# Room-Temperature Synthesis of Single-Phase Anatase $TiO_2$ by Aging and its Self-Cleaning Properties

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ARTICLE

**ABSTRACT** A facile process to synthesize single-phase anatase titanium dioxide nanocrystallites at room temperature was presented. The process included a sol–gel reaction in an aqueous media followed by aging at room temperature. The anatase $TiO_2$ was characterized using XRD, TEM and SEM. The cotton fabrics-coated by the anatase nanocrystallites possessed significant photocatalytic self-cleaning properties as demonstrated by their ability to decompose a colorant and degrade red wine and coffee stains, which was equivalent to that of prepared by heating or hydrothermal methods described previously. The anatase $TiO_2$-coated cotton substrate also showed a high UPF rating of 50+, which means excellent UV protection to human wearers. The study of the adhesion between the anatase $TiO_2$ and the cotton substrate showed that even after 20 times of repeated launderings, the-coated substrate was still capable of decomposing stains, which indicated its photocatalytic power, though this was reduced compared to that before laundering. The tensile strength results of the anatase $TiO_2$-coated cotton fabrics indicate that the anatase $TiO_2$ will not damage the cotton substrate even after 20 h of continuous UV irradiation. The method of preparing single-phase anatase $TiO_2$ revealed in this study not only eliminates the need for high temperature processing, which means energy saving, but also broadens its applications to poor acid-resistant and low thermal stability materials such as many of the biomaterials and cellulosic materials.

**KEYWORDS:** anatase titanium dioxide • aging • photocatalytic • self-cleaning • textiles

## 1. INTRODUCTION

In sol–gel processes, titania is usually prepared by the hydrolysis and condensation reactions of titanium alkoxides. It is well-known that titanium alkoxides hydrolyze vigorously in water, and many catalysts, typically various simple acids, for example, nitric acid (1), hydrochloric acid (2), and acetic acid (3), have been applied to control the reaction rates. Much work has been reported for the preparation of anatase coatings on low thermal resistant materials using sol–gel process at relatively low temperatures (4–10). However, most of the preparation methods use organic solvents, corrosive chemicals such as nitric acid and hydrochloric acid, and relatively high temperatures to obtain the anatase coatings, which are not desirable in scale up production. Moreover, some products in these studies are composed of both anatase and brookite, not pure anatase. Although some works use aqueous based sol–gel techniques, which are more environmentally friendly than those of using organic solvent, the destructive effect of strong acids used in sol–gel process for keeping aqueous sols in the peptized state prevent their applications to materials that have poor acid-resistance, such as cellulosic fibers. As for the preparation temperature of photocatalytic anatase coatings, low temperature, especially room temperature, is advantageous not only for energy saving, but also extending their applications to low thermally resistant materials such as biomaterials.

Aging of a sol is a process in which physical properties of the sol will be changed as the result of the following mechanisms: polymerization, coarsening and phase transformation (11). Various studies have shown that the amorphous $TiO_2$ sols crystallized into anatase through an aging process in boiling water, in HCl solution at 60 °C (12, 13) and in boiling $NH_4OH$ solution (14, 15). These studies mainly focused on the effects of aging on crystallization, specific surface area, crystallite size, phase transformation, and growth kinetics of $TiO_2$ nanocrystallites. Wu et al. (16) synthesized single-crystalline anatase $TiO_2$ nanowires using a room-temperature method involving the use of seed particles and a radio frequency magnetron sputter deposition technique. Hu et al. (17) prepared anatase $TiO_2$ sol by a sol–gel process at a low temperature of 65 °C. However, the photocatalytic activity of the anatase $TiO_2$ was not reported In fact, few studies in the past reported the formation of anatase nanocrystallites through aging at room temperature and atmospheric pressure. Recently, we investigated the coating of cotton and polyester with single-phase anatase $TiO_2$ sols and their photocatalytic self-cleaning effects (18–21). These sols were synthesized using an aqueous sol–gel process at a low temperature. The mechanical strength of $TiO_2$-coated cotton fabrics was reduced compared to that of the uncoated ones, which indicated the acid damage of the cotton fabrics by acidic sol, in which nitric acid was used.

In this study, anatase $TiO_2$ sols were fabricated by hydrolysis and condensation of titanium tetraisopropoxide in

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an aqueous medium with the use of acetic acid as a catalyst, followed by an aging process at room temperature (23 °C). With the use of milder acetic acid, the as-prepared anatase $TiO_2$ can be applied to materials with poor acid-resistance and low thermal stability, such as cotton fiber.. This study was also attempted to reveal the influence of aging on crystallization of anatase and its photocatalytic self-cleaning activities when-coated to cotton substrates. To characterize the self-cleaning activities, the decomposition of the colorant Neolan Blue 2G in a model photocatalytic reaction and the discoloration of red wine and coffee stains were studied

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Titanium tetraisopropoxide (98%) and acetic acid (99.8%) were purchased from Aldrich. All of the chemicals were reagent grade. The colorant Neolan Blue 2G was supplied by Ciba and was used as-received. Desized and scoured white twill woven cotton fabrics were used. The cotton fabrics were further washed by nonionic detergent at 80 °C for 30 min to remove any pretreatment chemicals on the fabrics. Deionized water was used throughout the study.

