectra of F/TiO<sub>2</sub> hybrid powder.



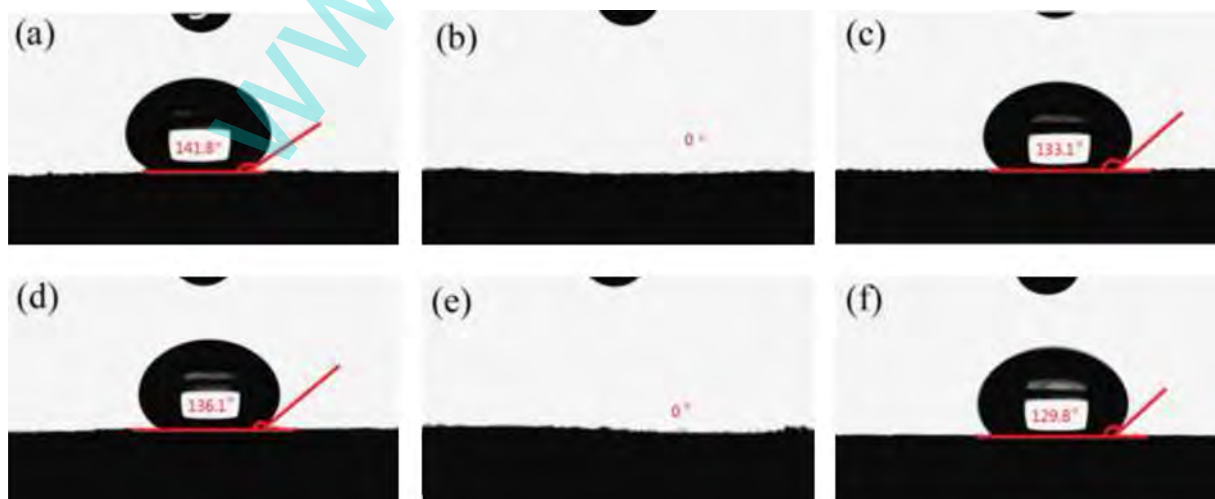
**Fig. 3.** Floatability of F/TiO<sub>2</sub> hybrid powder in water: (a) F/TiO<sub>2</sub> hybrid powder; (b) F/TiO<sub>2</sub> hybrid powder irradiated in UV for 24 h; (c) irradiated F/TiO<sub>2</sub> hybrid powder placed in dark for 48 h; (d) water surface; (e) floating of hydrophobic particle; (f) sinking of hydrophilic particle.

was in water. As the density of F/TiO<sub>2</sub> was larger than that of H<sub>2</sub>O, the gravity of the powder was higher than the buoyancy and the powder was sunk in water.

The irradiated F/TiO<sub>2</sub> hybrid powder was placed in dark, and the Ti<sup>3+</sup> was reverted back into the Ti<sup>4+</sup>. The -OH on the coating surface disappeared, and the wettability of the F/TiO<sub>2</sub> hybrid powder decreased, which led to hydrophobicity and floating on water (Fig. 3(c)).

### 3.3. Wetting conversion performance

The cotton and polyester fabrics were coated with F/TiO<sub>2</sub> hybrid sol. From Table 2, the weight increases of cotton and polyester were 6.7% and 6.1%, respectively. The F/TiO<sub>2</sub> hybrid sol on fabrics was gelled, and the F/TiO<sub>2</sub> hybrid coating increased the weight of the fabrics. The contact angle of cotton fabric coated with F/TiO<sub>2</sub> hybrid sol was 141.8° (Fig. 4), while the modified polyester fabric



**Fig. 4.** Contact angle changes: (a) coated cotton fabric; (b) coated cotton fabric irradiated for 24 h; (c) coated and irradiated cotton fabric in dark for 60 h; (d) coated polyester fabric; (e) coated polyester fabric irradiated for 38 h; (f) coated cotton fabric irradiated for 108 h.



