Cellulose (2016) 23:2143–2159
DOI 10.1007/s10570-016-0916-z

ORIGINAL PAPER

Microwave-assisted TiO_2: anatase formation on cotton and viscose fabric surfaces

Patrycja Giesz · Grzegorz Celichowski · Dorota Puchowicz · Irena Kamińska · Jarosław Grobelny · Damian Batory · Małgorzata Cieślak

Received: 4 February 2016 / Accepted: 20 March 2016 / Published online: 28 March 2016

Abstract The method of TiO_2-anatase film preparation on cotton and viscose fabric surfaces using the sol-gel process and microwave treatment is presented. Microwave treatment was used to change the amorphous TiO_2 form to anatase directly on the fabrics. The influence of microwave treatment conditions on the obtainable polymorphic form of TiO_2 was examined. Fabrics were pretreated with low-temperature air plasma (30 min). The root mean square height in the selected area increased from 44 to 166 nm (cotton) and from 9 to 112 nm (viscose). Infrared analysis showed the new band at 1748 and 1732 cm^{-1} corresponding to C=O stretching for plasma-treated cotton and viscose textiles, respectively. The plasma pretreatment also improved the wetting properties by TiO_2 sol and increased the surface free energy of fabrics. TiO_2 film thickness was 180 nm (12 %wg. Ti) and 140 nm (3 %wg. Ti) for cotton and viscose, respectively. TiO_2-modified cotton reduced the nicotine concentration three times more and TiO_2-modified viscose was two times higher under sunlight compared to raw fabrics. No changes in strength were observed for TiO_2-modified cotton, while the strength of TiO_2-modified viscose decreased about 45 %. No effect of UV irradiation on cotton and a slight reduction of the strength of raw viscose (7 %) and TiO_2-modified viscose (16 %) were observed. The Ti contents after washing decreased from 12 to 11 % (cotton) and from 3 to 2.6 % (viscose). The presented method allows obtaining TiO_2 film-anatase on the cotton and viscose fabrics, but its total effectiveness is better for cotton fabrics.

Keywords Microwave · TiO_2 · Sol-gel · Plasma · Cotton · Viscose

P. Giesz · D. Puchowicz · I. Kamińska · M. Cieślak (✉)
Scientific Department of Unconventional Technologies and Textiles, Textile Research Institute, 5/15 Brzezińska St., 92-103 Lodz, Poland
e-mail: cieslakm@iw.lodz.pl

P. Giesz · G. Celichowski · J. Grobelny
Department of Materials Technology and Chemistry, Faculty of Chemistry, University of Lodz, 163 Pomorska St., 90-236 Lodz, Poland

D. Batory
Institute Materials Science and Engineering, Lodz University of Technology, 1/15 Stefanowskiego St., 90-924 Lodz, Poland

Introduction

Titanium dioxide (TiO_2), especially in the anatase phase applied to the modification of textile materials, provides new properties such as photocatalytic, self-cleaning, bioactive, UV protective, superhydrophilic, antibacterial, flame retardant, etc. (Radetic 2013; Karimi et al. 2014; Morawski et al. 2013; Qi et al. 2006; Ibrahim et al. 2010; Karimi et al. 2010, Abidi et al. 2009). There are many methods to modify

materials with TiO_2; some of them require post-heat treatment to induce crystallization, e.g., the sol-gel method. At low temperature, it can be distinguished hydrothermally (Zhang et al. 2012) or using the sonochemical method (Behzadnia et al. 2014a, b). Both methods allow obtaining TiO_2 film in crystalline form. In the hydrothermal method, a long aging period is necessary to obtain the crystalline TiO_2 form. The sonochemical method was used to produce multifunctional wool fabric using titanium isopropoxide or butoxide in acidic media. Another method is the application of a TiO_2 dispersion or Ag-doped TiO_2 in the anatase form to the modification of the fibers and wovens surface (Cieslak et al. 2009). The most popular, fast, effective and easy method of producing TiO_2 thin films is a sol-gel method, but one of the disadvantages is the annealing post-treatment at high temperature (near 500 °C) to transform amorphous TiO_2 to the anatase form (Cieslak et al. 2015; Tung and Daoud 2011; Kadziola et al. 2014). Such treatment limits the ability to create films on textile substrates with low thermal resistance, such as cotton, viscose, wool, polypropylene, polyamide, polyester fibers, etc. (Liu et al. 2007). The microwave treatment is one of the methods in which TiO_2 in anatase form can be enhanced at lower temperature (below 200 °C). The application of microwave treatment may be useful for the modification of low-thermal-resistance textile materials. Some approaches using microwave treatment to obtain crystalline TiO_2 have been reported (Liu et al. 2007; Wilson et al. 2002; Vigil et al. 2001). Liuxue et al. (2007) obtained TiO_2 anatase on cotton fibers prepared via a microwave-assisted liquid-phase process with hexafluorotitanate as precursor. Microwaving improved the hydrolysis of the precursor and led to highly crystalline anatase at low temperature. Similar studies were carried out by Peiro et al. (2001), but the TiO_2 anatase film was deposited on glass substrates and silicon wafers. Li et al. (2010) prepared silver-modified TiO_2 via a microwave-assisted method. All papers presented the process of TiO_2 preparation and/or deposition on film during the microwave treatment. In this study, we show another method in which fibers with TiO_2 film (prepared using the sol-gel technique earlier) were only treated with microwaves to transform TiO_2 to the anatase form.

Materials

To prepare TiO_2 sol, titanium (IV) isopropoxide Ti(OC3H7)4 (TTIP, 97 %, Aldrich) as a Ti precursor, isopropanol (99.5 %, POCH S.A.) and hydrochloric acid (Chempur) were used. TiO_2 sol was applied to plain-woven cellulose fabrics whose characteristics are given in Table 1.

TiO_2 film was also applied on silicon (Si) wafer 100 (Cemat Silicon S.A.) with a thickness of 320–380 μm as a reference substrate material.

