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In situ Deposition of TiO_2 Nanoparticles on Polyester Fabric and Study of Its Functional Properties

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Abstract: *In situ* deposition of TiO_2 nanoparticles on polyester fabric has been carried out using hydrothermal method by changing the process conditions. The morphology and crystalline structure of as-deposited particles has been studied by using SEM and XRD. The chemical composition of nanoparticles was determined using energy dispersive spectroscopy. The treated sample exhibited photocatalytic solution discoloration and good washing fastness properties. The study of UV protection and moisture management of fabric showed that it had excellent UV protection factor and comfort properties.

Keywords: Titanium dioxide, Nanoparticles, Moisture management, Functional textiles

Introduction

Functional textiles are those which in addition to performing their routine job, provide additional functions such as UV protection, self-cleaning, lotus effect, superhydrophilicity, fire retardancy, moisture management, antibacterial activity etc. Due to growing market demand, the researchers have recently focused their research on development of multifunctional textiles using non-conventional techniques. These techniques include the use of nanotechnology or nanomaterials either to deposit nanoparticles on textiles to functionalize them or to develop nanofibers which are used for manufacturing of fabrics with functional characteristics. The development of nanofibers at industrial scale is still under investigation but the surface treatment of fabric with nanomaterials to impart functional properties is well known.

During the recent years, lot of work has been done to develop functional textiles using nanoparticles of ZnO, SiO_2, TiO_2 etc. The lotus effect on textiles has been developed by using different nanoparticles to generate roughness on fibers which were subsequently treated with hydrophobic compounds [1-5]. To impart self-cleaning function, the fabric has been treated with different photocatalysts like ZnO and TiO_2 which have ability to degrade color stains and decolorize dye solutions [6-11]. Antibacterial textiles have been developed by depositing nanoparticles of ZnO and silver [12,13]. The textiles having antibacterial and self-cleaning characteristics have been developed by using TiO_2 and silver [14-16]. The UV protection of textiles has been achieved by functionalizing them with TiO_2 and ZnO nanoparticles [17-20].

Another important functional property of textiles is moisture management due to which textile clothing transports moisture to outer surface of fabric so that the wearer feels comfortable. The usage of microfibers enhances the moisture management properties of fabrics due to decrease in capillary size and increase in number of capillaries in the yarn cross-section [21]. The moisture management capacity of fabrics can be further improved by developing nano-capillaries with deposition of nanostructures on textiles [22].

TiO_2 happens to be an excellent functionalizing agent due to its multifunctional properties and possibility to be deposited in the form of nanoparticles at low temperature. It is a very well-known photocatalyst and has been extensively used to degrade the coloring substances in effluent [23,24] as well as in the development of self-cleaning surfaces like glasses and textiles [25,26]. Due to its photocatalytic nature, it absorbs the light in UV region, thus providing protection against harmful rays of UV [27].

The present work is aimed at *in situ* deposition of TiO_2 nanoparticles on polyester fabric using seeding method and evaluation of multifunctional properties of the treated fabric such as photocatalytic discoloration of solutions, moisture management and UV protection. The thermo-physiological comfort properties of untreated polyester fabrics are not very good due to poor moisture regain. However, the functionalized polyester fabric would have good comfort properties due to hydrophilic nature of TiO_2 nanoparticles [28].

Experimental

Materials

Tetrabutyl orthotitanate (97 %) and titanium isopropoxide (98 %) were purchased from TCI Japan. HCl (37 %), granulated caustic soda, ethanol (99.9 %) and petroleum ether were purchased from Sigma Aldrich and were used without any further purification. A plain woven polyester fabric (areal density 110 g/m^2) was supplied by a local industry.

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Growth of Nanoparticles

The fabric was cleaned with petroleum ether using Soxhlet apparatus. The cleaned fabric was treated with 30 g/*l* caustic soda solution at 90 °C for 30 minutes. The growth of nanoparticles was carried out using a two steps process. In the first step, TiO_2 nanoseeds were deposited on caustic soda treated polyester fabric, and then nanoparticles were grown on these seeds in the subsequent step. The nano seeds were prepared using sol-gel method. Ethanol (50 m*l*) and acetic acid (1.5 m*l*) were taken in a round bottom flask. Then flask was placed in water bath on a hotplate. Then, tetrabutyl orthotitanate (5 m*l*) was added drop wise into flask with continuous stirring of solution at 60 °C. The solution became nearly transparent after 5 hours. The as-prepared seed solution was applied to caustic soda treated polyester fabric by padding. The fabric was immersed into the seed solution and was squeezed between rollers at a nip pressure of 2 bars and dried at 120 °C. This process was repeated 5 times and finally the fabric was cured at 150 °C.