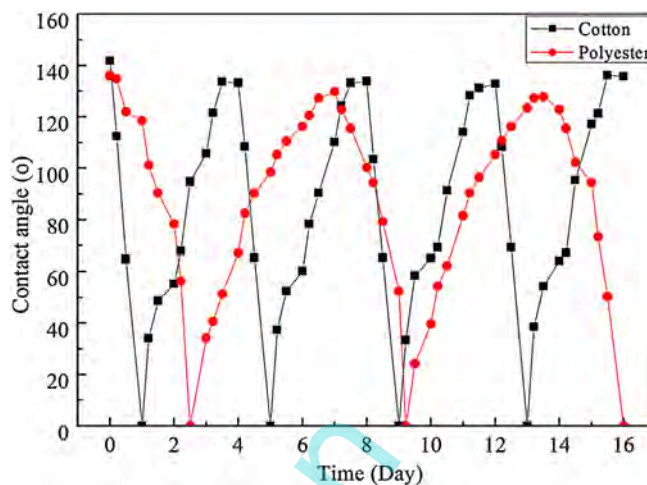
**Table 2**  
Weight increase of treated fabrics.

Fabric	Weight increase (%)
Cotton fabric	$6.7 \pm 0.1$
Polyester fabric	$6.1 \pm 0.2$

presented a contact angle  $136.1^\circ$ . Under UV light for 24 h, the contact angle of the cotton fabric coated with F/TiO<sub>2</sub> hybrid sol decreased to  $0^\circ$  after 24 h and the coated fabric was superhydrophilic. Although the contact angle of the coated polyester fabric was decreased to  $118.5^\circ$  after exposed in UV light for 24 h, the reduction was slight. The sample was sequentially irradiated the contact angle further decreased. The contact angle of the coated polyester sample was decreased to  $0^\circ$  while the irradiated time was 60 h. The superhydrophilic cotton and polyester samples were placed in dark, and the contact angles were increased slowly. The contact angle of the coated cotton sample was increased to  $94.7^\circ$  after stored in dark for 36 h, and the contact angle of the coated polyester sample was increased to  $67.2^\circ$ . Continuing to store in dark, the contact angles were further risen. While stored in dark for 60 h and 108 h, the contact angles of the coated cotton and polyester samples were increased to  $133.1^\circ$  and  $129.8^\circ$ , respectively, and they did not increase sequentially when kept on in dark again.

The dynamically modifiable wettability of the coated fabric was aroused by the F/TiO<sub>2</sub> hybrid component. TiO<sub>2</sub> in F/TiO<sub>2</sub> hybrid coating was a photosensitive material, and when the fabric was irradiated with UV light, the photogenerated hole in TiO<sub>2</sub> reacted with lattice oxygen to form surface oxygen vacancies, to which water molecules kinetically coordinated. This change improved the surface hydrophilicity greatly and resulted in a contact angle of about  $0^\circ$ . For the -OH group adsorption, the surface of TiO<sub>2</sub> transformed into an energetically metastable state, and the adsorbed -OH groups could gradually be replaced by atmospheric oxygen when the fabric was placed in dark. And the surface reverted back to its original state, and the surface wettability changed to hydrophobic again [11,24]. The fluoric component increased the hydrophobicity before irradiated in UV light and after in dark.

From Fig. 5, the process was repeated for several cycles. The cycle time of the cotton and polyester was 84 h and 168 h, respectively. The cycle time and the maximum/minimum contact angle in every cycle were nearly the same for every fabric sample.



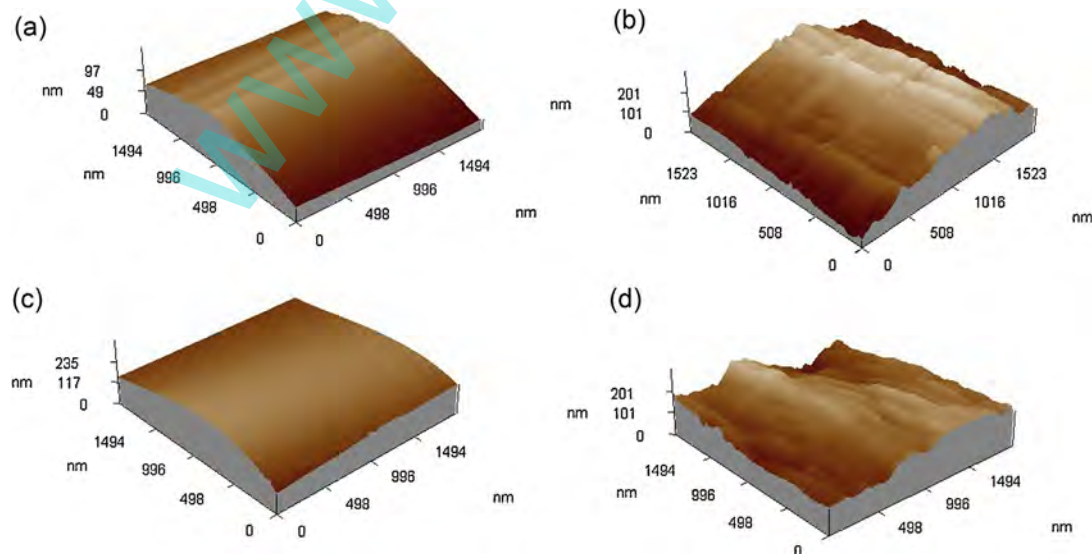
**Fig. 5.** Contact angle curves of the coated fabrics in UV light and dark.