Methods

TiO_2 thin film preparation

Titanium dioxide was prepared based on a sol-gel technique using Ti—titanium tetraisopropoxide as precursor. To the solution containing 1.2 g (0.00422 mol) TTIP in 13.2 g (0.22 mol) of isopropanol, 0.04 g (0.0011 mol) of hydrochloric acid (HCl 2 mol/l) was added dropwise. The prepared sol was stirred 30 min before deposition on the fabric samples and Si wafers. The surfaces of cotton and viscose fabrics were pretreated in low-temperature air plasma (45 W, 15.26 MHz, Zepto) for 30 min. TiO_2 sol was applied on the pretreated substrates by dip-coating technique using an NIMA dip coater (Technology LB, UK) with a constant rate of 25 mm/min. After the sol deposition, fabrics and Si wafers were dried at room temperature for 48 h. Next, the samples were placed in vessels filled with distilled water and treated with microwaves (MWs) using an Anton Paar Synthos microwave reactor. After the MW treatment, the samples were dried at room temperature. Different MW treatment conditions were tested (various powers and heating times), and the results of two selected conditions are presented in this article (MW power and heating time 650 W, 15 min at $T = 180$ °C and 500 W, 10 min at $T = 110$ °C) (Fig. 1). MW treatment was only used for conversion of the TiO_2 amorphous form deposited on the fabric surface to TiO_2 anatase.

Characterization

A thermogravimetric analysis (TGA) of viscose and cotton fabrics was carried out using a TG 209F1 Libra analyzer (Netzsch, Germany) with a heating rate of

Table 1 Characteristics of the studied fabrics

Fabric composition (%)	Weave	Mass per unit area (g/m^2)	Pick and end densities (1/cm)	
			Warp	Weft
Cotton 100	Plain	108	43	32
Viscose 100	Plain	104	45	25

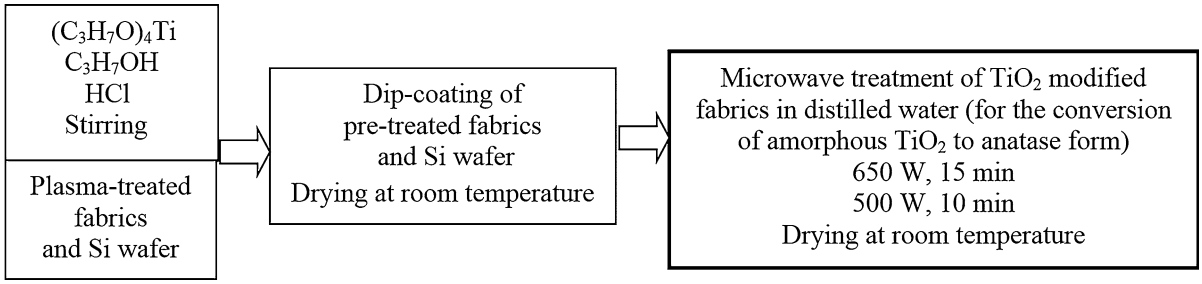

Fig. 1 Flowchart of thin TiO_2 layer preparation on fabrics and Si wafers

10 °C min^{-1} under a nitrogen flow rate of 20 ml min^{-1} over the range of 30–700 °C. The samples (4.0 ± 2 mg) were tested in a ceramic crucible. The initial (T_{Onset}) and final (T_{End}) temperature of degradation, temperature at peak maximum degradation ($T_{Max\ Peak}$) and loss of mass were evaluated. Fabrics were pretreated in low-temperature air plasma (50 W, Zepto) for 30 min. The surface morphologies of fabrics and Si wafers were studied with a scanning electron microscope (SEM) (Nova NanoSEM 450, FEI, USA). The thickness of the TiO_2 coating on the fiber surfaces was evaluated on the basis the SEM images of fiber cross sections. The elemental composition analysis and maps of Ti distribution were performed with an X-ray microanalyzer (INCA Energy EDS, Oxford Instruments Analytical, UK) connected to a Vega 3 SEM (Tescan, Czech Republic). The 3D SEM images were prepared using Alicona MeX software connected to a Vega 3 SEM. FTIR analysis of textiles before and after plasma treatment using the Thermo Scientific Nicolet iS50 FT-IR equipped with a Golden Gate ATR accessory with 4-cm^{-1} resolution was made. Raman spectra and mapping analyses of modified fabrics were performed using a Raman Renishaw InVia dispersive spectrometer (Renishaw, UK) with infrared $\lambda = 785$-nm laser excitation. The phase composition of the examined samples was measured using the X-ray diffraction technique. In the investigation, an Empyrean diffractometer (PANalytical) working in grazing incidence (GIXRD) mode with Co Kα (1.78901 A) radiation was used. The incidence angle (omega) was set to 2°. Further data processing was done using the ICDD PDF 4 database and HighScore Plus software. To evaluate the impact of plasma treatment on the surface free energy (SFE) of fabrics and the wettability of fabrics by TiO_2 sol, the contact angle was measured using the Drop Shape Analyzer (Krüss GmbH DSA 100, Germany) and three non-reactive standard liquids (droplet size of 5 µl): distilled water ($\gamma_l = 72.8$; $\gamma_l^d = 21.8$; $\gamma_l^p = 51.0$), diiodomethane ($\gamma_l = 50.8$; $\gamma_l^d = 48.5$; $\gamma_l^p = 2.3$) and formamide ($\gamma_l = 58.0$; $\gamma_l^d = 39.0$; $\gamma_l^p = 19.0$). On the basis of the obtained contact angle values, the SFE was calculated using the Owens–Wendt model (Owens and Wendt 1969; Cieslak et al. 2012). In this model, the SFE is calculated from the geometric mean of dispersion and polar interactions between the solid and liquid, according to Eq. (1):

$$\gamma_l(1+\cos\theta) = 2[(\gamma_l^d\gamma_s^d)^{1/2} + (\gamma_l^d\gamma_s^d)^{1/2}] \text{ and } \gamma_s = \gamma_s^d + \gamma_s^d \quad (1)$$

where θ is the contact angle, and γ_s^d, γ_s^p, γ_l^d and γ_l^p are the dispersion (^{d}) and polar (^{p}) components of the surface free energies of the solid ($_s$) and liquid ($_l$), respectively. The reversible work of adhesion (Wa) of the fabric and water was calculated using Dupre's Eq. (2) (Dupre 1869):

$$\text{Wa} = \gamma s + \gamma l - \gamma sl \quad (2)$$

where γs is the surface free energy of the solid, γsl is the solid/liquid interface tension, and γl is the surface free energy of the liquid.

