

# Structure and Properties of Cotton Fibers Modified with Titanium Sulfate and Urea under Hydrothermal Conditions

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## ABSTRACT

Cotton fibers were treated with titanium sulfate, urea and hexadecyl trimethyl ammonium bromide by low temperature hydrothermal method. The surface morphology, chemical structure, thermal stability and optical properties of cotton fibers before and after treatments were studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), thermal gravimetric (TG) and diffuse reflectance spectrum (DRS). The properties of tensile, friction and self-cleaning capability to discolor strawberry juice stain were also measured. The results showed that titanium dioxide ( $\text{TiO}_2$ ) nanoparticles in anatase phase with an average particle size of 50 nm were grafted on the surfaces of cotton fibers. The crystallites of  $\text{TiO}_2$  were less than 10 nm in size. In comparison with the original cotton fibers, the thermal properties of  $\text{TiO}_2$  coated cotton fibers had almost no change. The protection against ultraviolet radiation was obtained. However, the tensile properties decreased to some extent. The coefficients of static and kinetic friction increased because of the introduction of  $\text{TiO}_2$  nanoparticles. The strawberry juice stained on cotton fibers could be discolored exposure to UV radiation.

**Keywords:** Cotton fibers; titanium dioxide; modification

## INTRODUCTION

Titanium dioxide ( $\text{TiO}_2$ ) nanoparticles have recently attracted increasing attention because of their unique characteristics (inexpensive, non-toxicity and chemical stability) and promising applications in the fields of pigments, photocatalysts, solar energy cells, antimicrobial, etc. It is well known that when exposed to ultraviolet (UV) light, the photon energy generates an electron hole pair on the surface of  $\text{TiO}_2$ .

The hole in the valence band can react with hydroxyl ions ( $\text{OH}^-$ ) adsorbed on the surface to produce hydroxyl radicals ( $\cdot\text{OH}$ ), and the electron in the conduction band can reduce oxygen to produce peroxide ions ( $\text{O}_2^{2-}$ ). Both hydroxyl radicals and peroxide ions are extremely reactive particles, and they can decompose organic compounds upon contact with them [1]. It has been reported that the higher photocatalytic reactivity of  $\text{TiO}_2$  is mainly attributed to the strong UV absorption. The photodecomposition efficiency can be greatly improved under different illumination conditions. The photocatalytic activities of  $\text{TiO}_2$  are often dependent upon the crystallite size, morphology, phase, crystallinity and the porosity of the coating [2,3].

However, the large-scale application of  $\text{TiO}_2$  nanoparticles has been restricted by the problem of recycling the photocatalyst. Some processing techniques, such as sol-gel [4], microemulsion [5], hydrothermal [6], template method [7], chemical vapor deposition [8] as well as reverse micelle method [9], have been developed for the immobilization of  $\text{TiO}_2$  nanoparticles on different substrates with large surface areas. To impart cotton fabric with the properties of self-cleaning, antibacterial and UV protection, the preparation of  $\text{TiO}_2$  deposition has been realized using various coating methods. For instance, cellulose fibers were used as the templates to deposit  $\text{TiO}_2$  nanoparticles by using a sol-gel process at relatively low temperature. The resulting fibers showed the self-cleaning properties when exposed to sun light [10]. Also, the titania nanosol solution was applied to cotton fabric by a dip-pad-dry-cure process. A transparent thin layer of nano-crystalline titania formed on the fiber surface, which could degrade the coffee and red wine under UV radiation [1]. Likewise,

the self-cleaning fabrics were fabricated by depositing and grafting TiO<sub>2</sub> nanoparticles via an aqueous sol process at low temperature [11]. Moreover, TiO<sub>2</sub> nanoparticles in anatase and rutile structures were synthesized and deposited onto the surfaces of cotton fabrics by using ultrasonic irradiation [12].