Although the components and the coating condition were the same, the cycles for cotton and polyester were different. The cycle might be affected by the fabric construction and fiber morphology.

Table 3 showed the constructional properties of the cotton and polyester samples. The porosities of the cotton and polyester were 13.2% and 14.2%, respectively, and the polyester fabric was thin and porous. The air permeabilities of the cotton and polyester were 108.4 and 225.5 mm/s, respectively, which further indicated that the porosity of the polyester was more remarkable. According to Cassie model, porosity could increase the hydrophobicity by filling air in the pore and decreasing the contact area between coating and H<sub>2</sub>O. Actually, the experimental data were not the same as the Cassie model from fabric constructional [2,14]. Also from coefficient of kinetic friction and surface roughness, there seems not to be an obvious regular about the roughness and hydrophobicity.

To investigate the influencing factor on the contact angle, the surface morphologies of cotton and polyester fibers before and after coating were compared via AFM images.

The surface texture of cotton fiber presented groove construction and natural distortion from AFM (Fig. 6(a)), whereas the roughness is not drastic, which was slightly effect on the contact angle [25]. From Fig. 6(b), the micro-surface of cotton fabric coated



**Fig. 6.** Fiber surface morphologies: (a) original cotton fiber; (b) cotton fiber coated with F/TiO<sub>2</sub> hybrid sol; (c) original polyester fiber; (d) polyester coated with F/TiO<sub>2</sub> hybrid sol.

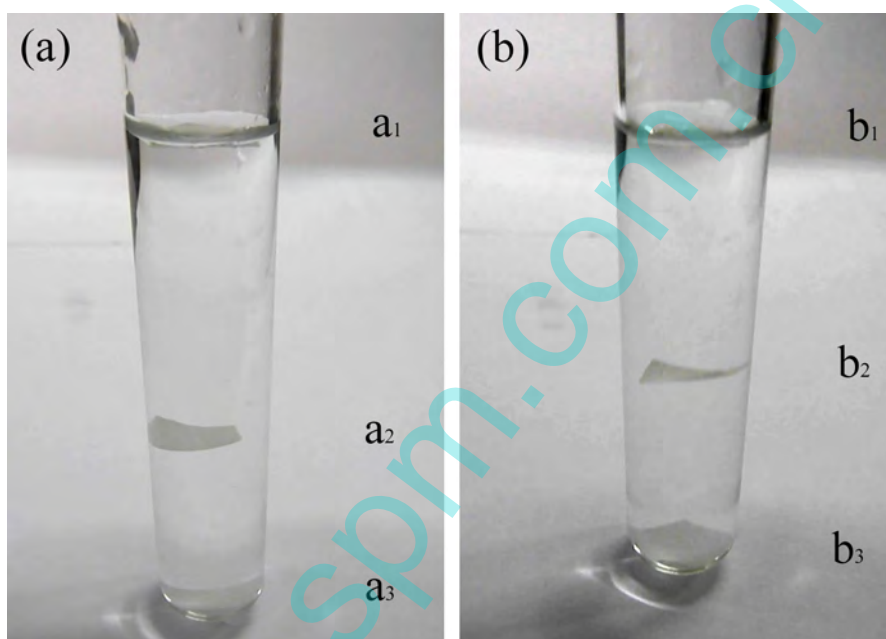
**Table 3**

The constructional properties of the cotton and polyester fabrics.