The photocatalytic properties were tested by the decomposition of nicotine adsorbed on cotton and viscose fabrics modified with TiO_2-anatase. The testing was performed at 21 ± 2 °C on the test stand as previously described (Cieslak et al. 2009; Cieslak et al. 2014). Briefly, ten samples of each fabric type were hung in a chamber (40 dm^3) and the chamber air was evacuated; 5 µl of nicotine (Fluka 72290, CAS 54-11-5, puriss. p.a. >99.0 %) was injected into a *U*-shaped tube placed in the bath warmed up to 250 °C, and nicotine vapor was supplied in a stream of air into the chamber. The chamber was protected from light with a black cover. After 24 h, two samples of each fabric type were removed from the chamber and subjected to chromatographic analysis to assess the initial concentration of nicotine. The rest of the samples were placed on a frame attached to the window and exposed to sunlight. Two sensors (CMP 3 and CUV 4, Kipp and Zonen B.V.) were used to measure the light intensity, which was in the 310–2800 nm and 305–385 nm range, respectively. Periodically, two samples of each type were taken to determine the nicotine concentration. The total irradiation dose was 405.8 kJ/m^2.

Tensile strength tests before and after modifications of the fabrics and UV irradiation were performed according to standard PN-EN ISO 13934-1:2013-07 using an Instron 3367 machine. The fabrics were UV irradiated (305–385 nm) with the use of a Xenotest Alpha HE apparatus (Atlas) with a total irradiation dose (P) of 5184 kJ/m^2. Five repetitions were carried out for each fabric type, and the average values of the breaking force and breaking elongation were determined.

Washing of the TiO_2-modified samples was performed according to standard PN EN ISO 6330:2012, procedure 4 N, method A. The Ti contents of samples before and after washing were evaluated on the basis of the SEM/EDS analysis.

Results and discussion

On the basis of the thermal analysis (Fig. 2), it was noticed that the thermal decomposition of cotton and viscose started at 320.9 °C (T_{Onset}) and 293.5 °C (T_{Onset}) with the maximum ($T_{Max\ Peak}$) at 366.0 and 343.3 °C, respectively. Cotton fabric is thermally stable up to about 320 °C and viscose fabric up to 293 °C; above these temperatures, degradation of fabrics was observed. Therefore, the experiments were carried out at lower temperatures of 110 and 180 °C.

The nano-roughness of plasma-treated fabric surfaces was higher than that of the untreated fabrics (Figs. 3, 4, 5). An etching effect of plasma treatment and uniform surface structure of both fabrics without any cracks or damages were observed. The 3D SEM pictures (Fig. 5) clearly showed the changes in the surface structure of fibers after plasma treatment. A significant increase in their roughness was observed. The root-mean-square height of the measured area of 64 μm^2 increased from 44 to 166 nm and from 9 to 112 nm for plasma-treated cotton and viscose, respectively (Fig. 5). Such nano-topography changes on the fabric surfaces are also described in the literature (Navaneetha Pandiyaraj and Selvarajan 2008; Shishoo 2007; Mihailovic et al. 2011). The surface development can provide a new pathway for the TiO_2 sol and improve its application. According to Mirjalili et al. (2015), corona treatment of cotton improves the adsorption of TiO_2 nanoparticles and thus ensures stable properties of materials, e.g., self-cleaning. In addition, TiO_2 film on cotton with corona pretreatment is stable even after 50 washing cycles. In the research of Mihailovic et al. (2011), the amount of TiO_2 for air RF plasma-pretreated cotton increased about 31 % compared to untreated fabric. Corona discharge/air RF plasma resulted in an increase in the binding efficiency of TiO_2 nanoparticles.

The effect of plasma treatment of fabric in the studies differs for each type of fiber. In the case of cotton fibers (Fig. 3), these changes are characteristic of the morphology of the surface layer, including the primary topography (irregularities on the cotton fiber). The higher roughness of cotton allows increasing the surface area and the amount of TiO_2 deposition. The viscose fiber texture is very even, also in the longitudinal recesses, but more amorphous viscose causes susceptibility to plasma etching (Fig. 4) (Prysiazhnyi et al. 2013).

The FTIR spectra of untreated and plasma-treated fabrics are demonstrated in Fig. 6. All spectra show characteristic broad bands around 3339, 3340 and 3392 cm^{-1}, which correspond to alcoholic OH stretching, and bands around 2900 cm^{-1} and in the region 1455, 1430 and 1429 cm^{-1} due to CH_2