Generally speaking, there are two main approaches to improve the binding strength between TiO<sub>2</sub> nanoparticles and supporting materials. One way is to modify the surface of fiber. For example, the TiO<sub>2</sub> nanoparticles were applied on the dyed cotton fabrics by the sol-gel and linking agent methods, which could withstand the various cycles of domestic washing [13]. Similarly, cotton fibers were modified with corona or RF plasma pretreatment prior to deposition of colloidal TiO<sub>2</sub> nanoparticles. The extraordinary photocatalytic activity of TiO<sub>2</sub> nanoparticles loaded on cotton fabrics was proved by self-cleaning of blueberry juice stains and photodegradation of methylene blue in aqueous solution under UV illumination [14]. The other way is to modify the surface of nanoparticles by chemical or physical modification. For example, TiO<sub>2</sub> nanoparticles were first modified with glycidoxypropyltrimethoxy silicone and polyoxymethylene, and then introduced into hybrid polytetrafluoroethylene/cotton fabric composites. The as-obtained composites exhibited a lower wear rate because of the improvement of interfacial adhesion between filler and matrix [15]. The cotton fabric was equally treated by the nano TiO<sub>2</sub>-polyacrylate hybrid dispersion synthesized by in-situ suspension polymerization or solution polymerization. The as-prepared fabric had the excellent photocatalytic self-cleaning ability to decompose the grape syrup [2,16]. Several reports suggested that the problem of stability and durability of TiO<sub>2</sub> nanoparticles could be resolved by the introduction of new functional groups to fiber surface. A layer of silica between TiO<sub>2</sub> nanoparticles and cellulose fibers was added to provide the best protection of the cellulose from the damage caused by the titanium particle when exposed to sunlight [17]. In addition, TiO<sub>2</sub> thin film was produced on cotton fabric from a colloidal sol by a simple dip-pad-dry-cure process in a short time. The adhesion between the TiO<sub>2</sub> film and the cotton support was enhanced, indicated by good fastness at 20 home launderings [18].

Although TiO<sub>2</sub> based cotton fabrics have been widely investigated with antimicrobial, self-cleaning, UV-protective properties and so on, the adherence of nano TiO<sub>2</sub> on the surface of fabric is usually not strong enough to immobilize the nanoparticle. Anatase TiO<sub>2</sub> nanocrystallites were successfully grown on cotton fabrics through a hydrothermal process for three hours after the fabric treatment using ethanol-based sol-gel titania [19]. More recently, we have fabricated TiO<sub>2</sub>-coated cotton fabric using titanium tetrabutyl as the precursor at low temperature by hydrothermal method [20]. Nano-sized TiO<sub>2</sub> was synthesized and simultaneously loaded on cotton fabric in a one-step fabrication procedure. The high pressure and hot water facilitated the binding of colloidal nanoparticles to fiber. However, the structure and properties of cotton fibers were not discussed. Herein, we employed an improved method to anchor TiO<sub>2</sub> nanoparticles on cotton fibers by using titanium sulfate and urea as the precursors and hexadecyl trimethyl ammonium bromide as the dispersing agent. The particle size of as-synthesized TiO<sub>2</sub> was controlled below 10 nm. The phase structures, morphologies, the chemical states and optical properties of cotton fibers before and after treatments were analyzed by using characterization methods such as scanning electron microscope (SEM), transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), thermal gravimetric (TG) and diffuse reflectance spectrum (DRS). The properties of tensile, friction and self-cleaning behaviors were also studied.

## **EXPERIMENTAL**

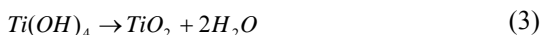
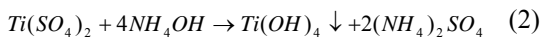
### **Materials**

The linear density of fine staple cotton fibers is 1.69±0.05 dtex and the upper half mean length is 29±2 mm. The chemical reagents, including titanium sulfate (Ti(SO<sub>4</sub>)<sub>2</sub>), urea ((NH<sub>2</sub>)<sub>2</sub>CO), hexadecyl trimethyl ammonium bromide ((C<sub>16</sub>H<sub>33</sub>)N(CH<sub>3</sub>)<sub>3</sub>Br, CTAB), sodium hydroxide, acetone and anhydrous ethanol were used without further purification. Distilled water was used for all the preparations.