**2.2. Preparation of $TiO_2$ Sol by Aging at Room Temperature.** Five milliliters titanium tetraisopropoxide (Aldrich, 98%) was added dropwise into 100 mL of deionized water containing 10 mL of acetic acid (Aldrich, 99.8%) under vigorous stirring at room temperature (23 °C). The mixture was then vigorously stirred at room temperature for 24 h. The as-prepared sample is named as A23. Freshly prepared A23 was stored without stirring at room temperature and atmospheric pressure. It became transparent within one week. This aged sample is named as TA23. The freshly prepared A23 and TA23 were used for preparation of $TiO_2$ powders. Only TA23 was used for preparation of $TiO_2$ coatings since precipitation occurs in the freshly prepared sol A23.

**2.3. Preparation of $TiO_2$ Coatings and $TiO_2$ Powders.** TA23 was used to prepare $TiO_2$ thin coatings on white woven cotton fabrics by a dip-pad-dry-cure process. Cotton fabrics were first dipped in TA23 $TiO_2$ sol for one minute and padded with an automatic padder (Rapid Labortex Co. Ltd., Taipei, Taiwan) with a fixed nip pressure to standardize the amount of $TiO_2$ on each of the cotton fabric (Wet pick-up is about 70%). The fabrics were then dried at 80 °C for 5 min in a preheated oven (Memmert ULE800 Universal Oven, Memmert, Schwabach, Germany) and finally cured at 120 °C for 3 min in a preheated curing machine (Mathis Labdryer Labor-Trockner Type LTE, Werner Mathis AG Co., Switzerland).

A23 and TA23 $TiO_2$ powders were extracted from the corresponding sols by adding adequate amounts of 0.3% sodium carbonate aqueous solution until precipitation occurred. The formed suspensions were centrifuged at 4000 rpm for 5 min using Boeco C-28 Centrifuge (Model BOE 1205−13, Boeckel & Co, Hamburg, Germany), followed by removal of the liquid phase. The precipitates were then washed three times with water and finally with acetone twice before being air-dried at room temperature overnight.

**2.4. Characterization of $TiO_2$ Nanoparticles.** The structure and morphology of the $TiO_2$ coatings on the cotton substrate were investigated using field-emission scanning electron microscopy (FESEM, JSM-6335F at 3.0 kV, JEOL, Tokyo, Japan). The crystal phases of the titania powder extracted from the sol were studied by X-ray diffraction (XRD, Bruker D8 Discover X-ray diffractometer) operating at 40 kV and 40 mA. The crystal phases of formed the titania coatings on cotton substrates were studied by low angle X-ray diffraction (XRD, Philips Xpert XRD system) at 3° of incident beam using Cu Kα radiation and detector scan mode operating at 40 kV and spectroscopy 30 mA. The lattice spaces were determined by a high-resolution transmission electron microscopy (HRTEM, JEOL JEM 2010 operated at 200 kV).

**2.5. Assessment of UV-Protection of $TiO_2$ coatings.** The ability of absorbing UV radiation is a special feature to titania coating, which can effectively protect the wearer of the clothes made with such-coated fabric. The ability to protect human skin from UV radiation is measured by UV protection factor (UPF) defined according to the Australian/New Zealand Standard AS/NZS 4399:1996 using a Varian Cary 300 UV spectrophotometer.

**2.6. Assessment of Photocatalytic Activities of the $TiO_2$ coatings.** The photocatalytic activities of the $TiO_2$ coatings on the white cotton substrate were assessed by analyzing the decomposition of Neolan Blue 2G under UV irradiation. In this experiment, a total of 5 g of fabrics were cut into 1 cm ×1 cm pieces. These pieces were placed in three 250 mL beakers containing 75 mL aqueous solution of Neolan Blue 2G (0.2 g $L^{-1}$). Then the beakers were exposed to UV radiation produced by Philip UV lamps ((365 nm, Philips TLD 18W/08) while under vigorous shaking (using an IKA KS260 Basic Orbital Shaker). The light intensity on the top of beakers was 1.1−1.3 mW $cm^{-2}$. Prior to UV irradiation, the colorant solution containing cotton pieces was kept in dark condition for 2 h under shaking to establish the fabric absorption−desorption equilibrium. After a predetermined duration, the colorant solution was taken out and centrifuged to precipitate cotton fibers at the bottom of the tube and the upper clear colorant solution was used for the determination of the change in concentrations before and after UV irradiation calculated from the change of the absorptions measured by a UV−vis spectrometer (Perkin-Elmer UV−vis spectrometer Lambda 18). The absorption measurement was performed at 630 nm, which is the maximum absorption wavelength for Neolan Blue 2G. For comparison, the same test was also performed using pure white cotton substrates. The assessment of photocatalytic activities of-coated cotton fabrics was repeated three times and the results were quite consistent with an error margin of ±5%. The average results were reported.

