SELF-CLEANING PROPERTIES OF COTTON FABRICS COATED BY Zn DOPED-TiO_2 THIN FILMS

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ABSTRACT
In this study, self-cleaning properties of cotton fabrics coated with zinc (Zn) doped and undoped TiO_2 thin films by sol-gel technique were investigated. As to this aim, Zn doped and undoped TiO_2 films were coated on cotton fabrics from the solutions prepared from Zn, Ti-based precursors, solvent and chelating agent at low temperature in air using sol-gel technique. In order to determine solution characteristics, which affect thin film structure, turbidity properties and pH values of the prepared solutions were measured by turbidimeter and pH meter, respectively. The microstructural properties of the coatings were characterized by using scanning electron microscopy (SEM). In addition, add-on values, whiteness values as Stensby, tensile strength, wash fastness, wettability and self-cleaning properties of the coated fabrics were determined by standard add-on value calculation, Minolta CM-3600d spectrophotometer, Instron 4411 Universal strength tester, Linitest plus apparatus, KSV Cam 100 instrument and UV/Vis spectrophotometer (Lambda 35, UV/VIS spectrometer, PERKIN ELMER) and visual evidence, respectively. In conclusion, the self-cleaning cotton fabric was fabricated using sol-gel processing. Zn doping in TiO_2 film improved the self-cleaning properties of the cotton fabric compared to Zn undoped-TiO_2 film.

Key Words: Sol-gel technique, self-cleaning, coating, cotton fabric

1 INDTRODUCTION
In recent years titanium dioxide-based films have been the subject of significant research for self-cleaning of various materials. Of particular interest here is the use of titanium dioxide based films on glass for self-cleaning purposes. Such films are typically dependent upon two phenomena for their desired self-cleaning behavior; photocatalytic activity and wettability (superhydrophilicity or superhydrophobicity). Of particular focus in this study is photocatalytic activity; in which for this system can be summarized with the following chemical reaction:

$$\text{Organic} + O_2 \xrightarrow{h\nu \geq E_{bg}(TiO_2)} CO_2 + H_2O \quad (1)$$

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with TiO_2 having an overall bandgap of approximately 3.2 eV, therefore requiring UV-light for the above photocatalytic reaction to proceed. Ultra-bandgap light, when coming in contact with the TiO_2 surface, produces photogenerated electrons and holes, with electrons reducing oxygen to water and holes oxidizing the organic. It has been suggested that oxidation reaction involves first oxidation of surface hydroxyl groups (OH–) to hydroxyl radicals (OH**.**), which in turn oxidize the organic reactant. However, although titanium dioxide photocatalysis has been studied for a number of years it is still not clear if the oxidation of the organic in Eq. (1) is the result of direct reaction with photogenerated holes, indirect reaction with hydroxyl radicals (OH**.**), or a combination of both [1].

Crystalline TiO_2 possess several applications such as photocatalyst, photovoltaics, UV-absorber, gas sensors and electrochromic display devices due to its photocatalytic activity and optic properties. Particularly, TiO_2 exists in three crystal forms including anatase, rutile and brookite, and amourphous structure. Of these crystalline forms, anatase phase of TiO_2 has the highest photocatalytic activity. Thus interest of photocatalytic activity of the anatase has been recently grown. Photocatalytic activity means decomposition of organic and inorganic pollutants under the ultraviolet (UV) light. It was an interesting point that there is a good relationship between the absorption intensity of UV radiation and the activity of the catalysts. The stronger the UV-absorption intensity of the crystal TiO_2, the higher the photocatalytic activity was [2]. Nevertheless, due to the fact that it is necessary to use high temperatures of 500–550 ^oC to produce these films, the production of photocatalytic TiO_2 films should be deposited at low temperatures on plastics and textiles that can not withstand high temperature treatment. W.A. Daoud et al. [3] produced the TiO_2 thin films on cotton fabric by sol-gel process at low temperature, e.g.150 ^oC, and they determined that the UV-protective factor (UPF) rating of the fabrics increased from 10+ UPF to 50+ UPF corresponding to excellent protection (see Table 1). It is necessary to obtain a good wash fastness of the coated textiles especially because textiles expose the much more times washing during wearing. Hence, they found to be withstand against 20 [3] and even 55 [4] home laundering of the applied the process to cotton fabrics in literature [5]. Therefore, it has strived up to now that mostly TiO_2 particles were bonded to fabric with organic binder or by mixing in detergents. By developing sol-gel technologies at the last years, it has been determined that the TiO_2 films were coated on fabric through Ti-based solutions without using organic binder and their UV-protective properties were improved. However the UV protective properties of the Zn-doped TiO_2 coated fabrics have not been investigated yet. It is possible to produce the higher UV protective properties of coated fabrics with Zn-doped Ti based solution together with higher washing fastness properties and the using of the less amounts of chemical agents.