### **Modification of Cotton Fibers**

About 5.0 g of raw cotton fibers was first treated with a 250 mL of sodium hydroxide solution (mass concentration 3.0 g/L) for 30 min at 80°C in order to

remove the natural waxes and impurities, and then washed with distilled water for 10 min thrice and dried at 80°C. A certain amount of titanium sulfate with a mass of 0.96 g was completely dissolved into 80 mL of distilled water. The designated amounts of urea (2.4 g) and CTAB (0.4 g) were subsequently added to the above solution. A half gram of pretreated cotton fibers was submerged into the resultant mixture for 10 min. The fiber sample together with the solution was transferred to a PTFE sealed can, which was put into the stainless steel autoclave. The autoclave was placed in a furnace and run at a speed of 200 r/min. The temperature was raised to 140°C at a heating rate of 2°C/min. After two hours, the cotton fibers was taken out and dipped in the acetone and ethanol solution for 15 min twice, respectively, and then washed with distilled water repeatedly, and dried at 80°C. The following reaction would be expected to occur during the hydrothermal treatment.



### **Characterization and Measurement**

The surface morphologies of cotton fibers before and after treatments were examined using field emission scanning electron microscope (FESEM, JEOL JSM-6700). The microstructure and phase identification of TiO<sub>2</sub> nanoparticles were carried out using transmission electron microscopy (JEOL JEM-3010). Fourier transform infrared spectroscopic (FTIR) measurements were conducted using a FTIR 7600 spectrophotometer (Lambda Scientific Systems, Inc). The spectra were recorded in the range of 400–4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup> as KBr pellets. The crystallinity index (*K*) was calculated by the following formula:  $K = (A_{1372}/A_{2900}) \times 100\%$  where  $A_{1372}$  and  $A_{2900}$  are the band intensities at wavenumber 1372 cm<sup>-1</sup> and 2900 cm<sup>-1</sup>, respectively [21]. The valence states of cotton fibers were obtained by X-ray photoelectron spectroscopy (XPS) spectra, which taken using non-monochromatic Al K $\alpha$  radiation (1486.68 eV) through a K-Alpha system with a base pressure of 4×10<sup>-6</sup> Pa. XPS data were corrected with the C-C binding energy at 284.6 eV and analyzed using the Thermo Advantage V4.51 software. The decomposition process of the fiber

sample was investigated by thermo gravimetric analysis using a GA/SDTA851e thermo gravimetric/differential thermal analyzer (TG-DTA) system. The change of relative mass vs temperature was evaluated at a heating rate of 10°C/min with a nitrogen flush rate of 10 mL/min over the range of 40–600°C. The optical properties of the fiber samples were determined using diffuse reflectance spectroscopy (DRS). The spectrophotometer (U-3010 UV-vis-NIR) equipped with an integrating sphere (ø150 mm) and BaSO<sub>4</sub> was used as reference. The spectra were recorded at room temperature in the wavelength range of 200–800 nm at a scanning speed of 600 nm/min.

The tensile properties of the fiber samples were measured on a YG001N electromechanical test instrument according to GB/T 14337–2008. The testing rate was 10 mm/min and the pretension was 0.1 g. More than 300 cotton fibers were measured to ensure a 95% confidence level. The friction properties of more than 50 fiber samples were evaluated using an Y151 single fiber friction instrument based on the capstan method. The coefficients of static and kinetic friction (a fiber over a metal rod) were calculated [22]. The strawberry juice was used as the stain to assess the self-cleaning ability of cotton fibers exposed to UV radiation. About 0.3 g of cotton fibers was pulled into a flat sliver by hands, and then fixed on the polyurethane foaming plate with pins. A half milliliter of strawberry juice (mass concentration 100%) was applied onto cotton fibers. After 5 min of absorption, the fiber sample was irradiated by a 30 W Philips UV ray lamp (wavelength 254 nm) at a distance of 15 cm. The optical graphs were viewed at given intervals (1 h) of irradiation.

