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Innovative self-cleaning and antibacterial cotton textile: no water and no detergent for cleaning

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ABSTRACT

In study, morphologically well-defined TiO_2 nano particles (NPs), prepared by sol-gel method was coated on the cotton textile surface to develop self-cleaning, UV blocking and antibacterial cotton textile surfaces. Commercially available Degussa P25 TiO_2 powder photocatalyst was used as benchmark for comparison. To evaluate the self-cleaning action of modified textile fabric, tea stains were introduced on the cotton fabric. Under sun-test illumination, decrease in the color of tea stain was followed over time for the determination of self-cleaning performance of the modified textile surface. The effects of TiO_2 treatments on the main functions of cotton fabric were investigated by the measurements of tensile strength, tear strength, wrinkle recovery angle and color fastness measurements. The modified cotton textiles with TiO_2 NPs and Degussa P25 TiO_2 powder showed strong self-cleaning performance under illumination and tea stain was completely removed in 30 min. TiO_2 coating improved UV protection factor of cotton textile by three fold. According to the untreated cotton textile, the modified textiles with sol-gel based TiO_2 NPs and TiO_2 powder showed much stronger antibacterial performance against *E. coli* and *S. aureus* bacteria.

Keywords: Antibacterial; Cotton textile; Nano particles; Self-cleaning; Titanium dioxide

1. Introduction

Most of the regular textile products are surfaces to be stained and soiled with any liquids, dirt, dust, foods, bloods or any other oily contaminations. Textile items are need to be frequently dry cleaned, washed, wiped or sponged using any type of detergent, soap or any other dirt removing media. Detergents are an extensively used group of chemicals with the annual worldwide use of surfactants exceeding 2 billion kg [1]. Large quantities of detergents and their components enter the environment. It is estimated that about 5% of all detergent and their components reaches the aquatic environment [2]. Concern over the potential environmental impact of detergents and some of the components has led to extensive study of their environmental effects [3]. Due to the hazardous and health effects of detergents, their additives and by-products, recently many studies were attempted to improve new environmentally friendly detergent and self-cleaning products. New improvements about self cleaning surface processing and challenging properties of nanotechnology have attracted textile industry

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in recent years. Nano particles (NPs) have been incorporated into textile products to create new functionalities such as soil resistance, wrinkle resistance, water repellency, anti-bacteria, anti-allergen, anti-static, self-cleaning, flame retardation, energy storing, and so on [4–11]. On-going research to provide environmentally safe, long-term stable and self-cleaning, low cost multi-functional nano-textiles is still major topic urging further innovative efforts. Photo-catalysts as self-cleaning agents have been receiving much attention, particularly for their complete destruction or mineralization of the toxic and non-biodegradable compounds to carbon dioxide and inorganic constituents. Among the photo-catalysts, titanium dioxide (TiO_2) is the most superior photo-catalyst due to its low cost, outstanding chemical stability, suitable band gap, blocking UV light, non-photocorrosion, and non-toxic nature [12–14].

Photocatalytic activity (PCA) is a photoassisted catalytic process utilizing a substance that converts light energy into catalytic work through chemical reactions. In PCA, a material creates an electron hole pair as a result of exposure to ultraviolet radiation [15]. These electron-hole pairs contribute to powerful oxidizing photo-electrochemical reactions that are capable of decomposing dirt, harmful microorganisms and organic contaminants into carbon dioxide and water [16,17]. As a semiconducting, which can be chemically activated by light, material TiO_2 is known for about 60 y. The photo activity of TiO_2 has been extensively studied because of its potential use in sterilization, sanitation, UV protection and remediation applications.

In this study, commercial TiO_2 and morphologically well-defined TiO_2 NPs, which were prepared by sol-gel method, were coated on the cotton textile surface. To evaluate antimicrobial activity and the self-cleaning action of modified cotton textile, tea stain were introduced on the cotton fabric and decrease in color was followed over time after irradiation of the sample in a solar simulator. The effects of commercial TiO_2 and TiO_2 NPs on the main functions of cotton textile were determined by measuring some textile properties before and after coating.