In the second step, hydrothermal method was used for the development of nanoparticles on the seeded fabric. A 60 m*l* aliquot of distilled water was mixed with 60 m*l* of HCl (37 wt%) in a conical flask and then different amounts of titanium isopropoxide were added in it and stirred for 10 minutes. The TiO_2 seeded polyester fabric was placed in the conical flask and then autoclaved at 121 °C and 15 psi for 1 h. After synthesis, the autoclave was cooled to room temperature and fabric was taken out from the flask and rinsed with distilled water. Then, the rinsed fabric was dried in an oven at 120 °C for 5 minutes.

Characterizations

Analysis of Nanoparticles

The morphology of nanoparticles grown on polyester fabric was characterized by using FEI Quanta 50 scanning electron microscope. The elemental analysis of nanoparticles deposited on the fabric was carried out using Energy-dispersive X-ray spectroscopy. PANalytical's X'Pert PRO Materials Research Diffraction System was used to study the crystalline structure of TiO_2.

Moisture Management Properties

Standard test method AATCC 195-2009 was used to evaluate the liquid moisture management properties of polyester fabric by using Moisture Management Tester. Five samples of 8×8 cm^2 were cut diagonally across the width of the fabric to ensure the presence of different sets of warp and weft yarns in the samples. The samples were then conditioned in an environment controlled at 21±1 °C (70±2 °F) temperature and 65±2 % relative humidity for 24 hours.

UV Protection Properties

Mean Ultraviolet Protection Factor (UPF), UVA and UVB blocking percentage of the samples were determined according to AATCC 183-2000 standard test method using UV Spectrophotometer (M550 SPF).

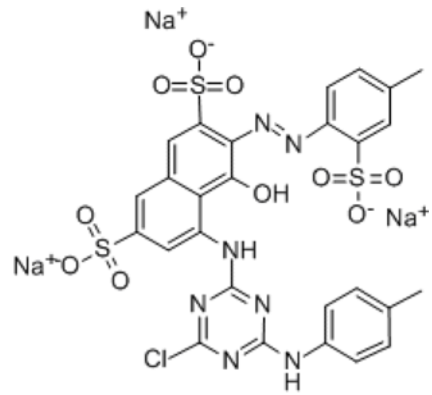

Figure 1. Chemical structure of C.I. reactive red 45.

Samples were conditioned for 4 hours at 21±1 °C temperature and 65±2 % relative humidity by laying each test specimen separately. After that each sample was cut into size 5×5 cm^2, andplaced on the flush against the sample transmission port opening in the sphere. Then first UV transmission measurement was taken with the sample oriented in one direction and second measurement was taken at 0.79 radian or 45 ° to the first and the third at 0.79 radian or 45 ° to the second.

Photocatalytic Effect

To study the photocatalytic discoloration effect, the nanoparticles functionalized sample with diameter 2.54 cm was placed in a beaker having 15 m*l* of C. I. Reactive Red 45 dye solution (The chemical structure is shown in Figure 1). This beaker was placed in light box carrying 20 W UV light (UV=315-400 nm with maximum emission at 368 nm). An aliquot was removed from the solution and its absorbance was measured at λ_{max} (540 nm) using BMS, UV-2800 UV-Vis spectrophotometer.

Results and Discussion

Deposition of Nanoparticles

As TiO_2 nanoparticles were grown by seeding method, therefore, the polar groups were generated on polyester fabric by treating with caustic soda before the seeding step. The caustic soda hydrolyzed the polymer chain by generating hydroxyl and carboxyl acid groups. These polar groups attached the nano seeds which are pre-requisite for the growth of nanoparticles [29-31]. Due to hydrolysis of chains, oligomers are formed which appear as small particles on the surface of fibers (Figure 2(B)) but no such particles were observed on untreated fabric (Figure 2(A)).