## **RESULTS AND DISCUSSION**

### **SEM Observation**

The SEM images of original and modified cotton fibers are shown in *Figure 1*. It can be clearly observed that the surfaces of the original cotton fibers are relatively smooth and clean with many tiny striations [*Figure 1(a)*]. After treatment with titanium sulfate, urea and CTAB, the surfaces of the modified cotton fibers were coated with a film of granular substances and dispersed with some agglomerated particles [*Figure 1(b)*]. From the high-resolution SEM image of modified fiber, the coating is made up of fine grains. The primary particle size is estimated to be less than 50 nm [*Figure 1(c)*].

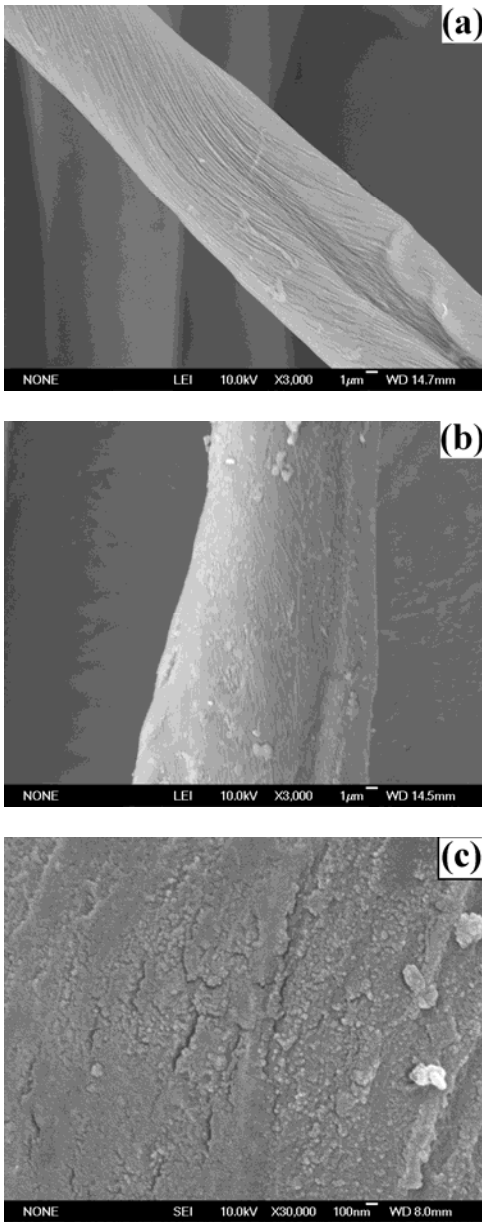


FIGURE 1. SEM images of the original (a) 3000 $\times$  and modified (b) 3000 $\times$  and (c) 30000 $\times$  cotton fibers.

### TEM Analysis

The TEM and HRTEM images and electron diffraction pattern of the synthesized particles are shown in *Figure 2*. It can be seen that the as-prepared nanoparticles have the hexagonal morphology. The particle sizes are in the low-nanometer range (less than 10 nm) [*Figure 2(a)*]. The interplanar crystal spacing (0.346 nm) is determined by the crystalline structure of nanoparticles, which is very close to the d-spacing 0.35 nm of (101) plane of TiO<sub>2</sub> [*Figure 2(b)*]. The electron diffraction pattern shows the planes (101), (004), (200), (105), (211) and (204) indexed to the anatase crystalline phase of TiO<sub>2</sub> [*Figure 2(c)*] [23].