2. Materials and methods

2.1. Materials

Bleached and optical whitened plain woven 100% cotton fabric had been used through experiments for preparation of each two specimen set of nano TiO_2 and TiO_2 powder (Degussa P25) coated fabrics and also control fabric.

2.2. Preparation of sol-gel based TiO_2 NPs

Titanium (IV) isopropoxide (Aldrich) was used as a precursor for preparing TiO_2 colloidal suspensions. After adding 25 ml of titanium isopropoxide to 5 ml nitric acid solution in 50 ml distilled water, the resulting precipitate was continuously stirred at 80 °C. A stable colloidal suspension occurred after 30 min mixing time period. This suspension was dialyzed against milli-Q water to pH 2.8 by using a Micropore 3500 MW cutoff membrane.

2.3. Antimicrobial activity test

Antibacterial efficiency of textile materials were performed using a method 'AATCC Test Method 100-1999, Antibacterial Finishes on Textile Materials: Assessment of' [15]. The two bacterial species were used throughout: *Staphylococcus aureus* ATCC 29213 and *Escherichia coli* ATCC 25922. Stock cultures of these bacteria were maintained on Nutrient Agar slants. Before each assay, the test bacteria were incubated at 37 ± 0.1 °C for 24 h by inoculation into Nutrient broth. The culture suspensions were prepared and adjusted to (1–2) × 10^6 cfu/ml (colony forming units per milliliter) by using 0.5 Mc Farland turbidity standard tubes. All cotton fabrics were prepared at 8 ± 0.1 cm^2 in quartz tubes and were sterilized by autoclaving at 121 °C for 15 min. As described in the AATCC Test Method, swatches of the textile materials were inoculated with test bacteria. Then, coated and uncoated fabrics incubated different times at SUNTEST equipment (500 w, 35 °C). After incubation the cotton fabrics were then transferred into 25ml of nutrient broth and shaken vigorously for 1 min. A 10-fold dilution with 0.85% (w/v) normal saline solution was prepared, spread at varying dilutions onto a NA plate, and further incubated at 37 °C for 24 h. All experiments were performed in duplicate. The number of bacteria in each sample (cfu per pieces of fabric) was reported.

2.4. Self-cleaning test

A commercial tea was added in boiled distilled water to prepare tea stain solution. Brownish tea solution which absorbs light at 200–500 nm (Fig. 1) was used to stain the cotton textile fabric. Fabric samples were dipped into the staining solution of tea and they were replaced in quartz rectangular tubes and illuminated in the sun-test solar simulator. Color changes on the textile surface were determined over time via CAMSPEC M350 UV_Vis spectrophotometer for the evaluation of self-cleaning performances of modified textile samples.

2.5. Finishing treatments of textile fabric

TiO_2 NPs were coated onto the cotton fabric via dipping coating technique. TiO_2 powder coating process is done via pad-dry method. Appropriate amount of TiO_2 powder was stirred at 2000 rpm for 5 h. Washed

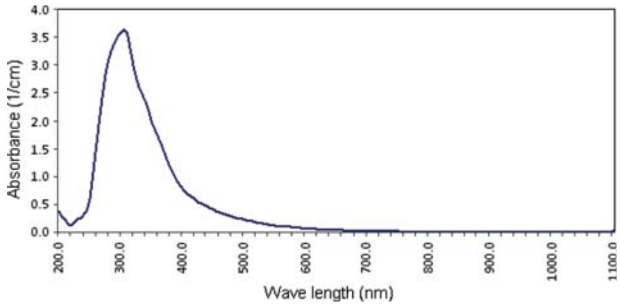

Fig. 1. Spectrophotometric analysis of tea as staining solution.

cotton fabric was immersed twice in the suspension solution containing TiO_2 for 1 min and then passed through a padding mangle to remove the excess solution. Later fabric was immersed into binder solution for 20 seconds and then passed through the padding mangle. After padding, the fabric was dried for 2 mins at 100 °C. Control fabric has only washed in the water and soap medium to remove undesirable dirt, simple stains and other soils from the fabric surface.

2.6. Measurements of textile main functions

Treated specimens were cut into appropriate sizes for the fabric performance tests. Table 1 shows the tests and their methods, applied to the prepared fabric samples.