When seeded samples were placed in solutions with different concentrations of titanium isopropoxide and heated up to 120 °C under pressure, the nanoparticles grew on them but their fiber coverage was different at different concentrations as shown in Figure 3. The coverage of fibers with nanoparticles increased with increase in the precursor concentration. With

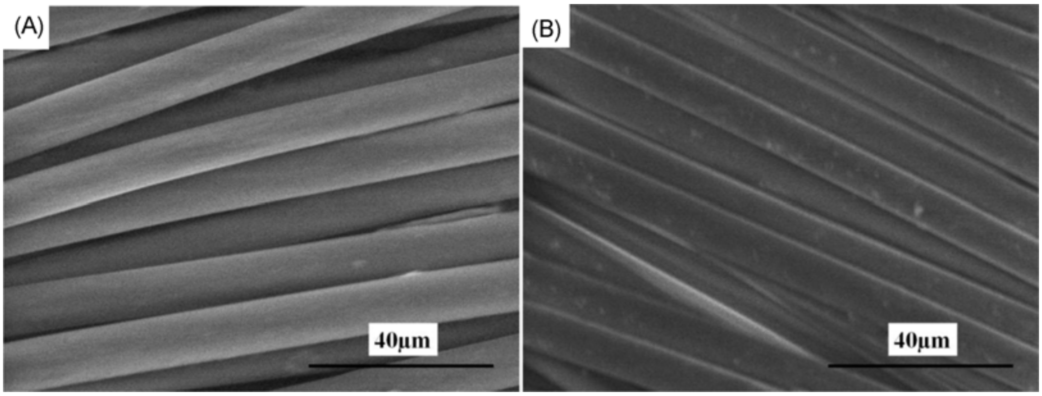

Figure 2. SEM micrographs of sample; (A) untreated polyester fabric and (B) caustic soda treated polyester fabric.