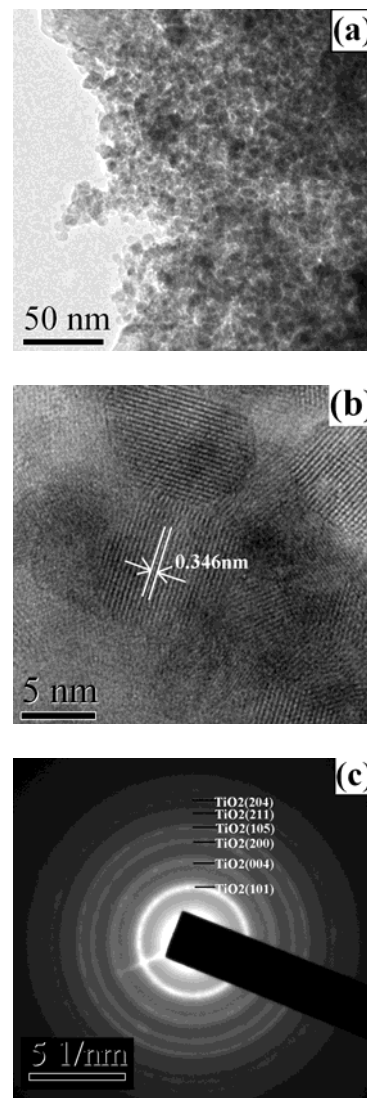


FIGURE 2. TEM (a) and HRTEM (b) images and electron diffraction pattern (c) of TiO<sub>2</sub> nanoparticles.

### FTIR Analysis

The FTIR spectra of the original and modified cotton fibers and TiO<sub>2</sub> nanoparticles are shown in *Figure 3*. Compared with the original cotton fibers, the peaks at 3436 cm<sup>-1</sup> (O–H stretching) and 2919 cm<sup>-1</sup> (CH<sub>2</sub> asymmetrical stretching) for the modified fiber are intensified to some extent, but the peak at 2859 cm<sup>-1</sup> (CH<sub>2</sub> symmetrical stretching) is weakened. That is due to the absorbed water or surface hydroxyl groups. The peaks at 1450 cm<sup>-1</sup> (CH<sub>2</sub> bending) and 1379 cm<sup>-1</sup> (CH bending) are shifted to 1432 cm<sup>-1</sup> and 1375 cm<sup>-1</sup>, respectively. The peaks at 1163 cm<sup>-1</sup> (C–O–C stretching at β–glucosidic linkage) and 1056 cm<sup>-1</sup> (C–O stretching at C–3 and C–C) are shifted to 1166 cm<sup>-1</sup> and 1061 cm<sup>-1</sup>, respectively [24]. At the same time, the peak at 668 cm<sup>-1</sup> (C–OH out of plane bending) is intensified and the peak at 603 cm<sup>-1</sup> (C–H bending) is shifted to 617 cm<sup>-1</sup>. The peak at 569 cm<sup>-1</sup> should be assigned to the O–Ti stretching band with respect to the spectrum of TiO<sub>2</sub> (586 cm<sup>-1</sup>). This is attributed to the formation of O–Ti covalent bonds between TiO<sub>2</sub> and cotton fibers. Thus, it may be deduced that TiO<sub>2</sub> nanoparticles react with cotton fibers [11]. The possible reaction mechanism is illustrated in *Scheme 1*. Moreover, the crystallinity index was reduced from 68.8% to 54.7% when cotton fibers were treated with titanium sulfate, urea and CTAB under hydrothermal conditions. This is due to the fact that the chemicals and hot water penetrated into the crystalline regions of cellulose fiber to some extent. So the crystalline to amorphous transition occurs.

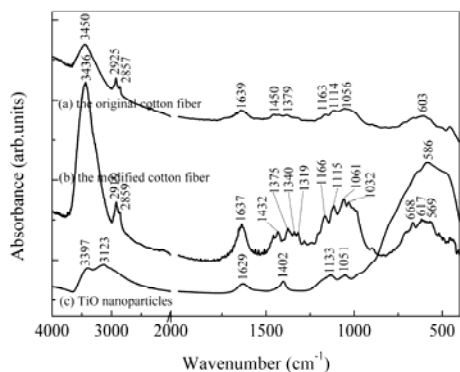
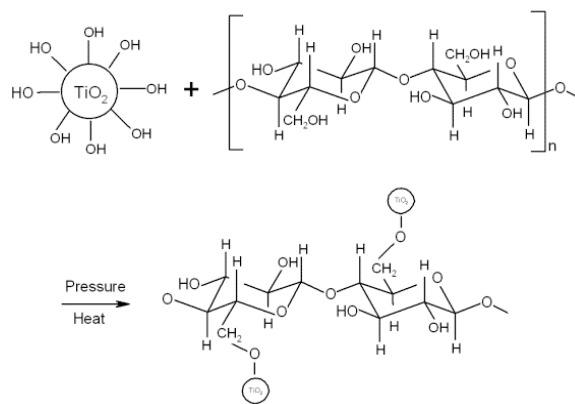