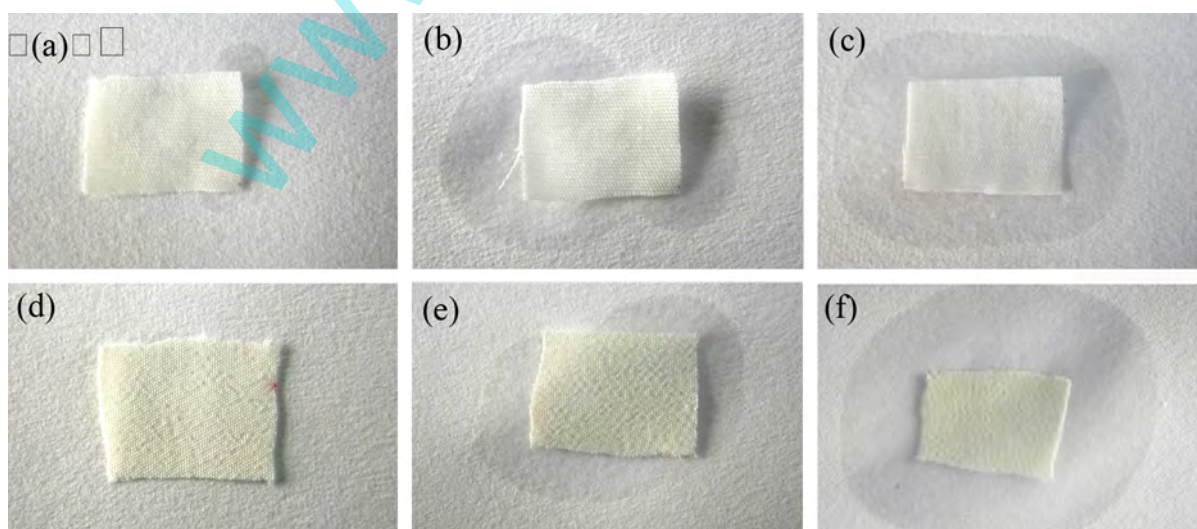
Sample	Porosity (%)	Air permeability (mm/s)	Coefficient of kinetic friction ( $\mu$ )		Surface roughness ( $\mu\text{m}$ )	
			Warp	Weft	Warp	Weft
Cotton fabric	13.2	108.4	0.16	0.15	5.6	2.8
Polyester fabric	14.2	225.5	0.22	0.15	2.6	3.5

with F/TiO<sub>2</sub> hybrid sol was relatively scraggy. About polyester fiber, the surface was smooth and there was nearly no groove construction (Fig. 6(c)). However, the surface component of fabric was changed and slightly rough surface was presented after coated with F/TiO<sub>2</sub> hybrid sol (Fig. 6(d)). Although the polyester was hydrophobic and the cotton was hydrophilic, the coating nearly covered all

the fiber surfaces, and the surface components were F/TiO<sub>2</sub> hybrid powder. From Fig. 6(b) and (d), the coated cotton fiber presented a rougher surface for the related rough fiber substrate. According to the Cassie model, the coated cotton fabric should show a larger contact angle, and it was consistent with the experimental results [26].



**Fig. 7.** Floatability of cotton (a) and polyester (b) fabrics in water: (a<sub>1</sub>) coated cotton fabric; (a<sub>2</sub>) coated cotton fabric irradiated for 14 h; (a<sub>3</sub>) coated cotton fabric irradiated for 24 h; (b<sub>1</sub>) coated polyester fabric; (b<sub>2</sub>) coated polyester fabric irradiated for 38 h; (b<sub>3</sub>) coated cotton fabric irradiated for 60 h.



**Fig. 8.** Water diffusion on paper from different fabrics: (a) coated cotton fabric; (b) coated cotton fabric irradiated for 14 h; (c) coated cotton fabric irradiated for 24 h; (d) coated polyester fabric; (e) coated polyester fabric irradiated for 38 h; (f) coated cotton fabric irradiated for 60 h.



### 3.4. Permeability of H<sub>2</sub>O

The fabric revealed different status in water for the dynamically modifiable wettability of the coated fabric. The coated cotton and polyester fabrics floated on water (Fig. 7(a<sub>1</sub>) and (b<sub>1</sub>)), and the fabrics would suspend in water after irradiated 14 h for cotton and 38 h for polyester, respectively (Fig. 7(a<sub>2</sub>) and (b<sub>2</sub>)). Continuing to irradiate in UV light, the fabric samples were deposited at the bottom of the test tube (Fig. 7(a<sub>3</sub>) and (b<sub>3</sub>)).