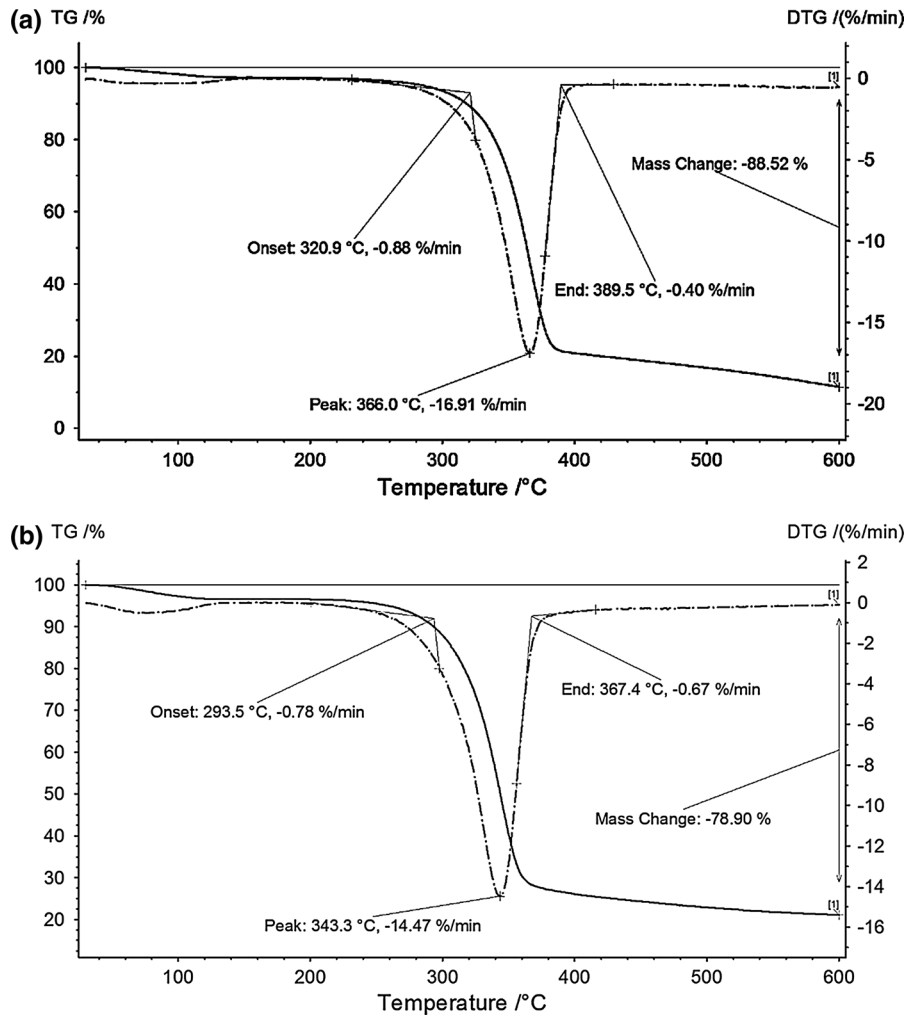

Fig. 2 TGA analysis of **a** cotton and **b** viscose fabrics

stretching and CH_2 bending, respectively. Carboxyl groups were noticed in the viscose and cotton plasma-treated samples with bands at 1732 and 1748 cm^{-1} (Fig. 6b,d) corresponding to C=O stretching. This proves that besides etching (confirmed by SEM analysis), surface oxidation of both fibers by plasma occurs. Also a higher intensity of bands was observed in the 1429–1061 cm^{-1} range. Bands near 1455–1061 cm^{-1} correspond to C–O stretching and in the range 1200–1400 cm^{-1} are O–H bending bands (Caschera et al. 2014; Ibrahim et al. 2012). Karahan and Özdoan (2008) did not obtain bands around 1740 cm^{-1} by atmospheric plasma treatment; however, they obtained this band by Ar plasma treatment. The FTIR results clearly show an increase in the intensity band at 3340 cm^{-1}, especially for cotton, which indicates the greater number of OH groups after 30-min plasma treatment. The more polar OH groups and the formation of new polar groups such as C=O (both of cotton and viscose) after plasma etching cause an increase in the hydrophilicity and the value of the surface free energy and adhesion properties. Similar observations were made by Kiwi and Pulgarin (2010). The increase in polar groups and roughness of the cotton surface during RF plasma treatment improved the effectiveness of the modification of the cotton surface with the nanomodifiers TiO_2 and Ag. After the plasma treatment of fabrics, a decrease in the contact angle was observed for all standard liquids. For water, the value of the contact angle decreased from 55° to 10° and from 50° to 7° for cotton and viscose fabric, respectively (Table 2). The values of SFE for cotton