**2.7. Assessment of Degradation of Red Wine and Coffee Stains.** The photocatalytic degradation of red wine stains (Carlo Rossi California Red, 11.5% alc/vol) and coffee stains (Nestle, 1.8 g 100% pure soluble coffee powder/150 mL hot water) were evaluated. Pure white cotton fabrics and the $TiO_2$-coated white cotton fabrics were cut into 4.5 cm ×6.5 cm. One drop of red wine or coffee was applied onto the cotton fabric using 10 mL medical syringe with pinhead close to the fabric surface when dropping. Then these stained samples were exposed to light irradiation for 8 and 20 h. The irradiation of all samples were carried out in a Xenotest Alpha LM light exposure and weathering test instrument (air cooled xenon arc lamp, irradiance 4.5 mW $cm^{-2}$ at 300−400 nm Wavelength, Xenotest Alpha LM, Heraeus Industrietechnik, Hanau, Germany). The staining grades of red wine and coffee stains on cotton substrates were evaluated according to AATCC Test Method 130−2000 using stain release replica.

**2.8. Durability of the $TiO_2$ Coatings on Cotton Substrates.** Laundering of the $TiO_2$-coated cotton fabrics was carried out following AATCC Test Method 61−2003 Test No. 2A at 49 ± 2 °C using AATCC Standard Instrument Atlas Launder-Ometer LEF. The laundering was carried out at 49 ± 2 °C for 1.5 h which was equivalent to 10 times of repeated home laundering. The durability of $TiO_2$ coatings on cotton fabrics was evaluated by comparing the decomposition activity of the-coated cotton fabrics to Neolan Blue 2G, before and after 10 and 20 launderings.

**2.9. Tensile Strength of the $TiO_2$-Coated Cotton Substrates.** The tensile strength of pure cotton fabrics and the $TiO_2$-coated cotton fabrics before and after 10 h, 20 h of light irradiation was measured by a Tensile Strength Tester Instron 4411 (Instron Co., U.K.) with Instron Series IX Software in

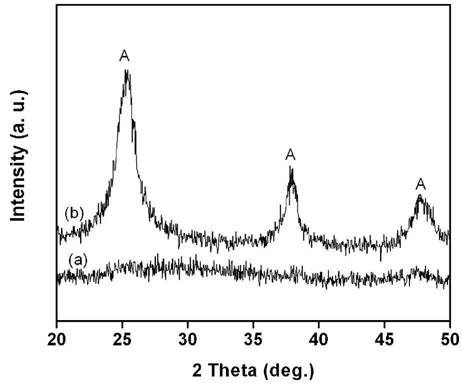


FIGURE 1. XRD patterns of powders extracted from (a) freshly prepared A23 and (b) the aged sample TA23 (A = anatase).

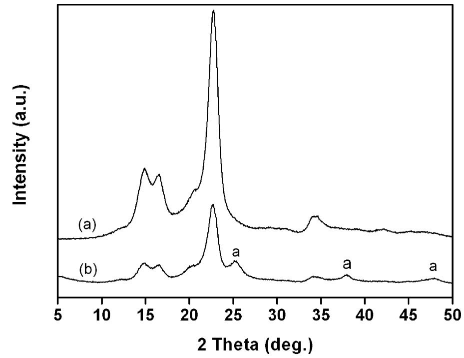


FIGURE 2. XRD patterns of (a) a pure cotton fabric and (b) aged titania sample TA23-coated the cotton substrate fabric (a = anatase).

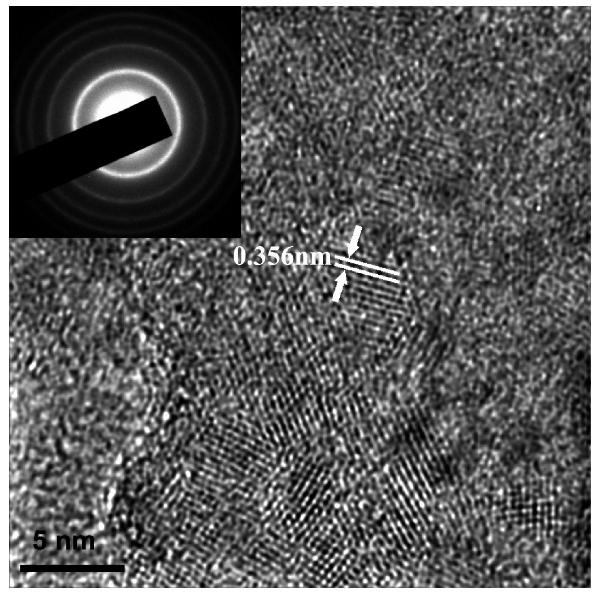


FIGURE 3. High-resolution TEM image of TA23. Inset located on the top left corner is the corresponding selected area electron diffraction (SAED).