FIGURE 3. FTIR spectra of the original (a) and modified (b) cotton fibers and TiO<sub>2</sub> (c) nanoparticles.



SCHEME 1. Possible reaction route of TiO<sub>2</sub>-coated cotton fibers.

### XPS Analysis

The broad scan XPS survey spectra, O<sub>1s</sub> and Ti<sub>2p</sub> XPS narrow scan spectra of cotton fibers before and after treatments are shown in *Figure 4*. From the survey scan in *Figure 4(a)*, it is obvious that the element of titanium at binding energy of 458.49 eV is found in the modified cotton fibers. The O/C atomic ratio for the original cotton fibers is 34.85:65.15. After treatment, the atomic concentrations for the elements O, C and Ti are 40.31%, 57.08% and 2.61%, respectively. In *Figure 4(b)* and (c) for the corresponding O<sub>1s</sub> spectra, the O<sub>1s</sub> spectrum for the original cotton fibers is fitted by decomposition into three Gaussian peaks. The peaks at 527.01 eV, 530.11 eV and 532.51 eV represent the O–H, C–O–C and O–C groups, respectively [25]. After treatment, the peaks representing H<sub>2</sub>O, O–Ti<sup>4+</sup> (TiO<sub>2</sub>) and O–Ti<sup>3+</sup>/O–H groups appear, indicating that TiO<sub>2</sub> nanosol reacts with cotton fibers. In *Figure 4(d)*, the peaks at binding energies of 457.82 eV and 463.53 eV are attributed to Ti<sup>4+</sup><sub>2p3/2</sub> and Ti<sup>4+</sup><sub>2p1/2</sub> (TiO<sub>2</sub>), respectively. The peaks at 459.58 eV and 465.01 eV are assigned to O–Ti<sup>3+</sup><sub>2p3/2</sub> and O–Ti<sup>3+</sup><sub>2p1/2</sub>, respectively [26,27]. This implies that the titanium atoms of TiO<sub>2</sub> are bound to oxygen atoms of cotton fibers. Therefore, it can be concluded that TiO<sub>2</sub> nanoparticles are not only loaded on fiber surface, but also grafted onto cotton fibers through the O–Ti<sup>3+</sup> band.