This paper devoted to the research of 2.68 % Zn-doped TiO_2 films prepared on cotton fabrics from solutions of Ti isoproxide, $ZnCl_2$, isopropanol and glacial acetic acid by using sol-gel technique without organic binder in order to improve their UV-protective, photocatalytic (self-cleaning) and washing fastness properties. According to this aim, turbidity and pH measurement of the prepared Ti and Zn based solutions were carried out. Surface morphology of the produced films was investigated using Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDS). The thickness, refractive index and band gap values of the produced films on glass was investigated using refractometer and spectrophotometer devices to estimate real thickness on fabric. In addition, wash fastness, UV-protection factor, whiteness value and contact angle of the coated fabrics were determined.

2 EXPERIMENTAL DETAILS

2.1 Nanosol preparation

To reach the aim of the study, nanosol solutions were prepared as flow chart on Figure 1. Zn-doped TiO_2 films were synthesized with the solutions which were prepared as follows. The Zn and Ti based precursors were weighted out in fume hood. Isopropanol (C_3H_8O) (Riedel, 99%) as solvent and glacial acetic acid (CH_3COOH) (Aldrich, 97%) as chelating agent were mixed in the powder form of $ZnCl_2$ precursor chemical agent (Horasan Chemistry, 98%). After this solution was stirred at room temperature for 30 min in air, the liquid form of titanium isopropoxide ($Ti(OC_3H_7)_4$, Alfa Easer, 97%) was added by droping to this solution. The obtained solution was stirred as to obtaining the transparent solution for 3 hours. The contents of the Zn in the solutions were x = 2.68 percent of atomic ratio (Zn:Ti mole ratio 1:50), where x was calculated as formula of x=[Zn/(Ti+Zn)]x100. The stability of the process is set by control of the hydrolysis and condensation reactions such that while the solutions are being dried, the solvent is lost or the temperature is elevated.