accordance with ASTM D 5034-95. Three samples were prepared in the warp direction. The irradiation of all samples was carried out in Xenotest Alpha LM light exposure and weathering test instrument with details given previously. The average of five repeated tests was reported as the average ± standard deviation in the following results and discussion section.

## 3. RESULTS AND DISCUSSION

**3.1. XRD Patterns.** The crystal phases of titania particles and titania coatings on cotton substrates were studied by XRD. Figure 1 shows the XRD patterns of titania powders obtained from freshly prepared A23 and aged transparent TA23. Freshly prepared A23 was a suspension of precipitated titania particles. However, it became a transparent sol with slightly bluish tint after it was stored at room temperature and atmospheric pressure for one week. It was stable without any precipitation for more than half a year. Freshly prepared A23 was amorphous phase as shown in Figure 1(a). However, after aging, A23 amorphous sol was transformed into single-phase anatase sol as shown in Figure 1(b) with the anatase peaks observed at 25.4°, 38.0° and 48.0° respectively. While the presence of brookite can be detected by XRD at 27.7°, 31.1°, etc. (22) and the presence of rutile can be detected by XRD at 27.5°, 36.0°, etc. (23), no traces of brookite or rutile could be found after careful examination of XRD pattern of aged TA23 sample in Figure 1.

Conventionally, amorphous-anatase transformation can be done in the temperature range from 250 to 400 °C (24). Yanagisawa and Ovenstone (25) studied the crystallization of anatase from amorphous titania using hydrothermal technique and realized the transformation from amorphous to anatase at temperatures between 120 and 250 °C. It was also reported that amorphous titania sols obtained at pH between 2.7 and 5.0 were transformed to titania consisting of anatase and brookite at 40 °C for several days (26). In another study by Ding and He (27), amorphous titania was converted into anatase and rutile titania after aging at room temperature for one year. Bischoff and Anderson (28) investigated the peptization process in the sol−gel preparation of titania and reported that an acidified (nitric or hydrochloric acid) sol peptized at room temperature leads to the formation of a mixture of anatase and rutile; the acidified sol under refluxing at elevated temperatures led to a mixture of anatase and brookite. In this study, amorphous titania in aqueous solution was transformed into pure anatase after aging at room temperature (23 °C) for only one week. Moreover, sharper anatase peaks with greater intensities for TA23 are observed indicating that better crystallization of anatase occurred in TA23. The single-phase anatase of TA23 obtained by aging at room temperature is similar to that of S60 $TiO_2$ sol obtained by heating at 60 °C reported previously (18).

Figure 2 presents the XRD patterns of a pure cotton fabric and the aged titania TA23-coated cotton fabric. In the profiles, the strong diffraction peaks at 14.9°, 16.6°, 22.8° and 34.7° are originated from the cotton substrate. Weak peaks at 25.4°, 38.0° and 48.0° are observed in Figure 2b, which match well with those observed anatase peaks in Figure 1. This finding further confirmed that nanocrystalline anatase was formed in TA23 with the aging process.

**3.2. TEM Analysis.** Figure 3 shows the existence of small nanocrystallites with lattice fringes of 0.356 nm, which are characteristic values of the anatase phase. The inset, located on the top left corner of the images, shows the corresponding selected area electron diffraction (SAED).