3. Results

3.1. Antimicrobial activities on the TiO_2 coated textile surface

The antimicrobial performances of textile materials against *E. coli* and *S. aureus* have been summarized in Table 2 and 3. The results showed that cotton fabrics which coated with nano TiO_2 and TiO_2 powder inhibited the growth of microorganisms in different rates. In general, coated fabrics had a less antibacterial activity against *E. coli* and strongly inhibited the growth of the *S. aureus*.

Table 1
Fabric sample evaluation tests

Name of the test	Test standard
Fabric tensile strength test	TS EN ISO 13934-1
Fabric tear strength test	TS EN ISO 13937-1
Crease recovery angle test	ISO 2313
Sweat fastness test	TS EN ISO 105-E04
Sun protective clothing-evaluation and classification	AS/NZ 4399:1996
Color change test (staining and self cleaning)	TS 12552

Table 2
Antimicrobial activity of fabrics coated with nano TiO_2, TiO_2 powder and uncoated fabrics (blank) against *E. coli* under sun-test illumination

Time (min)	*E. coli* (log cfu/cm^2)		
	Blank	TiO_2 NPs (Sole Gel)	TiO_2 powder (Degussa P25)
0	6.71 ± 0.17	6.63 ± 0.19	6.74 ± 0.3
5	6.23 ± 0.2	6.24 ± 0.2	6.06 ± 0.1
15	5.91 ± 0	5.57 ± 0.2	5.69 ± 0
20	5.91 ± 0	5.08 ± 0.5	5.2 ± 0.6
30	5.55 ± 0	4.36 ± 0	2.79 ± 0

Table 3
Antimicrobial activity of fabrics coated with nano TiO_2, TiO_2 powder and uncoated fabrics (blank) against *S. aureus* under sun-test illumination

Time (min)	*S. aureus* (log cfu/cm^2)		
	Blank	TiO_2 NPs (Sol-gel)	TiO_2 powder (Degussa P25)
0	6.36 ± 0.11	6.38 ± 0.18	6.38 ± 0.14
5	6.09 ± 0.02	5.59 ± 0.29	6.12 ± 0.19
15	5.87 ± 0	5.1 ± 0.13	6.05 ± 0.01
20	5.87 ± 0	4.81 ± 0.18	4.98 ± 0.01
30	4.39 ± 0	2.60 ± 1.17	1.87 ± 0

Compared with the control fabric, about 10 times more *E. coli* were inactivated on the TiO_2 coated cotton textile. In 30 min illumination time, 6.6 log cfu/cm^2 initial number of *E. coli* on the sol-gel based TiO_2 NPs coated textile fabric was reduced to 4.3 log cfu/cm^2. In the same time period, a higher *E. coli* inactivation was achieved on the TiO_2 powder coated textile fabric and 6.7 log cfu/cm^2 initial number of *E. coli* was reduced to 2.7 log cfu/cm^2. In terms of inactivation of *S. aureus*, TiO_2 treated samples showed strong antibacterial performances and after 30 min sun-test illumination, 6.25 log cfu/cm^2 *S. aureus* initial numbers *on* the sol-gel based nano TiO_2 and TiO_2 powder coated textile fabrics were reduced to 2.6 log cfu/cm^2 and 1.8 log cfu/cm^2 respectively.

3.2. UV blocking performances of the modified cotton textiles

Determination of the UV transmission of textile surfaces was done in accordance to AS/NZ 4399:1996 for sun protection clothing with the use of Camspec M350 UV/Visible Spectrophotometer apparatus. The absorption of UV rays by the specimen fabrics has found different between treated and