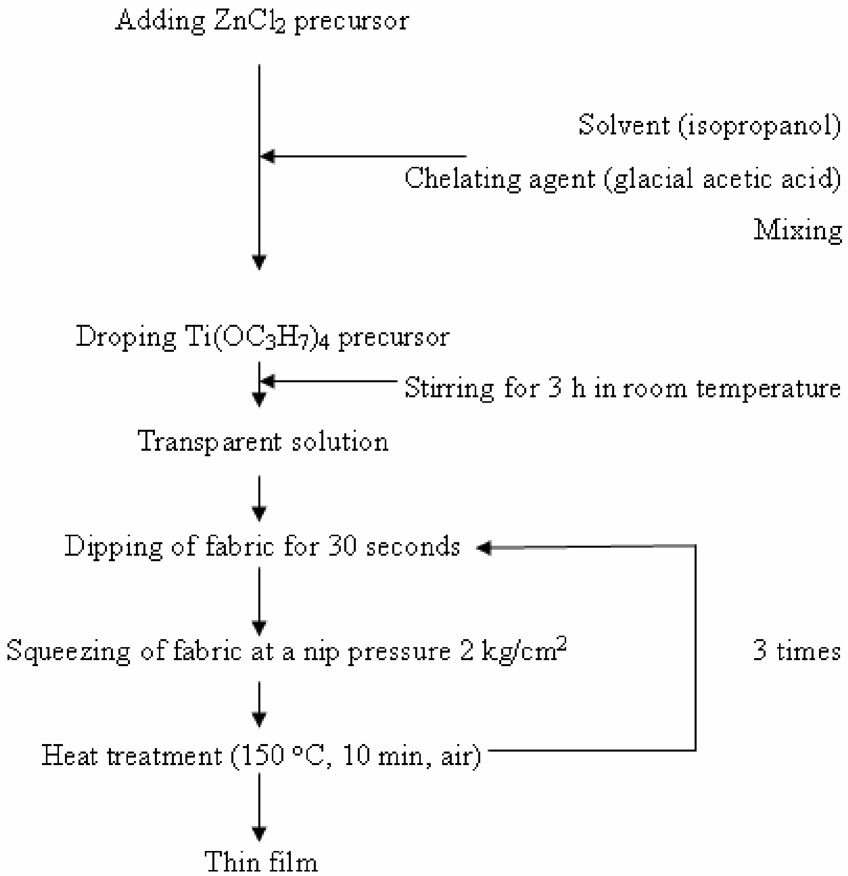

Figure 1. The diagram of flow chart for sol-gel process.

2.2 Solution characterization

In order to determine solution characteristics which affect thin film structure, turbidity and pH values of the prepared solutions were measured.

2.3 Coating process

A 40x10 cm dimensioned cotton fabric, which desized, scoured and bleached, (weft density of 22 yarn/cm, warp density of 26 yarn/cm, a weight density of 138 g/m^2) was dipped at 25°C for 30 sec into the solutions and then padded fabrics were squeezed twice using an Fulard (Model P-A1, Labortex) for 100 % A_F (pick-up) at a nip pressure of 0.75 kg/cm^2. We repeated this procedure for three layers. Then the padded fabrics were cured at 150 °C or 10 minute using a preheated oven (Nüve KD400 Oven) (see Figure 1 for details).

2.4 Film characterization

Prior to deposition of cotton fabrics, Zn-doped TiO_2 films with single layer on the glass substrates were carried out by the sol-gel drop-coating method. The coated glass substrates were dried at 300 °C for 10 min and then sintered at 500 °C for 1 h in oven [6]. Film thickness and band gap values of the produced Zn-doped and undoped TiO_2 films were evaluated using refractometer and spectrophotometer machines. Refractive indexes of thin films were measured in the VIS region by a high-accuracy Abbe refractometer at room temperature.

2.5 Textile characterization

In order to better understand textile properties of the coated fabrics, add-on value, wash fastness, UV-protection factor, whiteness value, contact angle, tensile strength and self-cleaning properties of the coated fabrics were investigated. The add-on values of the coated fabric were calculated according to Eq. 2.

$$W_{add-on}(\%) = \frac{W_2 - W_1}{W_1} x100 \quad (2)$$

where W_1; of the dry weight of the untreated fabric, W_2; of the dry weight of the treated fabric and W_{add-on}; of the add-on value of the untreated fabric. The wash fastnesses of the samples were determined according to BS EN ISO 105- C06- A1S standard (without balls) by the using Linitest plus apparatus (Atlas, Germany). Washing processes were achieved as three times and ten times. The microstructures of coated fabrics were studied by the using of SEM (JSM–6060 JEOL Model), operating with 3 kV with X2000 magnification. The UV-protective characteristics of the coated fabrics were determined according to AS/NZS 4399:1996 by using Camspec M350 UV/Visible spectrophotometer. The whiteness values of prepared fabrics were determined by the using Minolta 3600d spectrophotometer. The contact angle of the fabrics was determined using KSV CAM 100 Instruments order to determine the properties of water repellent of fabrics. The tensile properties (in warp direction) of treated and untreated fabrics were determined by using an Instron 4411 tester according to ASTM D5035-90 (strip test). Self-cleaning properties of the coated fabrics was evaluated by visual evidence based on photo-induced discoloration of red wine stains on Zn-doped and undoped TiO_2 coated cotton textiles. UV/Vis absorption spectra of reaction products of methylene blue solutions photocatalyzed by TiO_2-based thin films on glass substrate were recorded by using UV/VIS spectrometer. Since the methylene blue ($C_6H_{18}ClN_3S{\cdot}2H_2O$, Merck) is a dye used as an oxidation– reduction indicator, it can be activated by light to an excited state which in turn activates oxygen to yield oxidizing radicals as demonstrated in Zeman and Takabayashi [7]. The produced TiO_2 films with single layer on the glass substrates were immersed in methylene blue solution of 2 ppm for 3 h under sunshine. The coating surface covered with methylene blue was irradiated with visible light. This process was repeated for both Zn-doped and undoped TiO_2 film.