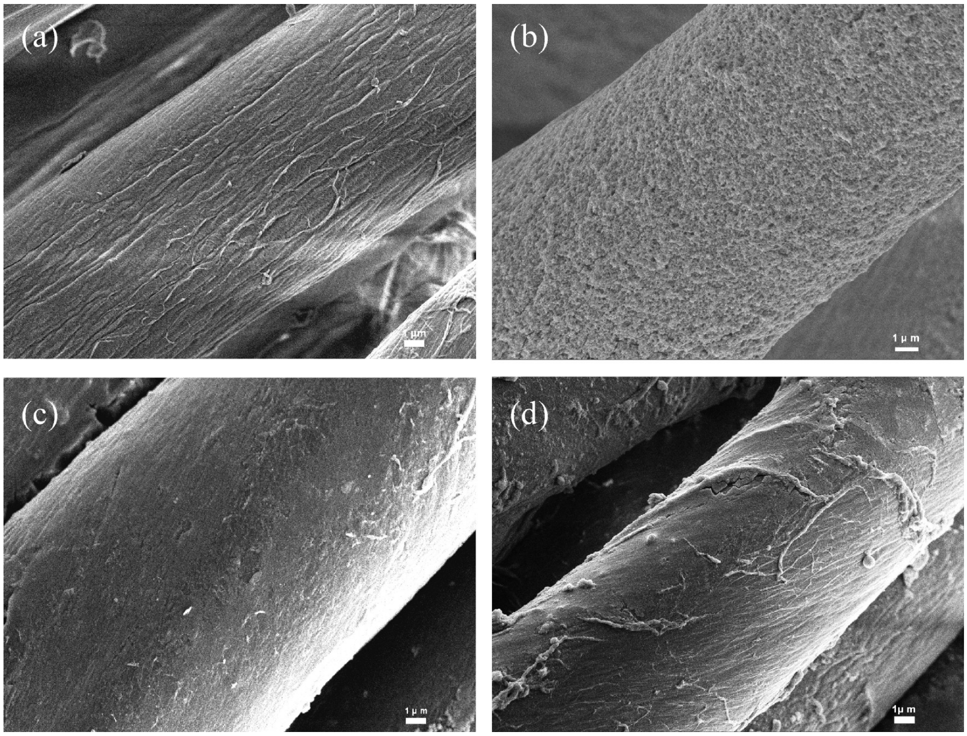


**FIGURE 4. SEM images of (a) pure cotton fibers, (b) TA23-coated cotton fibers, (c) TA23-coated cotton fibers after 10 launderings, and (d) TA23-coated cotton fibers after 20 launderings.**

Measurement of lattice spacing from the corresponding SAED pattern indicates that the nanocrystals of TA23 were anatase. From Figure 3, it can also be seen that the average crystal size of TA23 was 5−7 nm. Sharp and intense Deby−Scherrer rings were observed in Figure 3. Extra effort was devoted to find any traces of brookite or rutile phase. However nothing could be found. With the average crystal size of 5−7 nm, anatase phase of TA23 is similar to that of S60 $TiO_2$ reported previously (18).

**3.3. SEM Observations.** Figure 4 shows the representative SEM micrographs of $TiO_2$-coated cotton fibers. Compared to the SEM image of pure cotton fibers (Figure 4a), SEM observation of TA23-coated cotton fibers (Figure 4b) revealed that $TiO_2$ layers have been formed on cotton fibers. After 10 and 20 launderings, the titania coatings were still observed on cotton fibers as shown in Figure 4c and Figure 4d. However, the titania layer was leached out to certain degree after 20 launderings.

**3.4. UV Protection.** The UV-absorption property of the cotton fabrics can directly evaluated by Ultraviolet Protection Factor (UPF). Strengthened UV absorption is beneficial for UV blocking (29). UV absorption study of TA23-coated white cotton fabrics before laundering showed a high UPF value of 357.6 and thus a high UPF rating of 50+ according to the Australian/New Zealand Standard, started from a low UPF value of 6.1 which was rated as nonratable of the pure cotton fabric. After 20 launderings, UPF value of TA23-coated cotton fabrics was 281.0, which was lower than that before laundering but still much higher than that of the pure cotton fabric. The high UPF values of the-coated fabric after 20 launderings belong to an excellent protection classification.

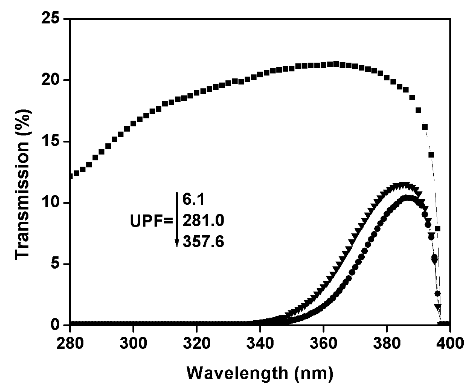


**FIGURE 5. UV absorption of pure cotton fabric (■), TA23-coated cotton fabric (●), and TA23-coated cotton fabric after 20 launderings (▼).**

**Scheme 1. Structure of Neolan Blue 2G**

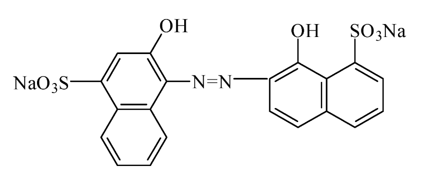


Figure 5 also shows that UV transmissions of TA23-coated white cotton fabrics can completely cut off the UV−B radiation (280−315 nm) before and after repeated launderings. In the UV-A spectral region (315−400 nm), UV transmissions of these-coated cotton fabrics were relatively higher yet still much lower than that of the pure cotton fabric. Stronger UV-absorption indicates higher the photocatalytic activity. From the UV-absorption results, it is certain that TA23 coatings on cotton fabrics should have good photocatalytic activity.