The densities of the cotton and polyester were 1.54 g/cm<sup>3</sup> and 1.38 g/cm<sup>3</sup>, respectively, and the F/TiO<sub>2</sub> hybrid powder was 4.0 g/cm<sup>3</sup>. The average densities of coated cotton and polyester were larger than that of water, and they deposited to the bottom in water if there was no air pore in the fabric according to buoyancy principle. Actually, the cotton and polyester fabric coated with F/TiO<sub>2</sub> hybrid sol presented excellent hydrophobicity, and water did not fill the small pore in the fabric, and there were a lot of air pore in the coated fabric. The fabric floated on water (Fig. 7(a<sub>1</sub>) and (b<sub>1</sub>)) when the average density of sample, including coated fabric and air pore, was smaller than that of water. Via irradiating in UV light, the wettability of the fabric increased, some air pore was filled with water and the average density increased. While the average density was the same as that of water, the fabric was suspended in water. Consequently, continuing to irradiate in UV light, the air pore in fabric was further decreased, and the average density was larger than that of water, the fabric deposited at the bottom of water.

To confirm the wettability and content of the air pore, the water diffusion on absorbent paper was tested.

From Fig. 8(a) and (d), there were nearly no water diffusion on the absorbent paper while the cotton and polyester fabrics coated with F/TiO<sub>2</sub> hybrid sol were placed on the paper. It indicated that there was nearly no water in the fabrics. The fabrics were irradiated 14 h for cotton and 38 h for polyester, and the water diffusion was obvious around the fabrics. It revealed that there was some water in the fabrics. The coated cotton fabric was irradiated 24 h and the coated polyester fabric was irradiated 60 h, the water stain area on the absorbent paper was increased, which indicated the water was more in the fabrics. These results were consistent with the conclusions in Fig. 7.

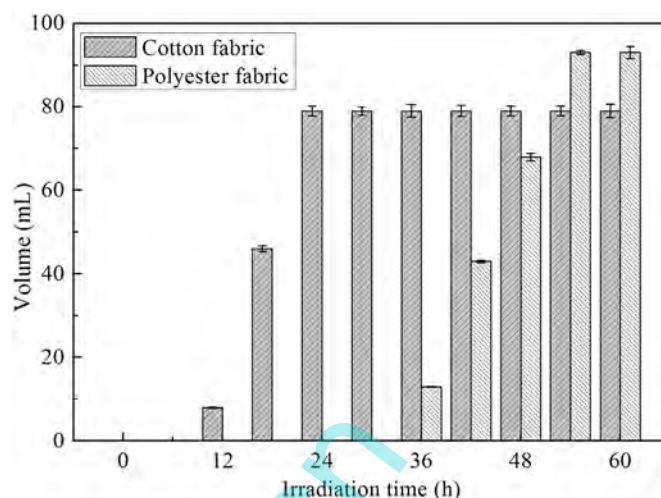


Fig. 9. Permeable volume of the fabrics irradiated different time in UV light.

The permeability of the H<sub>2</sub>O was another support to the wettability. From Fig. 9, Without UV irradiation, the permeable capacities of cotton and polyester coated with F/TiO<sub>2</sub> hybrid sol were 0 mL, and water was wholly resisted by the fabric. With UV irradiation for 12 h, the permeable capacity of cotton fabric was 8.1 mL and continuing to treat in UV light for another 6 h, the permeable volume increased to 46.0 mL. The permeable volume reached to 79.2 mL when the irradiated time was more than 24 h. However, the permeable capacity of polyester fabric was only 12.9 mL after irradiated in UV light for 36 h. The permeable volume increased to 93.0 mL while the polyester fabric was treated for 54 h, and the permeable volume reached the maximum value. The changes of the permeable capacities were related to the wettability of the F/TiO<sub>2</sub> hybrid coating within irradiation in UV light and revert back in dark. The results were coincident with the water diffusion experiment.