3 RESULTS AND DISCUSSION

3.1 Solution characteristics

Turbidimetric measurements have been used to reveal the completely dissolution of powder based precursors in the solutions. Their turbidity values of Zn doped and undoped Ti based sols were found as 0.31 and 0.13 ntu respectively, indicating that powder based chemical precursors were completely dissolved in the solutions. By adding $ZnCl_2$ powder to the solutions, no significant change of the turbidity is observed. Now that pH value of titania sols is an important factor influencing the formation of the polymeric three-dimensional structure of the gel during the gelation process, it should be taken into consideration while preparing solutions. While ramified structure is randomly formed in acidic conditions, separated clusters are formed from the solutions showing basic characters as explained in Ref. [8]. The pH values of Zn doped and undoped Ti based sols have mild acidic of pH value as 4.1 to 4.7 respectively and Zn doping did not significantly change the acidity of the titania sol.

3.2 Film characteristics

3.2.1 Microstructural properties

SEM images of untreated and treated fabrics with Zn doped and undoped Ti based sols were taken. The presence of TiO_2 layer on fiber surfaces could be observed at SEM images of treated fabric with Zn doped and undoped Ti based sols. Moreover it was observed from SEM images of the coated fabric with each film that the cracks formed on the surface of fiber and the micrometer ordered particles on the fiber surface occurred as coating islands. The mean thickness of the fibers determined to be 13 μm by using SEM. What is the increasing amount of the thickness of fiber of coating was not determined so that the thickness of fiber has quite variations in fabric. The refractive index, thickness and band gap values of the films on glass substrates were determined. The refractive index of the prepared films with Zn doped and undoped Ti based sols on glass substrate were measured as 1.6116 and 1.6156 respectively. Film thicknesses of the coated fabrics were estimated by using optical technique. Hence the thicknesses of Zn-doped TiO_2 films on cotton fabrics were roughly estimated before textile application. The thicknesses of Zn undoped and Zn-doped TiO_2 films were respectively measured as 373 nm and 238 nm using optical method after a layer deposition. The thickness of the film can be modified and the roughness could be improved by appropriate changes of the preparation conditions of the solutions and of the deposition procedure. TiO_2 have an overall bandgap of approximately 3.2 eV, therefore requiring UV-light for the photocatalytic reaction to proceed [1]. The band gap values of our produced thin films based on Zn doped and undoped TiO_2 on glass were determined 3.2713 and 3.2429, respectively.

3.3 Textile characteristics

3.3.1 Self-cleaning properties

Figure 2 shows the images of the untreated, treated with Ti based sol, treated with Ti based sol and then washed with 10 times, treated with Zn doped Ti based sol, treated with Zn doped Ti based sol and then washed with 10 times fabrics stained with red wine and then waited under sunshine for 3 h. The fabric treated with Zn doped TiO_2 sol, which stained with red wine and waited under sunshine for 3 h, shown the higher whiteness index value (66.176) as Stensby and lower yellowness index value as 16.951 for ASTM D 1925 and 13.590 for ASTM E 313 standards. Zn doping was increased slightly whiteness values of the fabric treated with TiO_2 sol.