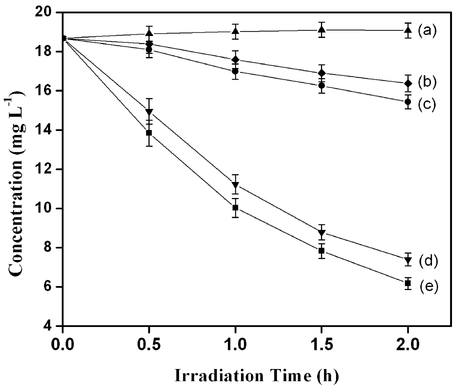


**FIGURE 6. Variations in concentration of Neolan Blue 2G in an aqueous solution as a function of UV irradiation time for (a) pure cotton, (b) TA23-coated cotton after 20 laundering, (c) TA23-coated cotton after 10 laundering, (d) TA23-coated cotton before laundering, and (e) S60 $TiO_2$-coated cotton substrates.**

**3.5. Colorant Decomposition Activities.** Self-cleaning property of TA23-coated cotton substrates was evaluated by the decomposition of the colorant, Neolan Blue 2G, in an aqueous solution under UV irradiation. For comparison, S60 anatase $TiO_2$-coated cotton fabrics, which was reported by us previously (18), were also used. The durability of TA23 coating on the cotton substrate was investigated by comparing the colorant decomposition activities of TA23-coated cotton fabrics before and after 10 and 20 launderings according AATCC Test Method Test No. 2A at 49 ± 2 °C. The chemical formula of Neolan Blue 2G is shown in Scheme 1.

Figure 6 shows the photocatalytic activities of TA23-coated cotton fabrics before and after 10 and 20 launderings and S60 $TiO_2$-coated cotton fabrics. It can be seen from Figure 6d that the colorant concentration under UV irradiation was reduced dramatically by TA23-coated cotton fabrics before laundering, which suggests that TA23 has high colorant decomposition activity or high photocatalytic power. This is considered to be attributed to single-phase anatase with high crystallinity and small crystal size 5−7 nm of TA23 as shown by XRD and TEM results. It is well-known that the photocatalytic activity of titania coatings is strongly influenced by several factors such as the crystallinity of the anatase phase (30, 31), particle size (32, 33), and surface area (34). While TA23 is single-phase anatase $TiO_2$ which is considered to be the most active photocatalyst, its high crystallinity is also beneficial for enhancing the photocatalytic activity, as anatase $TiO_2$ with high crystallinity has relatively little disruption in its electronic band structure and high crystallinity diminishes the $e^-$−$h^+$ recombination (25). Furthermore, TA23 has small particle size of 5−7 nm. Particle size is important for photocatalysis since it directly impacts the specific surface area of a photocatalyst. As the photocatalytic reaction occurs at the $TiO_2$ surface, the large contact area between the $TiO_2$ surface and the target material surface facilitates effective photocatalytic activity. With a smaller particle size, surface area increases and photonic efficiency will be enhanced through a higher surface charge carrier transfer rate in photocatalysis (32). Therefore, TA23 anatase $TiO_2$ with high crystallinity and smaller particle size 5−7 nm possesses high photocatalytic activity. Figure 6 also shows that the reduction in colorant concentrations are similar for both TA23 (Figure 6d) and S60 $TiO_2$-coated cotton fabrics (Figure 6e) though the latter shows slightly more reduction. These results suggest that the titania synthesized by aging can achieve similar photocatalytic activity comparing to that synthesized by the heating method described previously (18).