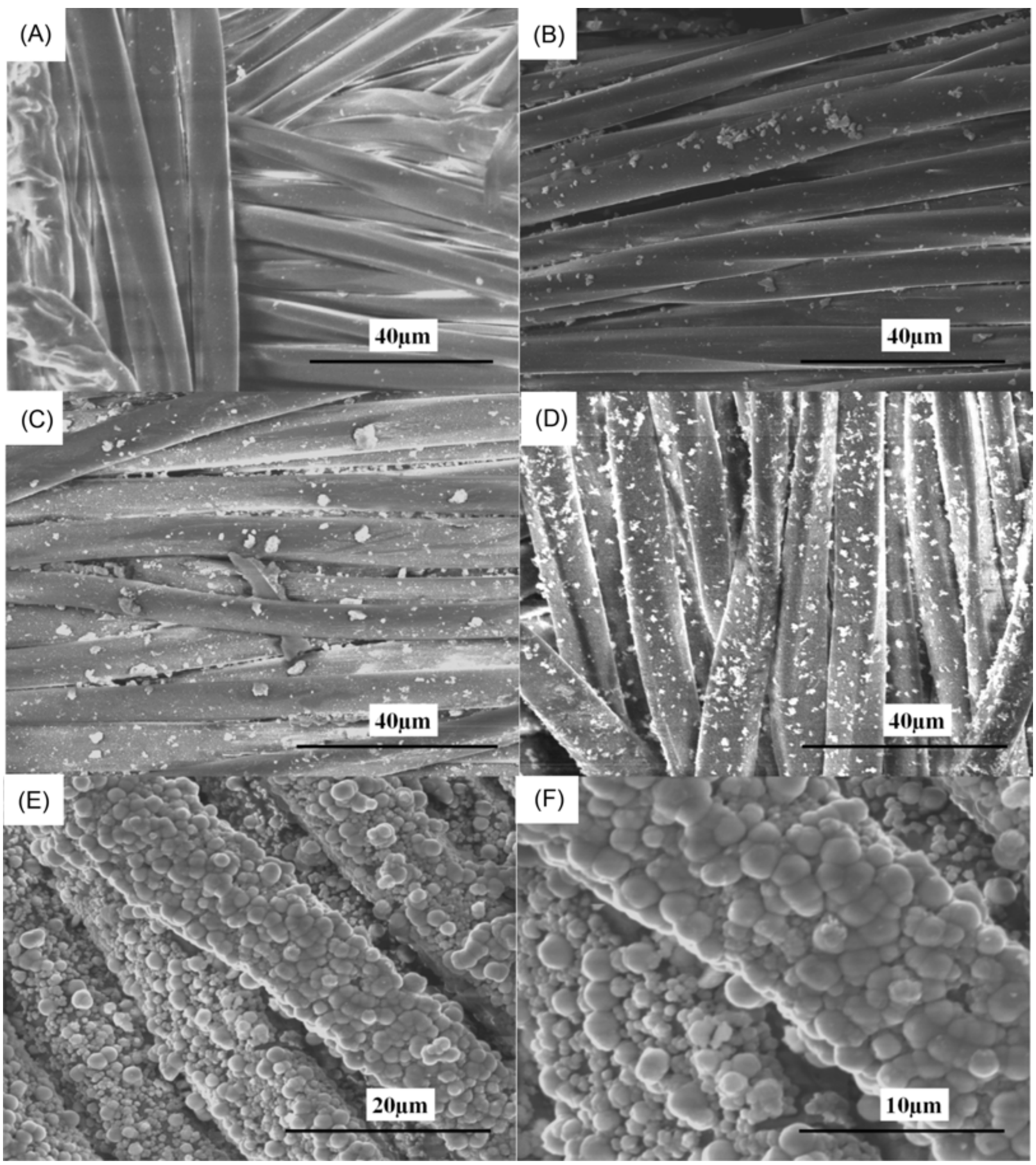

Figure 3. SEM micrographs of sample; (A) seeded sample, (B) seeded sample treated with 5 m*l* titanium isopropoxide, (C) seeded sample treated with 10 m*l* titanium isopropoxide, (D) seeded sample treated with 15 m*l* titanium isopropoxide, (E) seeded sample treated with 20 m*l* titanium isopropoxide, and (F) high resolution of sample E.

the increase in titanium isopropoxide concentration, more and more growth species were generated in the solution which led to increased deposition of TiO_2 on fibers and hence their fiber coverage was increased. Experiments to grow nanoparticles on bare polyester fabric (without nano seeds) were also performed but no growth of nanoparticles was observed. This shows that nano seeds are necessary for the growth of nanoparticles. These seeds provide the site for nucleation of growth species [32]. The tensile strength of the treated fabric was decreased by 13±2 % which can be attributed to the hydrolysis of polyester chains due to treatment with caustic soda.

The elemental analysis of the nanoparticles was done on the sample completely covered with nanoparticles (sample S3, Figure 3(E),(F)) using energy dispersive spectroscopy analysis, which shows that Ti, O and C are present on surface of fibers (Figure 4). The little carbon content is due to the polyester fibers but no other impurity was observed, which indicates that the nanoparticles are made of TiO_2.

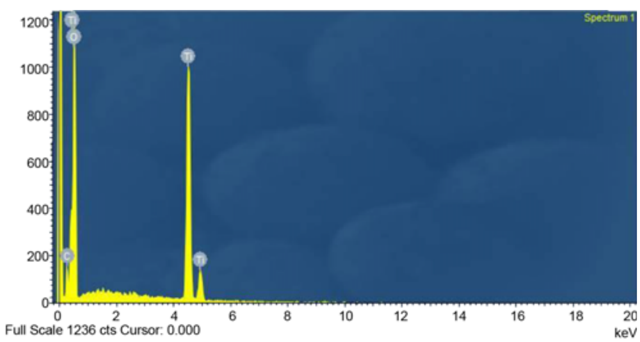

Figure 4. EDS spectra of treated fabric.

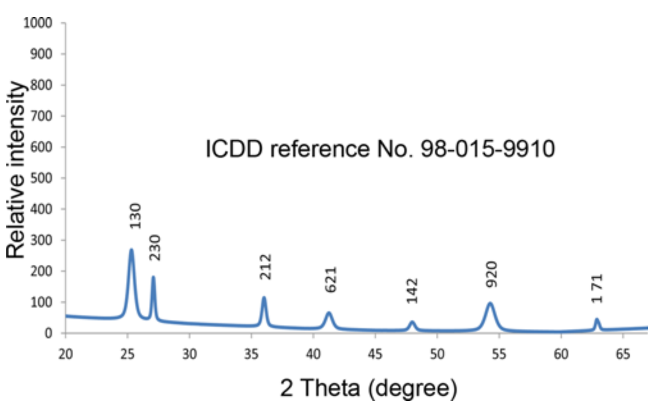

Figure 5. XRD Pattern of TiO_2 nanoparticles.