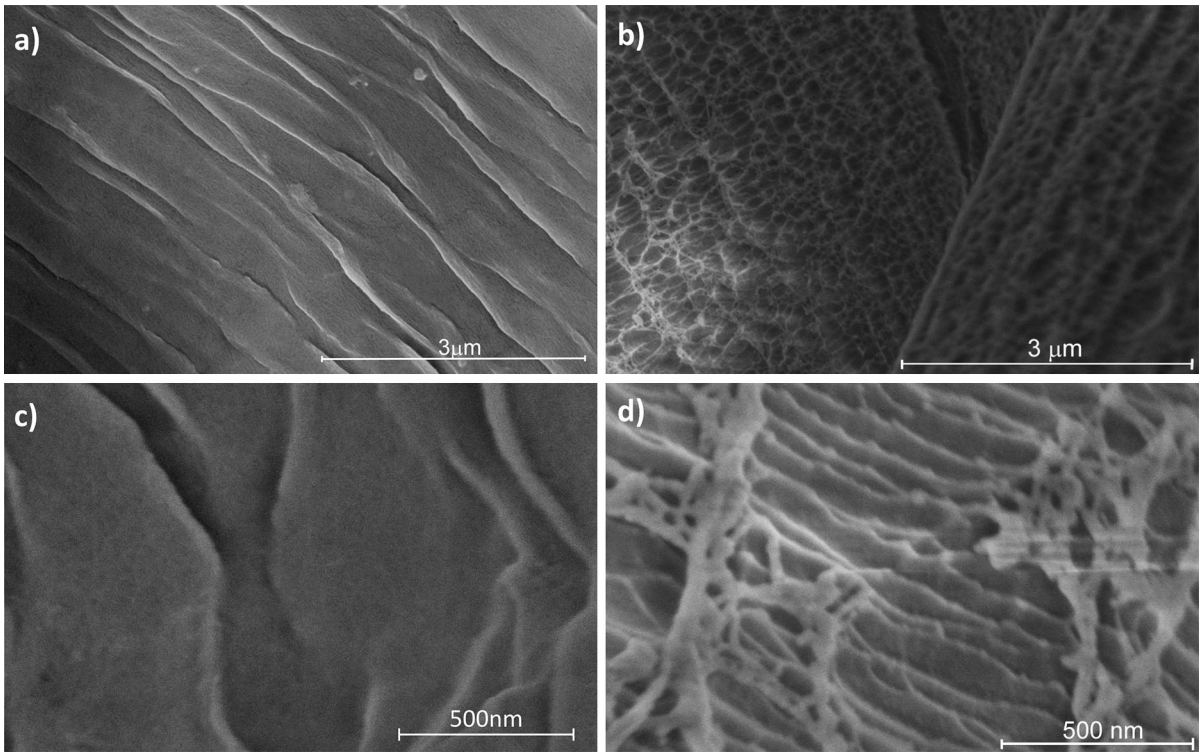

Fig. 3 SEM images of raw cotton (**a**, **c** ×30,000 and ×120,000 magnifications) and 30-min plasma-treated cotton (**b**, **d** ×30,000 and ×120,000 magnifications)

and viscose increased by about 26 and 23 mJ/m^2, respectively (Table 2). A larger increase in the polar component was observed for cotton (twofold) than for viscose (30 %). For the dispersion component, it rose by 25 and 35 % for cotton and viscose, respectively. This was mainly due to the polar groups, such as C=O, formed on the fabric surfaces. This resulted in an increase of the polar components of SFE and consequently improved the wettability. The W_{adh} for water increased to 145 mJ/m^2 for both fabrics. The adhesion properties of fabrics were higher, and for both fabrics the coating process with TiO_2 sol should be more effective (Lam et al. 2011; Calvimontes et al. 2011; Caschera et al. 2014; Navaneetha Pandiyaraj and Selvarajan 2008). This is confirmed by the results of a wettability study with TiO_2 sol (Fig. 7).

Generally, both fabrics are very well wettable by TiO_2 sol, but there are some differences in the wettability process. For cotton, the drop of sol spreads on both samples wherein it penetrates immediately to the structure of the plasma-pretreated fabric. In the case of viscose, a flat drop of sol is formed, and the contact angles before and after plasma treatment are 23° and 18°, respectively (Fig. 7). Under the same conditions of the sol application, the content of TiO_2 is higher for cotton, which is confirmed by the results of the SEM/EDS (Figs. 14, 15).

The impact of MW treatment is presented on the basis of SEM images of cotton fabric (Fig. 8). No changes or damage of the cotton fiber surface morphology was observed. The same results were observed for the viscose fabric (not shown). The effect of microwave treatment on the fibers was evaluated by Raman analysis (Fig. 9). In the case of cotton (Fig. 9a), the characteristic bands are stretching COC at 1098 cm^{-1}, a group of four bands (353, 411, 457 and 580 cm^{-1}), bending COC and CCC, methylene bands (900, 1270, 1378, 1468 cm^{-1}) and C–H stretching at 2898 cm^{-1}. No changes after MW treatment were observed between raw cotton (spectrum I) and MW-treated cotton (spectrum II). Characteristic viscose bands included stretching COC at 1100 cm^{-1}, bending COC and CCC at (332, 381, 438, 454), methylene bands (920, 1297, 1341, 1384, 1482 cm^{-1}) and C–H

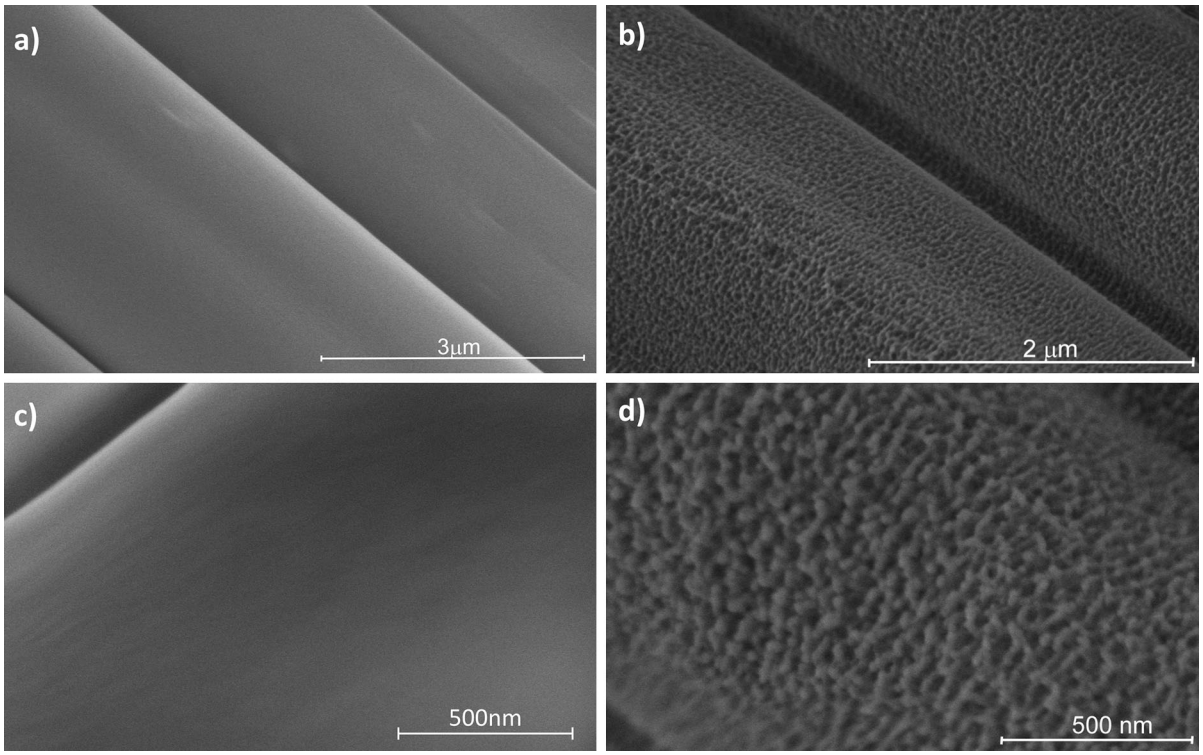

Fig. 4 SEM images of raw viscose (**a**, **c** ×30,000 and ×120,000 magnifications) and 30-min plasma-treated viscose (**b**, **d** ×30,000 and ×120,000 magnifications)