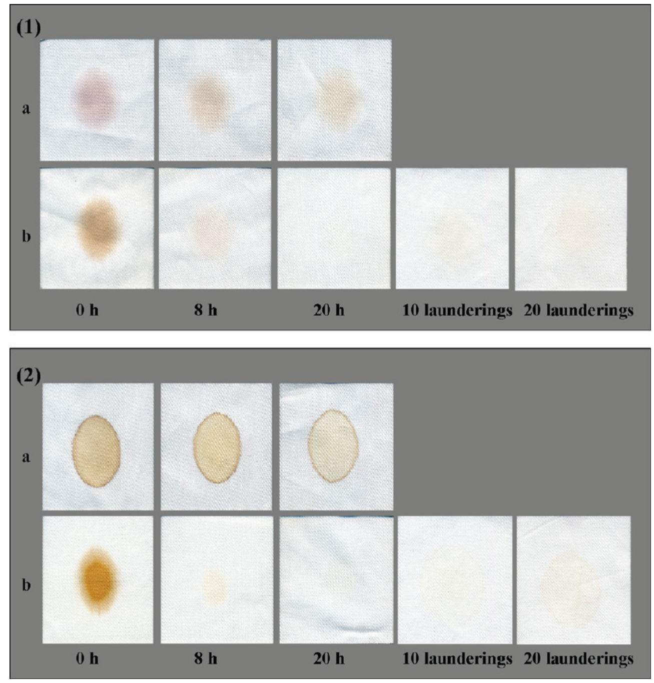


**FIGURE 7. Stain decomposition test using (1) a red wine stain and (2) a coffee stain. The images shown in (1) and (2) are the exposed side of (a) pure cotton fabrics and (b) TA23-coated white cotton fabrics before laundering subjected to 0 h, 8 and 20 h of light irradiation, and the TA23-coated cotton fabrics after 10, 20 launderings subjected to 20 h of light irradiation.**

When $TiO_2$ is subject to irradiation with UV light, the photon energy generates electron−hole pairs on the $TiO_2$ surface. The generated electron−hole pairs can induce the formation of reactive oxygen species, such as OH• and $O_2^{-}$•. The reactive oxygen species generated on TA23 surface decomposed the colorant under UV irradiation by participating in a series of oxidation reactions resulting in carbon dioxide. The molecule of Neolan Blue 2G contains one azo bond (−N═N−), which is more reactive and can be oxidized by positive hole, hydroxyl radical, or reduced by electron, superoxide ion (35). The discoloration of Neolan Blue 2G indicates that the chromophoric azo bond attached to the naphthalene ring was destroyed.

The durability of $TiO_2$ coatings on cotton substrates was investigated by comparing the colorant decomposition activities of $TiO_2$-coated cotton fabrics before and after 10 and 20 launderings according to AATCC Test Method 61-2003 Test No. 2A at 49 ± 2 °C, shown in Figure 6. Although the rates of colorant decomposition of TA23-coated samples were decreased after 10 launderings (Figure 6c) and after 20 launderings (Figure 6b) compared to that before laundering, they still possess some significant photocatalytic power compared to that of pure cotton substrates. Moreover, the

Table 1. Staining Grades of Red Wine and Coffee Stains

| | staining grades | | | |
|---|---|---|---|---|
| | red wine | | coffee | |
| irradiation time | pure cotton fabric | TA23-coated cotton fabric | pure cotton fabric | TA23-coated cotton fabric |
| 0 h | 1 | 1 | 1 | 1 |
| 8 h | 1 | 4 | 1 | 4 |
| 20 h | 1.5 | 5 | 1 | 5 |
| 20 h after 10 launderings | | 4.5 | | 4.5 |
| 20 h after 20 launderings | | 3.5 | | 3.5 |

Table 2. Tensile Strength Study in Warp Direction

| | tensile Strength (N) ± standard deviation (N) | | |
|---|---|---|---|
| samples | before light irradiation | after 20 h of light irradiation | reduction (%) |
| pure cotton | 652.90 ± 11.71 | 623.50 ± 5.8 | 4.50 |
| TA23-coated cotton | 648.00 ± 9.24 | 633.37 ± 8.08 | 2.26 |

colorant decomposition of the TA23-coated cotton substrates after 20 launderings was only slightly lower than that after 10 launderings, which suggests that the durability might be maintained or is very slowly reduced after 20 launderings. This may be attributable to the formation of covalent bonding at their interface as a result of dehydration reactions between the cellulosic hydroxyl groups and the hydroxyl groups of titania (36, 37). It can also be found that under the same UV irradiation, the colorant concentration in contact with pure cotton substrates without $TiO_2$ coatings remained almost at the same level during UV irradiation (Figure 6a), which means that this type of cotton substrates has no colorant decomposition ability and the dye itself would not be decomposed by UV radiation.

**3.6. Degradation of Red Wine and Coffee Stains.** Self-cleaning property of the TA23-coated cotton fabrics can be assessed by the degradation of organic stains such as red wine or coffee stains. Figure 7 presents the degradation pictures of red wine and coffee stains on pure cotton fabrics and TA23-coated cotton fabrics before and after launderings under 8 and 20 h of light irradiation in Xenotest Alpha LM light exposure and weathering test instrument. Table 1 shows the corresponding staining grades of red wine and coffee stains before and after launderings under light irradiation according AATCC 130 test method using stain release replica. Grade 5 represents the best stain removal and grade 1 represents the poorest stain removal. The stains on TA23-coated cotton fabrics after 10 and 20 launderings but before irradiation were not shown in Figure 7 as they were similar to those before laundering and irradiation.