With the water repellency spray test, the switchable wettability was shown in Fig. 10. The cotton and polyester coated with F/TiO<sub>2</sub> hybrid sol were nearly no water droplets on fabrics after spray (Fig. 10(a) and (e)). According to the AATCC 22-2010 standard

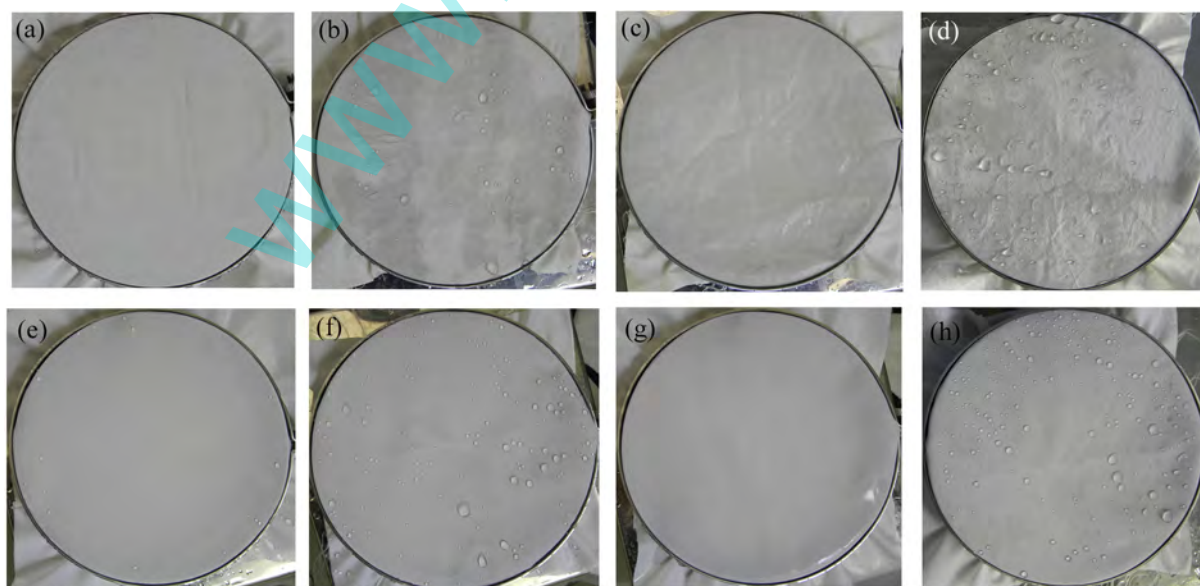


Fig. 10. Water repellency spray properties of cotton and polyester fabrics; (a) coated cotton fabric; (b) coated cotton fabric irradiated for 14 h; (c) coated cotton fabric irradiated for 24 h; (d) coated cotton fabric washed for 30 times (e) coated polyester fabric; (f) coated polyester fabric irradiated for 38 h; (g) coated cotton fabric irradiated for 60 h; (h) coated polyester fabric washed for 30 times.

spray test rating chart, the spray test rating were 100. Within UV irradiated for 14 h and 38 h, respectively, some water droplets could be seen on cotton and polyester fabrics from Fig. 10(b) and (f), and they were about 80 scores. When the samples were irradiated for 24 h and 60 h, respectively, both of the cotton and polyester samples were completely wetted, and the spray test rating were 0 (Fig. 10(c) and (g)). These properties were consistent with the contact angle property. The cotton and polyester fabrics coated with F/TiO<sub>2</sub> hybrid sol were tested according to the AATCC 22-2010 standard, the spray test rating were about 80 (Fig. 10(d) and (h)), which still presented good water repellency. During gelation process, Ti–O–Ti, Si–O–Si, Si–O–Ti formations [27] were generated on fiber surface, which could improve the washing property.

#### 4. Conclusions

F/TiO<sub>2</sub> hybrid sol was synthesized via sol–gel technology and coated on cotton and polyester fabrics to present dynamically modifiable wettability. The contact angle of cotton fabric coated with F/TiO<sub>2</sub> hybrid sol was 141.8°, and it was decreased to 0° by UV irradiation for 24 h. The contact angle of the coated polyester sample was increased to 133.6° after stored in dark for 72 h, revealing that the contact angle was nearly completely reverted. The polyester fabric showed similar properties to cotton except a longer cycle time 168 h. The fiber morphology had a significant effect on the hydrophobicity and switchable wettability. The F/TiO<sub>2</sub> showed different valence state in UV irradiation and dark storage, which was verified by the XRD spectrum. The floatability of powder and fabric, water diffusivity, permeable capacity and water repellency spray test were significantly affected by UV irradiation or storage in dark.