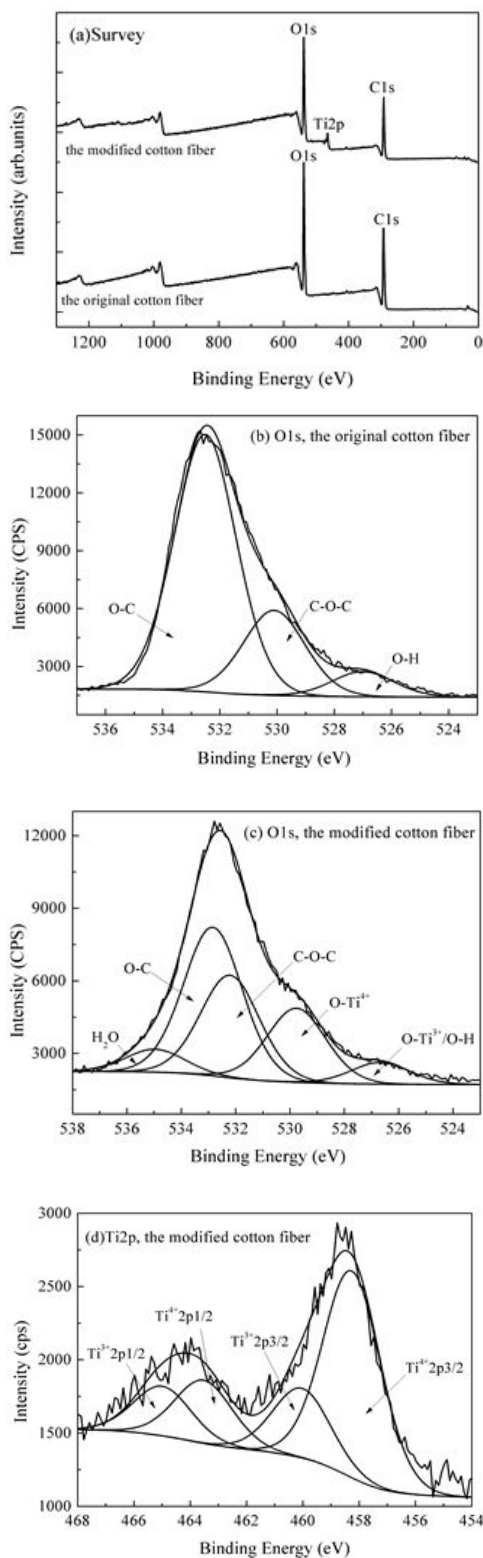


FIGURE 4. XPS survey spectra of cotton fibers (a); XPS O<sub>1s</sub> spectra of the original (b) and modified (c) cotton fibers; XPS Ti<sub>2p</sub> (d) spectra of modified cotton fibers.

### TG Analysis

The TG/DTA profiles of cotton fibers before and after treatments are shown in Figure 5. The thermal decomposition processes have only one period for both samples. The weight loss for the original cotton fibers is 81.4% in the temperature range between 298.2°C and 391.8°C, which should be attributed to the decomposition of cellulose component. But for the modified cotton fibers, the weight loss from 302.5°C to 380.8°C increases to 83.8%, which is due to the introduction of TiO<sub>2</sub> coating. The onset and endset decomposition temperatures are reduced from 330.6°C to 329.6°C and from 364.2°C to 356.8°C, respectively. The corresponding endothermic peak decreases from 347.7°C to 342.6°C. So the hydrothermal processing in the presence of titanium sulfate, urea and CTAB has a little effect on the thermal properties of cotton fibers.

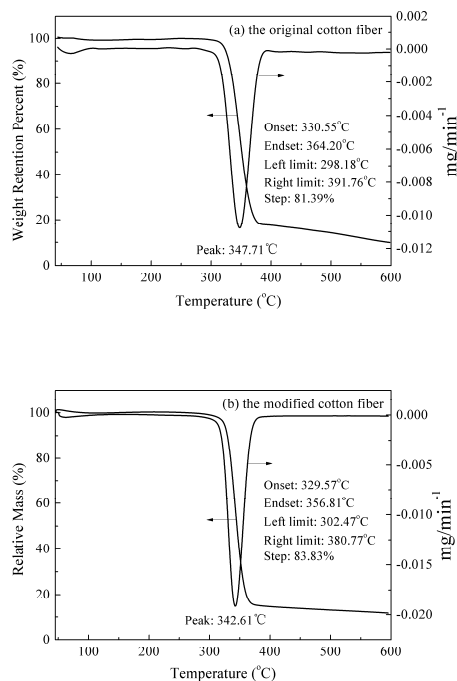


FIGURE 5. TG and DTA curves of cotton fibers before (a) and after (b) treatments.

### DRS Analysis

The diffuse reflectance spectra of the original and modified cotton fibers are shown in Figure 6. It is evident that the original cotton fibers cannot block the irradiated UV rays. After treatment, there is a significant decrease in the reflectance at UV wavebands. The mean reflectance percentage of modified cotton fibers in the 200–400 nm range increases by 21.0% compared with the original one.

This is ascribed to the evenly distributed TiO<sub>2</sub> coating. The reflectance for both samples is almost overlapped in the 400–800 range, implying that the thin film of TiO<sub>2</sub> has little absorption to the visible light.