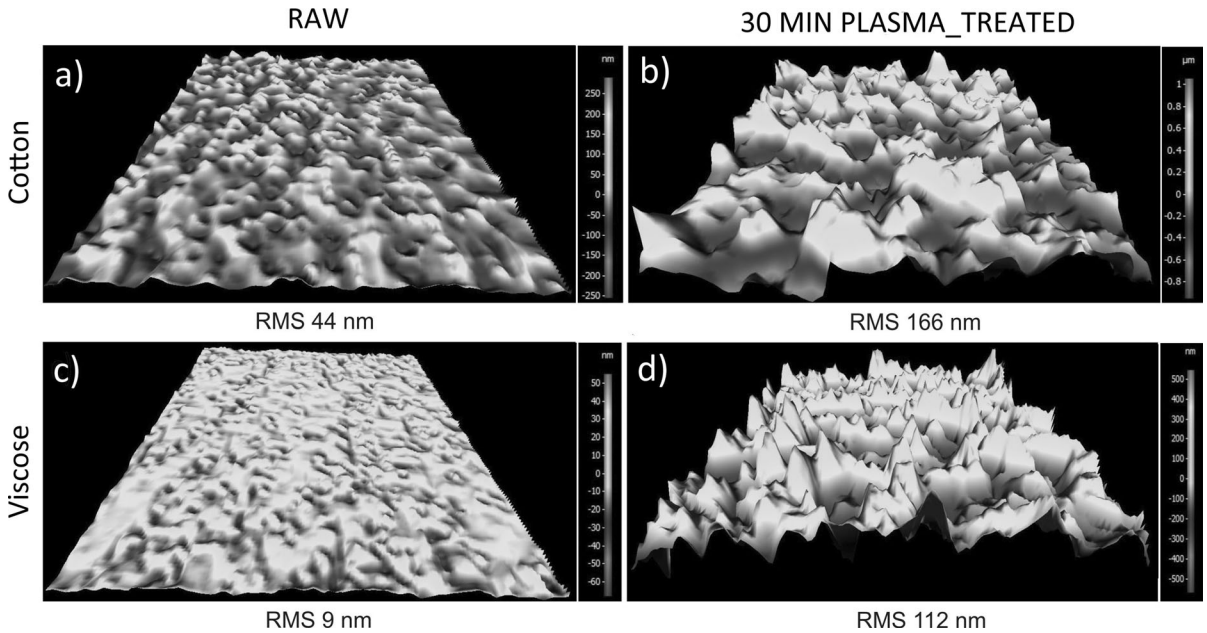

Fig. 5 The 3D SEM pictures of **a** raw cotton, **b** 30-min plasma-treated cotton, **c** raw viscose and **d** 30-min plasma-treated viscose with the root-mean-square-height value in the selected area

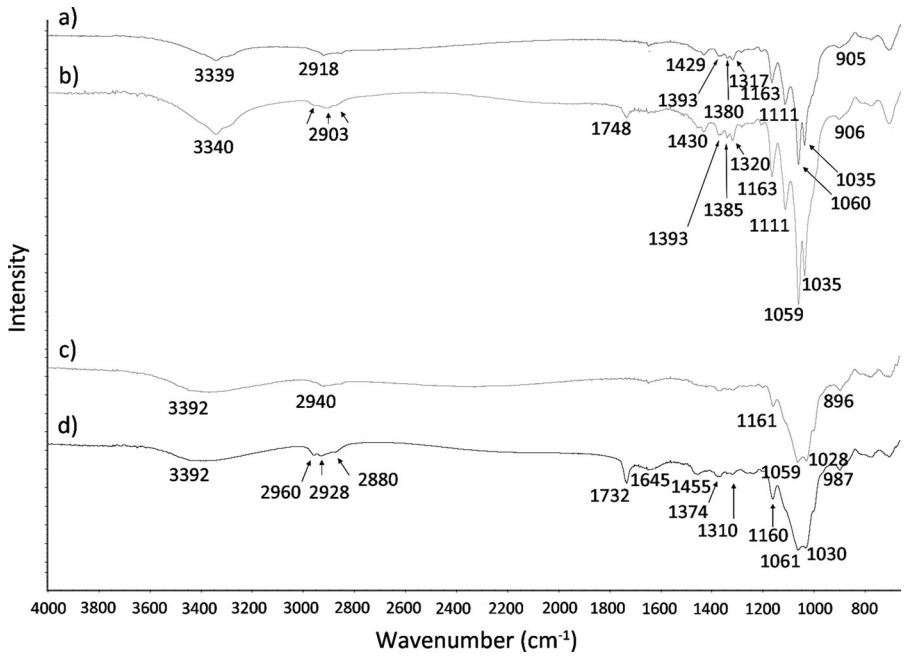

Fig. 6 FTIR analysis of **a** raw cotton, **b** 30-min plasma-treated cotton, **c** raw viscose and **d** 30-min plasma-treated viscose

Table 2 Contact angle, surface free energy and work of adhesion of cotton and viscose fabrics

Standard liquid	Cotton fabric		Viscose fabric	
	Raw	Plasma-treated	Raw	Plasma-treated
Contact angle (°)				
Water	55 ± 5	10 ± 2	50 ± 3	7 ± 2
Diiodomethane	40 ± 3	4 ± 2	56 ± 5	18 ± 4
Formamide	60 ± 7	8 ± 3	52 ± 4	16 ± 2
Surface free energy (SFE) (mJ/m^2)				
SFE	47 ± 3	73 ± 2	49 ± 4	72 ± 2
γ^d	31	41	26	40
γ^p	16	32	23	32
Work of adhesion (Wa) (mJ/m^2)				
Wa	115	145	120	145