Figure 5 shows the XRD Pattern of TiO_2 nanostructures deposited on fabric surface. XRD reference pattern used for analysis of TiO_2 are ICDD 98-015-9910. All the peaks which appear in 2theta pattern of XRD correspond to TiO_2 which means that the nanostructures are made of 100 % pure TiO_2.

Moisture Management Properties

Table 1 represents the moisture management test results of cleaned (S1), caustic soda treated (S2) and nanoparticles treated (S3) samples. The sample S2 has lower top and bottom wetting times than S1. This shows that due to caustic treatment, the carboxyl acid and hydroxyl polar groups were generated due to hydrolysis which enhanced wettability of fabric. The sample S3 has lowest wetting time (2.51 s) as compared to S2 and S1. Similarly, top and bottom absorption rates, maximum wetted area and spreading speeds of S3 are higher than S2 and S1. It is due to two possible reasons. The first important reason is the covering of TiO_2 nanoparticles with -OH groups. The amount of these groups further increases on exposure to sunlight which contains UV [33]. Due to hydrophilic nature of -OH groups, the nanoparticles treated sample becomes highly hydrophilic. The second reason is the capillarity. The deposition of nanoparticles on fabric also generates the submicron spaces between them which act as capillaries. The water moves quickly through these capillaries in all directions. It passes across the fabric as well as spreads over the surface. Due to aforementioned reasons, the S3 has better overall moisture management capability (OMMC) as compared to S2 and S1.

Ultraviolet Protection Properties

UV-protection property of samples was tested according to AATCC 183-2000 standard testing method. Table 2 shows the results of UV protection factor (UPF), percentage blocking of UVA and UVB of cleaned, caustic soda-treated, seeded and nanoparticles-treated samples. Cleaned and caustic soda treated samples showed lowest UPF and UVA and UVB blocking percentage as compared to all other samples. Seeded sample provided very high UPF and UV blocking percentage. TiO_2 nanoparticles treated sample showed 100 % UVA and

Table 1. Moisture management results

Sample	Wetting time top (sec)	Wetting time bottom (sec)	Top absorption rate (%/sec)	Bottom absorption rate (%/sec)	Top max wetted radius (mm)	Bottom max wetted radius (mm)	Top spreading speed (mm/sec)	Bottom spreading speed (mm/sec)	OMMC*
S-1	7.15	25.23	32.34	43.34	8	10	5.98	0.75	0.39
S-2	4.79	6.32	33.63	50.14	22	22	2.93	2.99	0.51
S-3	2.51	2.55	52.42	53.09	30	30	12.69	9.30	0.62

*Overall moisture management capacity, S-1=cleaned sample, S-2=caustic treated sample, S-3=nanoparticles treated sample.

Table 2. UV-protection results for various samples

Sr. No.	Sample name	Mean UPF	UVA blocking (%)	UVB blocking (%)
1	Cleaned sample	46.95	86.3	99.2
2	Caustic treated sample	49.1	86.9	99.3
3	Seeded sample	338	97.7	99.8
4	Nanostructures functionalized sample	*	100	100

*UV-protection of nanoparticles treated sample was so high that it was beyond the range of the instrument.

UVB blocking ability. The UPF of this sample was so high that it was beyond the upper limit of instrument measuring capability.

The results show that UV protection of nanoparticles treated fabric is due to combined effect of textiles as well as TiO_2. The interaction of light with textile is quite complex. A part of incident light is reflected while some is scattered and absorbed. Due to this, only a small quantity of light is able to pass through the fabric which is revealed here in this study that cleaned and caustic soda treated samples have more than 85 % blocking of UVA and UVB. The UV absorption is the natural property of titanium dioxide. TiO_2 is a kind of semiconductor oxide with a large band gap between its low-energy valence band and its high-energy conduction band. On illumination, the electrons in conduction band jump to valence band due to absorption of UV light. These excited electrons and holes then result in two competing consequences: either combining with other holes or electrons, or being captured by the absorbents surrounding TiO_2 and initiating reduction and oxidation reactions. The combining of electrons and holes is the mechanism of UV protection of TiO_2 [27]. The combined effect of textile and TiO_2 provide excellent UV protection against UVA and UVB with very high UPF.

Photocatalytic Effect

Figure 6 represents the absorbance of solution during the course of UV irradiation. The absorbance decreases with the passage of time which indicates that the concentration of dye in solution decreases due to photocatalytic degradation. To check the UV fastness of dye, an untreated sample was placed in the dye solution and exposed to UV light. It was observed that the dye had good fastness properties as there was no significant decrease in absorbance after 24 hours (Figure 6).