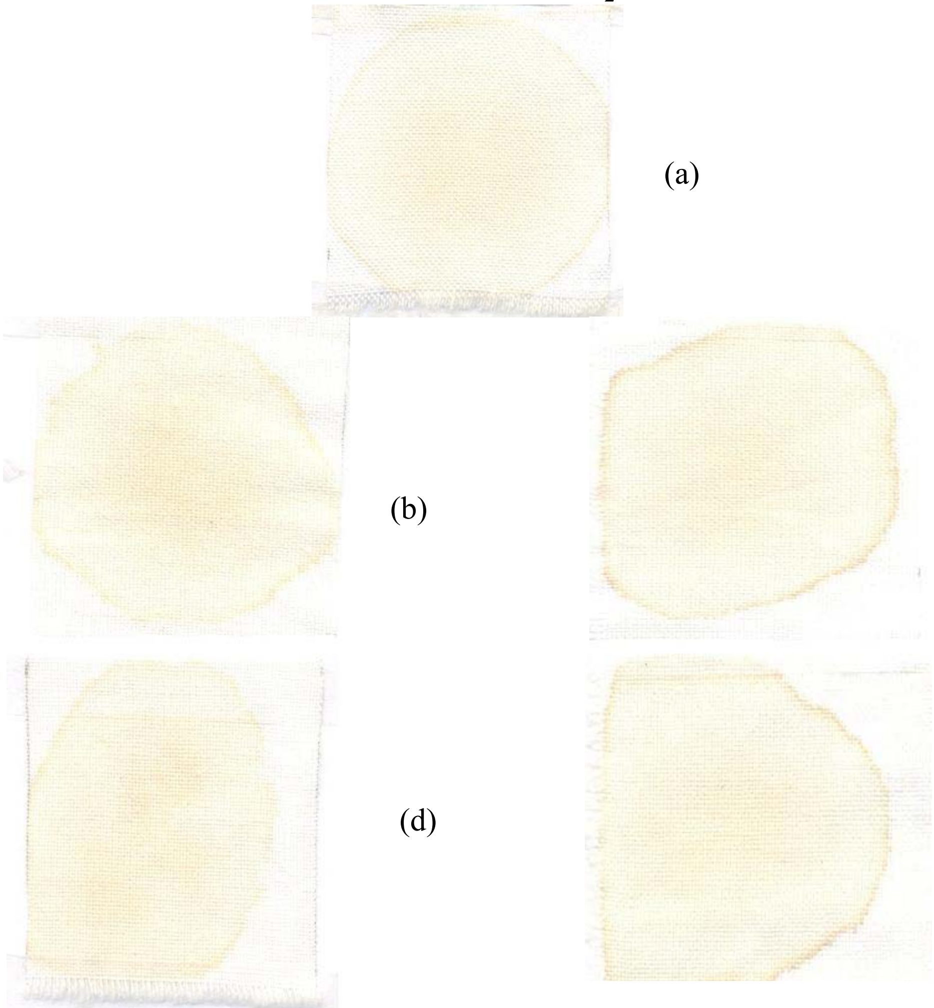

Figure 2. The images of the untreated (a), treated with Ti based sol (b), treated with Ti based sol and then washed with 10 times (c), treated with Zn doped Ti based sol (d), treated with Zn doped Ti based sol and then washed with 10 times (e) fabrics stained with red wine and then waited under sunshine for 3 h.

3.3.2 UV protective characteristics of the treated fabrics

The UPF has been proposed as a parameter for the UV protection of fabrics. As with sunscreens, this protection factor will mainly indicate the degree of protection against UV. Our study has attempted to determine whether a fabric with a high UPF value could offer an adequate protection in the UV light range. It was determined that the both fabrics treated with Zn doped and undoped Ti based sols have 10+ UPF rating with increasing as 10 degree than the untreated fabric (0). These fabrics subsequently washed with 10 times gave 15+ UPF rating corresponds to good protective factor according to relevant standard. Furthermore, it was considered that the silicate forms contained on the composition of ECE Phosphate Reference Detergent (B) as BS EN ISO 105- C06-

A1S standard could increase the UV-protective ratings of the fabrics after multiwashing. It was observed that the rated UPF values of the treated fabrics with Zn doped and undoped Ti based sols before and after washing with 3 and 10 times in Table 1.