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#### References

- [1] W. Hou, Q. Wang, *Journal of Colloid and Interface Science* 316 (2007) 206–209.
- [2] H.S. Lim, D. Kwak, D.Y. Lee, S.G. Lee, K. Cho, *Journal of the American Chemical Society* 129 (2007) 4128–4129.
- [3] Z. Mazrouei-Sebdani, A. Khoddami, *Progress in Organic Coatings* 72 (2011) 638–646.
- [4] Q. Zhu, Q. Gao, Y. Guo, C.Q. Yang, L. Shen, *Industrial & Engineering Chemistry Research* 50 (2011) 5881–5888.
- [5] A. Chaudhary, H.C. Barshilia, *Journal of Physical Chemistry C* 115 (2011) 18213–18220.
- [6] T. Sun, G. Wang, L. Feng, B. Liu, Y. Ma, L. Jiang, D. Zhu, *Angewandte Chemie International Ed. In English* 43 (2004) 357–360.
- [7] Y.J. Park, D.H. Lim, H.J. Kim, D.S. Park, I.K. Sung, *International Journal of Adhesion and Adhesives* 29 (2009) 710–717.
- [8] E. Krijnen, M. Marsman, O. Holweg, *Journal of Industrial Textiles* 24 (1994) 152–161.
- [9] H. Irie, H. Mori, K. Hashimoto, *Vacuum* 74 (2004) 625–629.
- [10] J. Zhang, X. Lu, W. Huang, Y. Han, *Macromolecular Rapid Communications* 26 (2005) 477–480.
- [11] K.S. Guan, B.J. Lu, Y.S. Yin, *Surface & Coatings Technology* 173 (2003) 219–223.
- [12] J.F. Wu, S. Fernando, K. Jagodzinski, D. Weerasinghe, Z. Chen, *Polymer International* 60 (2011) 571–577.
- [13] M.J. Jiang, Z.M. Dang, S.H. Yao, J.B. Bai, *Chemical Physics Letters* 457 (2008) 352–356.
- [14] C.-J. Chang, E.-H. Kuo, *Thin Solid Films* 519 (2010) 1755–1760.
- [15] M.N.N. Mintsas, L. Lecamp, C. Bunel, *European Polymer Journal* 45 (2009) 2043–2052.
- [16] P. Castell, M. Wouters, H. Fischer, *Journal of Applied Polymer Science* 106 (2007) 3348–3358.
- [17] G. Caputo, R. Cingolani, P.D. Cazzoli, A. Athanassiou, *Physical Chemistry Chemical Physics* 11 (2009) 3692–3700.
- [18] J. Yang, Z. Zhang, X. Men, X. Xu, X. Zhou, Q. Xue, *Journal of Colloid and Interface Science* 366 (2012) 191–195.
- [19] J. Yun, S. Lee, T.S. Bae, Y. Yun, S. Lee, J.D. Kwon, G.H. Lee, *Plasma Processes and Polymers* 8 (2011) 815–831.
- [20] T. Karakouz, B.M. Maoz, G. Lando, A. Vaskevich, I. Rubinstein, *ACS Applied Materials & Interfaces* 3 (2011) 978–987.
- [21] E. Sawada, H. Kakehi, Y. Chounan, M. Miura, Y. Sato, N. Isu, H. Sawada, *Composites Part B: Engineering* 41 (2010) 498–502.
- [22] Y. Sun, X. Chen, X. Wang, *Journal of Textile Research* 32 (2006) 83–88.
- [23] Q.J. Liu, X.H. Wu, B.L. Wang, Q.A. Liu, *Materials Research Bulletin* 37 (2002) 2255–2262.
- [24] S.M. Trey, P. Sidenvall, K. Alavi, D. Stahlberg, M. Johansson, *Progress in Organic Coatings* 64 (2009) 489–496.
- [25] J. Vince, B. Orel, A. Vilcnik, M. Fir, A.S. Vuk, V. Jovanovski, B. Simoncic, *Langmuir* 22 (2006) 6489–6497.
- [26] A. Cassie, S. Baxter, *Transactions of the Faraday Society* 40 (1944) 546–551.
- [27] Y.J. Yin, C.X. Wang, Y.J. Wang, *Colloids and Surfaces a-Physicochemical and Engineering Aspects* 399 (2012) 92–99.