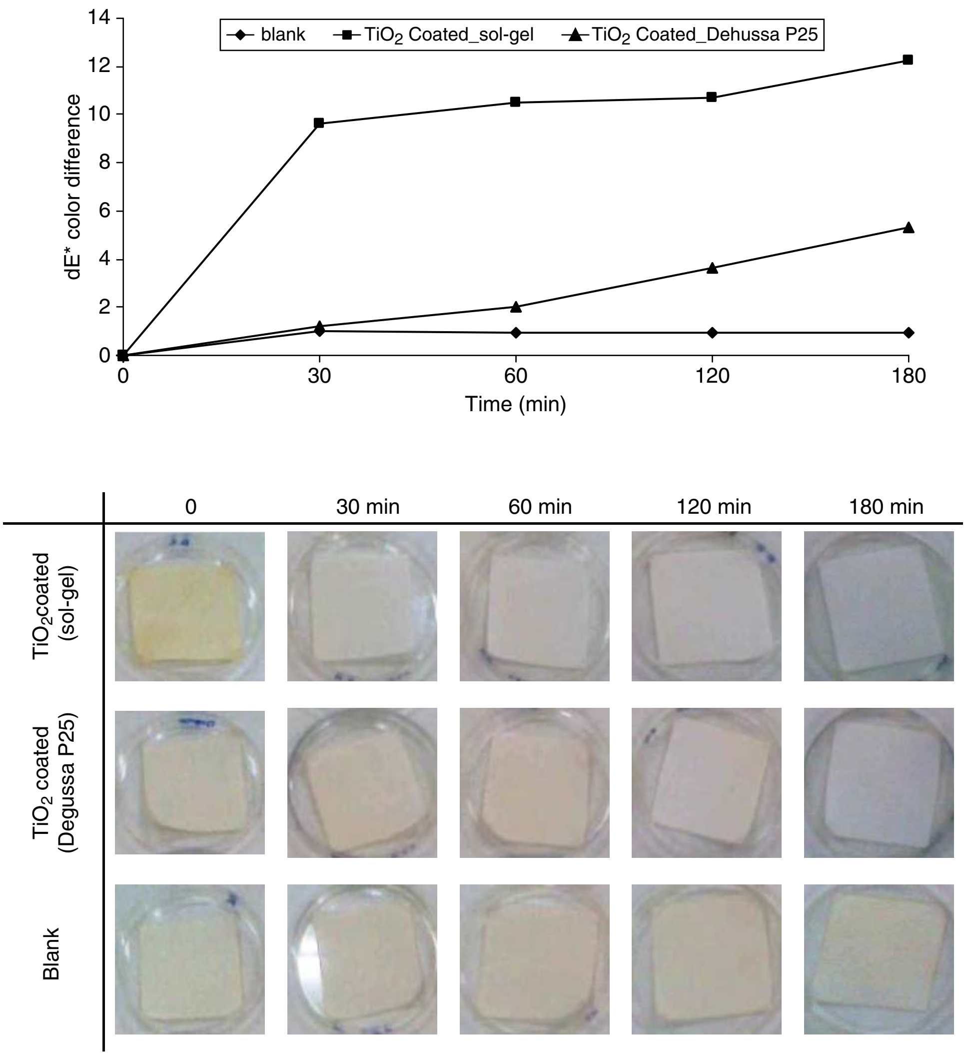

Fig. 2. dE* color difference values and visualized stain fading of light-tea stain.

Table 4
UPF and UVR (%) values of treated and untreated specimens

Sample	Mean UPF	Rated UPF	Protection category	% UVR blocked
Nano TiO_2	25.2	20	good	93.3–95.9
TiO_2 powder	22.4	15	good	93.3–95.9
Control sample	8.6	5	poor	–

untreated fabrics (Table 4). Nano TiO_2 and TiO_2 powder treated specimens has UPF value of 25.2 and 22.4 respectively while untreated fabric has only 8.6 The UPFs for both two TiO_2 treated specimens were in the "good" protection category (blocking 93.3 to 95.9% of UVR) while it was in "poor" category for untreated textile fabric.

3.3. Self cleaning performances of the modified cotton textiles

All textile samples were dipped into tea solution to stain. As illustrated in Fig. 2, according to the raw sample, very strong color occurred on the textile surface which is treated with sol-gel based TiO_2 NPs. Results reflect the fact that the cotton textile surface strongly attracts sol-gel based TiO_2 NPs and thus hydrophilic TiO_2 NPs adsorb much more tea stain on the textile surface. Commercial TiO_2 Degussa P25 did not show same effect because of weak adsorption of TiO_2 Degussa

P25 particles on the cotton textile surface (not published data). Both TiO_2 coated textile samples showed self-cleaning effect and after 30 min illumination time period color was removed on the surface of modified textile samples. On the textile surface, self-cleaning performance of sol-gel based TiO_2 was found to be higher than that of TiO_2 Degussa P25. Results showed that TiO_2 NPs provide textile products very efficient self-cleaning and antibacterial properties.