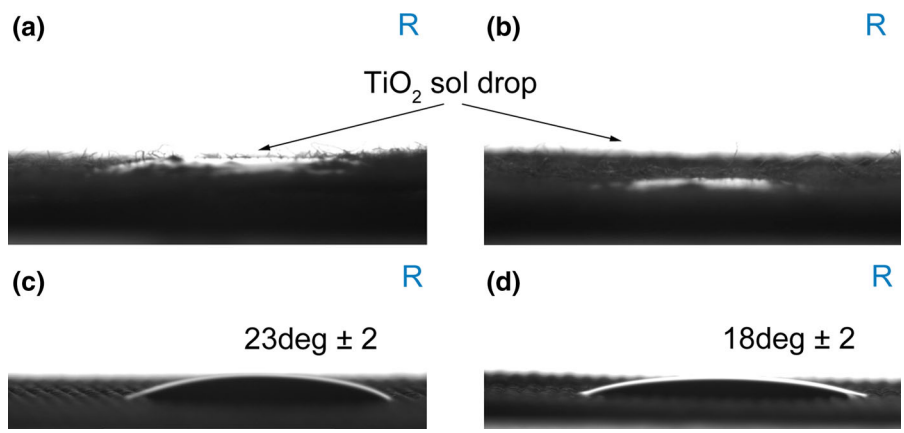

Fig. 7 The wettability of **a** raw cotton, **b** 30-min plasma-treated cotton, **c** raw viscose cotton and **d** 30-min plasma-treated viscose

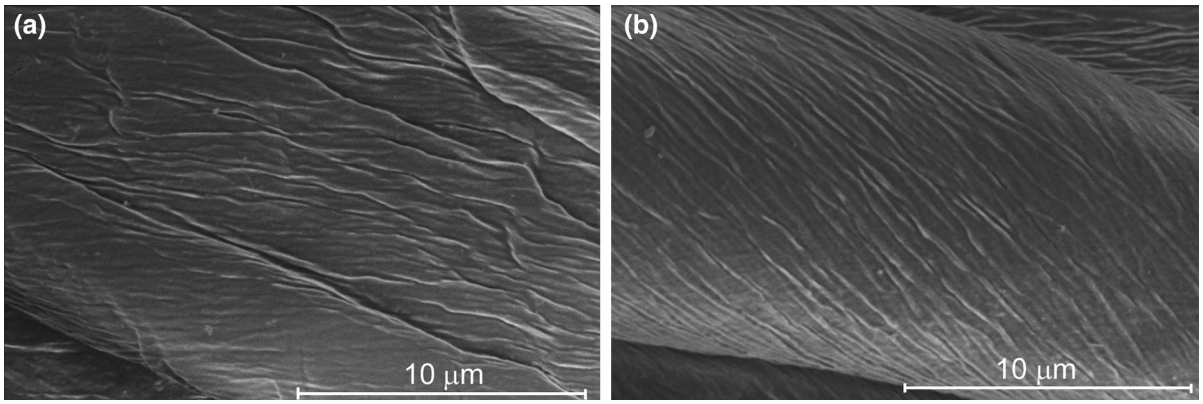

Fig. 8 SEM images of **a** raw cotton fabric and **b** cotton fabric after MW treatment at 650 W, 15 min with ×10,000 magnification

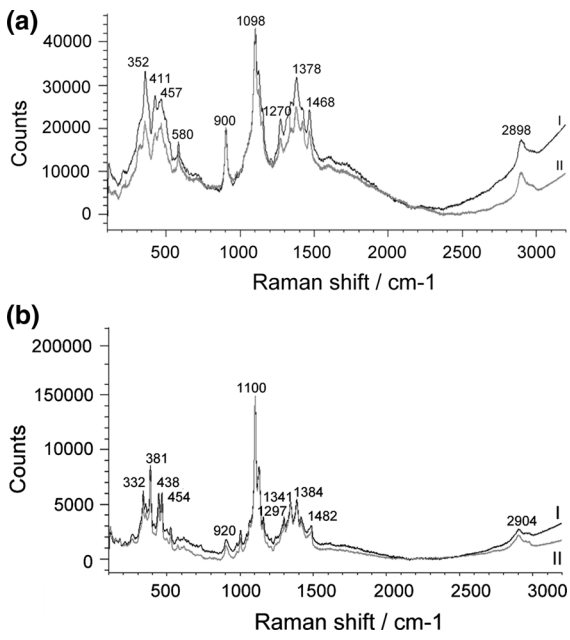

Fig. 9 Raman spectra of **a** cotton and **b** viscose fabrics: raw (*I*) and after MW treatment, 650 W, 15 min (*II*)

stretching at 2904 cm^{-1} (Fig. 9b); this also did not reveal changes between raw viscose (spectrum I) and MW-treated viscose (spectrum II) (Kavkler and Demšar 2011).

Raman spectra and map pictures obtained for cotton (Fig. 10a) and viscose (Fig. 10b) fabric modified with TiO_2 sol and MW treated at 650 W for 15 min are presented. The detected spectra prove that on both fabrics TiO_2 is present in the anatase form (band at 150 cm^{-1} for cotton and 153 cm^{-1} for viscose) (Fig. 10a, b, respectively). These strong sharp peaks are analogous to the 142-cm^{-1} anatase O–Ti–O bending vibration (Ohsaka et al. 1978). As a result of the physical interaction between the titania and fabric, the main anatase band is shifted to larger wavelengths. Other anatase bands at 194, 393, 515 and 637 cm^{-1} (Ohsaka et al. 1978) were not observed because there are strong bands of cotton and viscose fibers in this range. Raman map pictures show the distribution of TiO_2–anatase on the fiber surface. The dots on the pictures indicate where the Raman spectra were collected and the main anatase characteristic band was found.