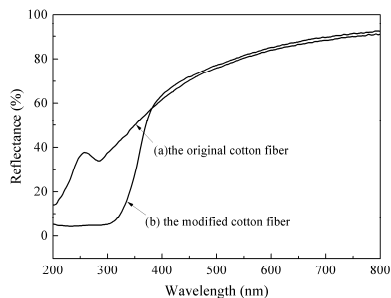


FIGURE 6. UV-vis reflectance spectra of the original (a) and modified (b) cotton fibers.

### **Tensile Property Analysis**

The tensile properties of cotton fibers revealed that when cotton fibers was treated with titanium sulfate, urea and CTAB in the high pressure hot-water system for long time, the breaking strength decreased from 3.26 cN/dtex to 2.35 cN/dtex. The corresponding elongation at break was reduced from 11.8% to 10.0%. This is due to the degradation of cotton fibers as a result of the change of crystalline structure of cellulose.

### **Friction Property Analysis**

The friction testing results of cotton fibers indicated that the coefficient of static friction increased from 0.38 to 0.62 distinctly, while the coefficient of kinetic friction increased from 0.27 to 0.30 slightly. The TiO<sub>2</sub> nanoparticles adhered on cotton fibers obviously resulted in the rough point contact between the mating surfaces.

### **Self-cleaning Property Analysis**

The self-cleaning abilities of cotton fibers before and after treatments are assessed by the degradation of strawberry juice. The optical graphs of stained fiber sample exposed to UV light at different time are shown in *Figure 7*. The color of stains on the original cotton fibers has almost no change even though it is radiated by UV ray for three hours. As the irradiation time increases, strawberry juice stains on the modified cotton fibers are gradually discolored. The color is totally disappeared after three hours

irradiation. The results clearly indicate that the TiO<sub>2</sub> coating on cotton fibers discolor the strawberry juice. The amount of CO<sub>2</sub> generated from the organic stains increased with exposure time to UV daylight.

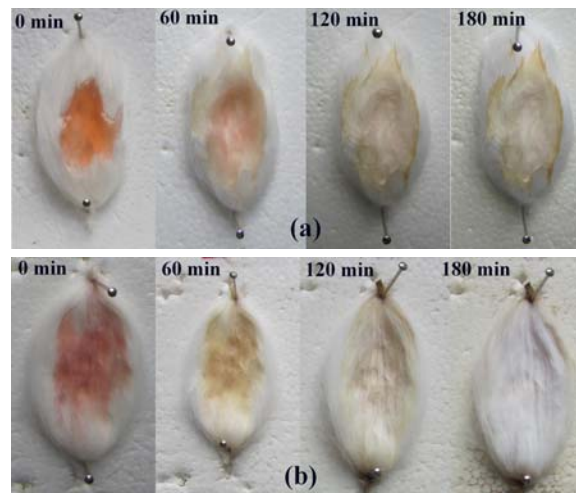


FIGURE 7. The optical graphs of cotton fibers before (a) and after (b) treatments stained with strawberry juice irradiated by UV light at different time.

### **CONCLUSIONS**

In this study, TiO<sub>2</sub> nanoparticles were first prepared by a facile low temperature hydrothermal method, and then coated on the surface of cotton fibers by using titanium sulfate and urea as the precursors and CTAB as the dispersing agent. SEM and TEM results show that pure anatase phase TiO<sub>2</sub> nanoparticles are synthesized. The crystal size is about 10 nm. FTIR and XPS results show that nanocrystalline TiO<sub>2</sub> is grafted onto cotton fibers by the O-Ti<sup>3+</sup> group. TG and DRS results show that the thermal stability of TiO<sub>2</sub> coated fiber changes a little. The protection against UV illumination is gained. The performances of tensile, friction and self-cleaning show that the tensile strength and elongation at break of the modified fiber decrease compared with the original one. The coefficients of static and kinetic friction increase. The self-cleaning property to degrade strawberry juice is obtained.

### **ACKNOWLEDGEMENT**

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