Table 1 shows that the grades of red wine and coffee stains on pure cotton fabrics and TA23-coated cotton fabrics at 0 h were equals to 1, respectively. For TA23-coated cotton fabrics before laundering, a remarkable discoloration of a red wine stain and a coffee stain was observed after 8 h of light irradiation and a complete discoloration was achieved after 20 h of light irradiation, as shown in Figure 7, while the corresponding grades of red wine and coffee stains on TA23-coated cotton fabrics were equal to 4 and 5 respectively, as listed in Table 1. On the other hand, almost no discoloration of red wine and coffee stains on pure cotton fabrics was observed after 10 and 20 h of the light irradiation (Figure 7), which corresponds to grades ranged from 1 to 1.5 as seen from Table 1. These results clearly indicate that TA23 coatings on cotton fabrics can effectively degrade red wine and coffee stains, whereas pure cotton substrates have no decomposition ability at all. Comparing to the discoloration of red wine and coffee stains on TA23-coated cotton fabrics before laundering and after 20 h irradiation, there was no significant reduction observed in the discoloration of these stains on the-coated cotton fabrics after 10 launderings and 20 h irradiation (Figure 7). The grades of both a red wine stain and a coffee stain on TA23-coated cotton fabrics were scored as 4.5 and 3.5 after 10 and 20 launderings respectively. From these results, it can be concluded that TA23 coating imparts significant photocatalytic ability to cotton substrate and this ability still remains after 20 launderings.

While significant discoloration of red wine and coffee stains was observed on the exposed side of TA23-coated cotton fabrics after 8 h of light irradiation, the color of the red wine stain and coffee stain on the unexposed side of TA23-coated cotton fabrics could still be clearly observed. However, a complete discoloration of these stains on the unexposed side of TA23-coated cotton fabrics was achieved after 20 h of light irradiation (See Figure S1 in the Supporting Information). After 10 and 20 launderings, the discoloration of these stains on the unexposed side of TA23-coated cotton fabrics were decreased slightly compared to that before laundering. The degradation activity of $TiO_2$ prepared by aging at room temperature toward red wine and coffee stains is similar to that of S60 $TiO_2$ prepared by heating method (18).

**3.7. Tensile Strength.** Table 2 shows the tensile strengths and standard deviations of pure cotton fabrics and TA23-coated cotton fabrics before and after 20 h of light irradiation in Xenotest Alpha LM light exposure and weathering test instrument. Before light irradiation, the tensile strength in warp direction of TA23-coated cotton fabrics was similar to that of the pure cotton fabric, which means that the TA23 aging sol prepared using acetic acid as a catalyst reduces the acid damage to cotton fabric compared to previous sols prepared using strong nitric acid and acetic acid as catalysts (18). After 20 h of light irradiation, the tensile strengths of both the pure cotton fabrics and TA23-coated cotton fabrics were reduced. However, the reduction in the tensile strength of the pure cotton fabrics was 4.50%, while the reduction in that of TA23-coated cotton fabrics was 2.26%. The standard deviations of tensile strengths of the pure cotton fabrics and TA23-coated cotton fabrics in Table 2 show that the distribution of the tensile strengths is narrow with an error margin of $\pm 2\%$. This suggests that there is no photocatalytic decomposition of the molecular chains of cotton caused by the TA23 layers. On the contrary, the titania layers reduced the drop of tensile strength due to its ability to absorb UV irradiation, which to a certain extent, protects the cotton fiber, which is in agreement with the results published previously (18).

## 4. CONCLUSIONS

Single-phase anatase $TiO_2$ nanocrystallites were prepared by a simple sol–gel process in an aqueous media, followed by aging at room temperature. The aging process at room temperature promotes the crystallization of anatase phase. The anatase nanocrystallites on the cotton substrates-coated by the TA23 anatase nanocrystallites show significant photocatalytic self-cleaning performance as demonstrated by the colorant decomposition and degradation of a red wine stain and a coffee stain under UV irradiation. This photocatalytic self-cleaning ability still remains after 20 launderings. The anatase titania prepared at room temperature has similar photocatalytic power compared to that prepared by heating method reported previously (18). The anatase $TiO_2$ coatings did not damage the cotton substrate as demonstrated by the comparison study of the tensile strengths of-coated and uncoated cotton fabrics before and after prolonged light irradiation. Instead, the coating can even slightly protect the cotton substrate. Moreover, the $TiO_2$ sol reduced the acid damage to cotton fabrics because of the use of acetic acid as a catalyst compared to previous sols prepared using strong nitric acid and acetic acid. The method of preparing single-phase anatase $TiO_2$ in this study not only eliminates the need for high temperature operations, but also extends their applications to poor acid-resistant materials and low thermal resistant materials such as biomaterials and cellulosic materials.

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**Supporting Information Available:** The degradation images of red wine and coffee stains on the unexposed side of pure cotton fabrics and TA23 $TiO_2$-coated white cotton fabrics before and after light irradiation. This material is available free of charge via the Internet at http://pubs.acs.org.

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