3.4. Effect of TiO2 coating on the main functions of cotton textile

3.4.1. Fabric strength

To explain the influence of the TiO_2 treatments on the strength properties of the 100% cotton woven fabric, specimens were examined in the weft and warp directions. Breaking strength of the TiO_2 treated specimens are increased in the weft direction while it is decreased in the warp direction of the specimens comparing to untreated control fabric (Fig. 3). Breaking elongation of the specimens is also changed depending on the treatments. Nano TiO_2 treatment causes increased breaking strength and elongation values comparing TiO_2 powder treatment.

TiO_2 treatments have caused a decrease in the tear strength of the treated cotton textile fabric (Fig. 4). Decrease in tear strength can be explained with the increasing friction level between warp and weft yarns and decreasing yarn movement freedom with the deposed TiO_2 NPs around yarns.

Fabric crease recovery angle; The results of crease recovery angle test of TiO_2 treated specimens are shown in the Fig. 5. In the weft direction crease recovery angle increased after TiO_2 NPs treatment while it decreased

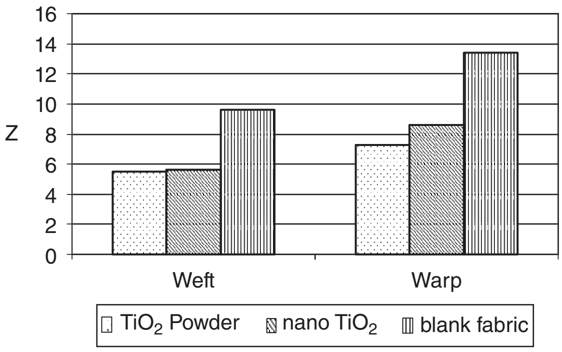

Fig. 4. Tear strength of specimen fabrics-weft and warp direction.

after TiO_2 powder treatment. Decrease in the crease recovery angle of the specimens with the TiO_2 treatments can be explained with the TiO_2 particle collection among the warp and weft yarns. Particle collection limits the movement possibility of the yarns over each others and shape recovery possibility of the fabrics becomes tougher.

3.4.2. Fabric color fastness against sweat

Influence of the TiO_2 treatments on the color fastness against the sweat of the 100% cotton woven fabric has been examined for the determination of color fastness. As can be seen from Table TiO_2 treatments influenced the color of the specimens. Acid and alkali sweat fastness measurement show that fading properties of specimens are influenced slightly by acidic and alkali sweat fastnesses. Thus, sweat fastnesses on the treated samples are found in the acceptable range of 4 to 4/5 (Table 5).

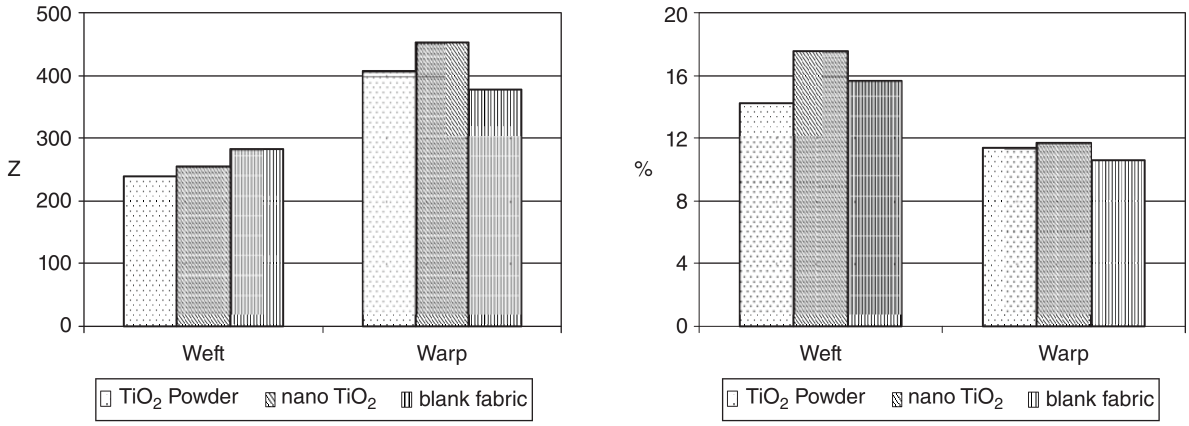

Fig. 3. Breaking strength and elongation of specimen fabrics-weft and warp direction.