Table 1. Rated UPF of untreated fabric and treated fabrics before and after washing with three times and with 10 times

	Ultraviolet Protection	**Blank fabric**	**Coated fabric with TiO_2 sol**	**Coated fabric with Zn doped TiO_2 sol**
Before washing	Rated UPF	0	10	10
	Mean UVA (315 to 400 nm)	45.0 %	20.0 %	19.2 %
	Mean UVB (290 to 315 nm)	37.1 %	7.2 %	6.4 %
After washing with 3 times	Rated UPF		15	15
	Mean UVA (315 to 400 nm)		12.1 %	15.7 %
	Mean UVB (290 to 315 nm)		4.4 %	3.7 %
After washing with 10 times	Rated UPF		15	15
	Mean UVA (315 to 400 nm)		16.2 %	15.5 %
	Mean UVB (290 to 315 nm)		4.4 %	3.9 %

3.3.3 The tensile strength of the fabrics

A slightly increase on tensile strength and extension of fabric treated with Zn-doped and undoped TiO_2 solutions could be observed from 63.65 to 68.75 and 70.17 kgf as well as from 46.45 to 52.70 and 51.05 % respectively.

3.3.4 Add-on value

The add-on values of the treated fabrics with Zn doped and undoped Ti based sols were 4.72 and 4.46 % respectively. Of these values, add-on value of the treated fabric with Zn doped Ti based sols was slightly higher than that with Zn undoped Ti based sols.

3.3.5 Contact angles on the fabric

To evaluate the hydrophobic properties of fabrics, the contact angle measurements were performed on the fabrics. The water drop sink into the untreated cotton fabrics in short time less than 20 seconds, thus in this case the contact angle was not detectable. After treatment with Zn doped and undoped Ti based sols, the contact angles of fabrics increased to the degree of 147^o. Figure 3 shows the image of contact of water on treated fabric with Ti based sol. While the untreated cotton fabrics have got hydrophilic property, the fabrics which treated with Zn doped and undoped Ti based sols have got hydrophobic property. The contact angles on treated fabrics after washing with 10 times were not detectable. It was concluded that there was not durability of the treatment against multiwashing.

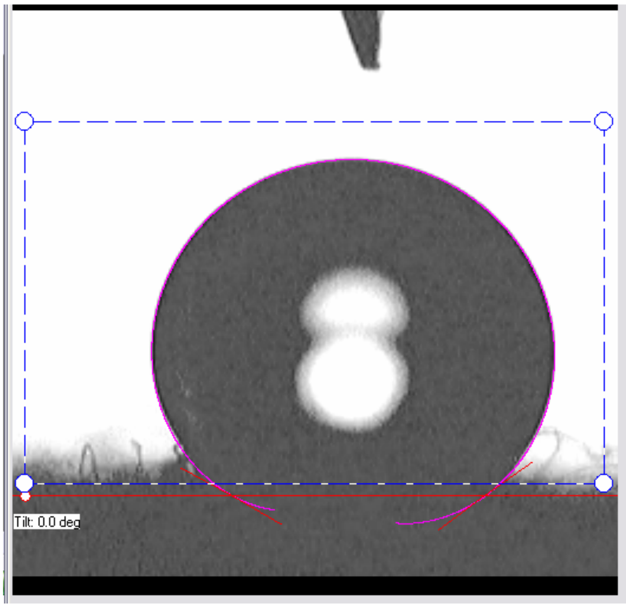

Figure 3. The contact image of water on cotton fabric treated with Zn undoped Ti based solution.

4. Conclusions

In this study, self-cleaning properties of treated fabrics with Zn doped and undoped Ti based sols by using sol-gel technique were investigated. In conclusion, the self-cleaning cotton fabric was fabricated by using sol-gel processing. The self-cleaning properties of treated fabric with Zn doped Ti based sol slightly improved in comparison with the properties of treated fabric with Zn doped Ti based sol. Multifunctional cotton fabrics including UV-protective, self-cleaning and water repellent properties were developed in our study. However there were not durability of the treatment against multiwashings with regard to self-cleaning and water repellent properties.

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