The fastness properties of the treated fabric were characterized using repeated solution discolorations with the same sample. After each discoloration, the degraded solution was drained and new solution was added. Figure 7(A) shows the results of repeated discolorations of dye solution. The time to decolorize solution increases after first and second turn. This is due to the deposition of degraded dye on fabric as it was not rinsed after each discoloration to remove degraded products. This deposition blocks some sites of TiO_2 which caused slower degradation of dye. The treated sample also has good washing fastness properties. Figure 7(B) shows that there is no significant reduction of solution discoloration

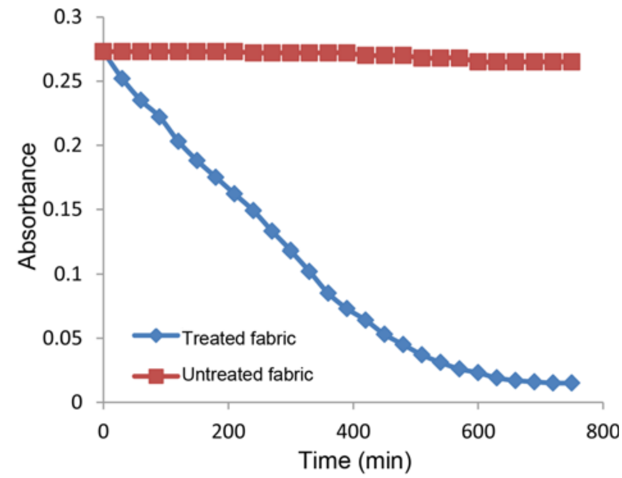

Figure 6. Absorbance evolution of dye solution during UV irradiation.

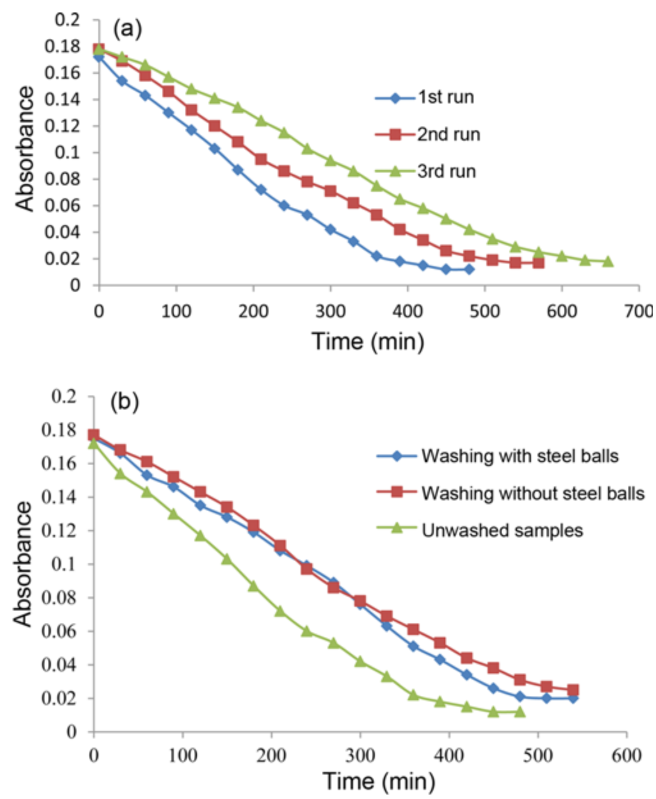

Figure 7. (A) Repeated discoloration of solution with same TiO_2 treated sample and (B) discoloration of solution by treated sample before and after washing tests.

ability of treated samples after washing in the presence of steel balls and without them. This shows that the treated sample has good washing fastness properties.

Conclusion

The TiO_2 nanoparticles have been successfully deposited on polyester fabric using *in situ* technique. The treated samples showed excellent UV protection and photocatalytic self-cleaning properties as well as good moisture management capability. The multi-functional properties obtained were found quite durable to washing. However, it was found that the caustic soda pre-treatment followed by a pre-seeding step was important for better deposition of the nanoparticles in the subsequent step. In the future work, the authors are investigating different possibilities to make the nanoparticle deposition process more efficient by reducing the number of steps involved.

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