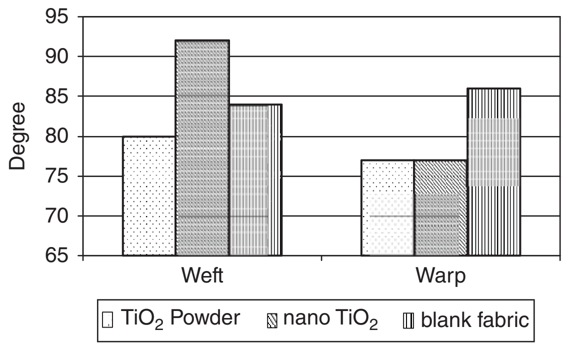

Fig. 5. Crease recovery angle changes of specimens-weft and warp direction.

Table 5
Sweat fastness of raw and treated cotton textile samples

Sample	Sweat fastness-fading	
	ac*	al*
Nano TiO_2	4	4
TiO_2 powder	4/5	4
control sample	4	4

ac*: acidic sweat fastness test; al*: alkali sweat fastness test; sweat fastness value is changed between 1 (worse) and 5 (best).

4. Conclusions

In this study, 100% cotton fabric samples were coated with TiO_2 powder and TiO_2 NPs to provide self-cleaning, antibacterial and UV blocking properties on the textile surface. According to the experiments conducted, the following conclusions can be drawn;

- Antibacterial performances of powder TiO_2 treated and untreated textile fabrics were determined by antibacterial tests against two type bacteria (*E. coli* and *S. aureus*). Compared with the control fabric, about 10 times more *E. coli* and 100 times more *S. aureus* were inactivated on the TiO_2 coated cotton textile samples. It is observed that TiO_2 coated textile fabrics are more effective on *S. aureus* than *E. coli*. Inactivation rates of *S. aureus* and *E. coli* on the treated fabrics reflect the fact that the TiO_2 powder coated textile is superior than the sol-gel based TiO_2 coated textile.
- Much more tea stain adsorption occurred on the surface of treated cotton fabric due to the hydrophilic nature of TiO_2. As a result, after staining textile samples into the tea solution the color of tea stain on the modified cotton fiber was found to be much stronger than that on the untreated cotton fiber. But under illumination both TiO_2 coated textile samples showed very efficient self-cleaning performance and after 60 min illumination the tea stain was completely removed from the surface of modified textile samples. Compared to the TiO_2 modified fibers, the color change on the stained raw textile fiber was insignificant under the same illumination time period. Otherwise self-cleaning performance of sol-gel based TiO_2 was found to be higher than that of TiO_2 Degussa P25.
- UV protection level of modified cotton fabric was not excellent but the UV absorption rate of the TiO_2 treated specimens was quite substantial and changed UV protection performance of cotton fabric from poor level to good category.
- The effect of TiO_2 coating on the main function of cotton textile fabric was evaluated by measurement of the breaking strength, tear strength, wrinkle recovery angle and sweat fastness. It is concluded that TiO_2 treatment influences the physical properties of cotton fabric. Fabric strength properties are found negatively influenced by the TiO_2 treatments. Wrinkle recovery angle measurement test results give idea about the stiffness change of the specimens. TiO_2 treated specimens gets softer comparing to control fabric. Sweat fastness results of the treated fabrics show that TiO_2 treatment does not cause fading on the cotton fabric.

Very high self-cleaning and antibacterial activities were achieved on the TiO_2 NPs coated textile fabrics. Therefore the results reflect the fact that development of self-cleaning textile fabric may reduce the required water, energy and detergent consumptions for the home textile cleaning. As a result, in the future, smart nano textiles may become an important environmentally friendly technology to decrease the effects of hazardous cleaning products in the environment.

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