The XRD results for TiO_2 coatings on both fabrics confirmed the formation of crystalline TiO_2. Figure 11 presents the XRD spectra of cotton (Fig. 11a) and viscose (Fig. 11b) modified with TiO_2. The characteristic peaks centered at two theta around 29.50; three peaks that appeared as one wide one (43.22; 44.24; 45.11) and 56.00 are visible, being characteristic for the TiO_2–anatase phase (ref. pattern no. 00-064-0863). The intensity of the registered peaks is rather low; moreover, they are more pronounced in the case of TiO_2-modified cotton fabric. This is also consistent with the results of Raman spectroscopy.

After reducing the power and time of MW treatment to 500 W and 10 min, the TiO_2 film on the fibers surface was a mixture of the anatase and amorphous form (Fig. 12). Besides the characteristic anatase bands, two bands at 440 and 620 cm^{-1} assigned to the amorphous form of titania were found (Zhang et al. 1998), clearly visible for viscose

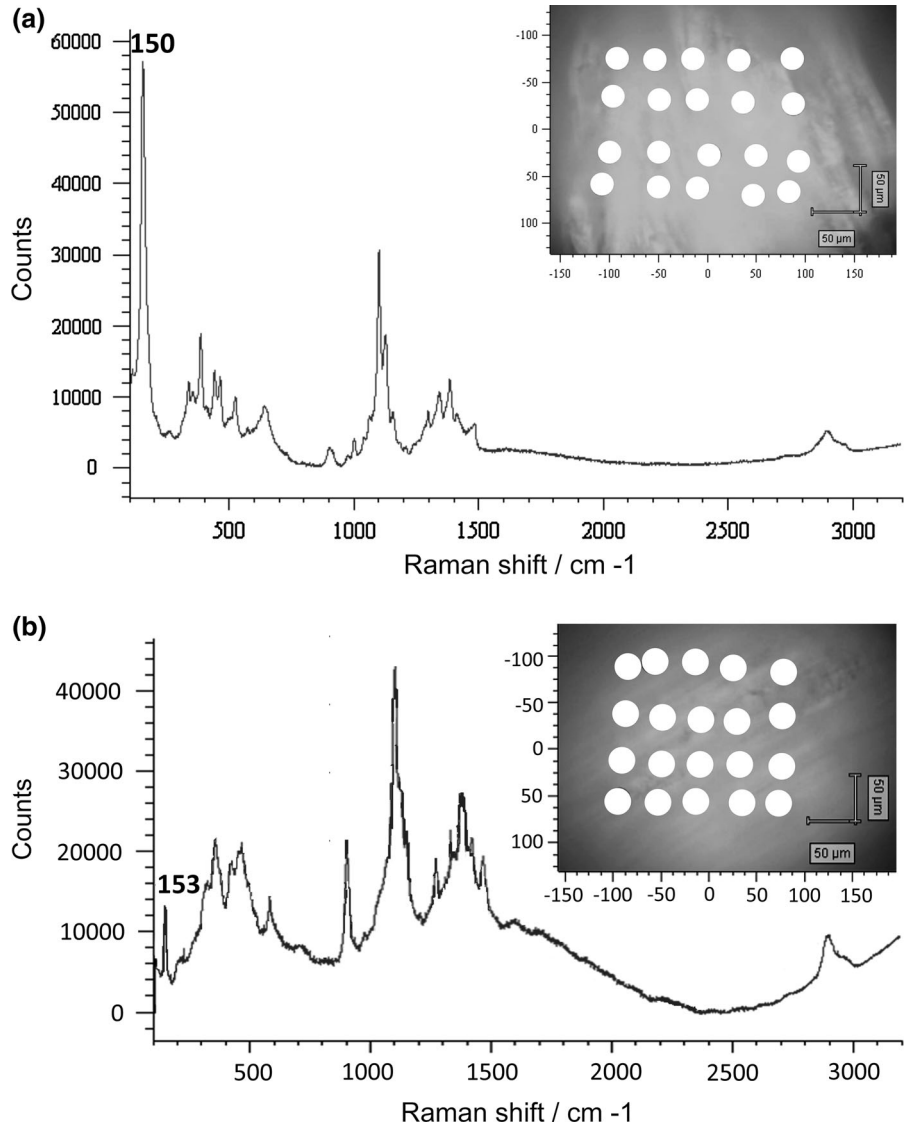

Fig. 10 Raman spectra and Raman maps of **a** cotton and **b** viscose fabrics with TiO_2 after MW treatment at 650 W, 15 min (*white dots* on the map—TiO_2 anatase)

(Fig. 12b). In the case of cotton (Fig. 12a), the band at 440 cm^{-1} is an overlap with the cotton bands present in this region. Results of Raman analysis show that for the transformation of TiO_2 to the anatase form, suitable MW treatment conditions must be selected.

SEM images of TiO_2 coatings in the anatase form on the Si wafers and fibers are presented in Figs. 13, 14 and 15.

TiO_2 film on the Si wafer (Fig. 13) creates a film with varied surface topography compared to smooth TiO_2 film–anatase on the Si wafer obtained by calcination for 2 h at 500 °C (Cieslak et al. 2015). TiO_2 forms a continuous coating on the cotton and viscose fibers without any gaps or agglomerates (Figs. 14, 15). SEM/EDS maps show that Ti is distributed on all fibers, white dots—Ti (Figs. 14c, 15c). The thickness of TiO_2 film is 180 ± 7 and 140 ± 8 nm for cotton and viscose, respectively. The content of Ti evaluated on the basis of SEM/EDS analysis is nearly four times higher for cotton. It can be concluded that compared to the roughness of the fiber surface of viscose, the thickness of the TiO_2 layer and Ti content are higher for cotton fabrics.

The different behaviors of both of the studied cellulose fabrics toward plasma pretreatment and the effect of TiO_2 sol application are related to differences

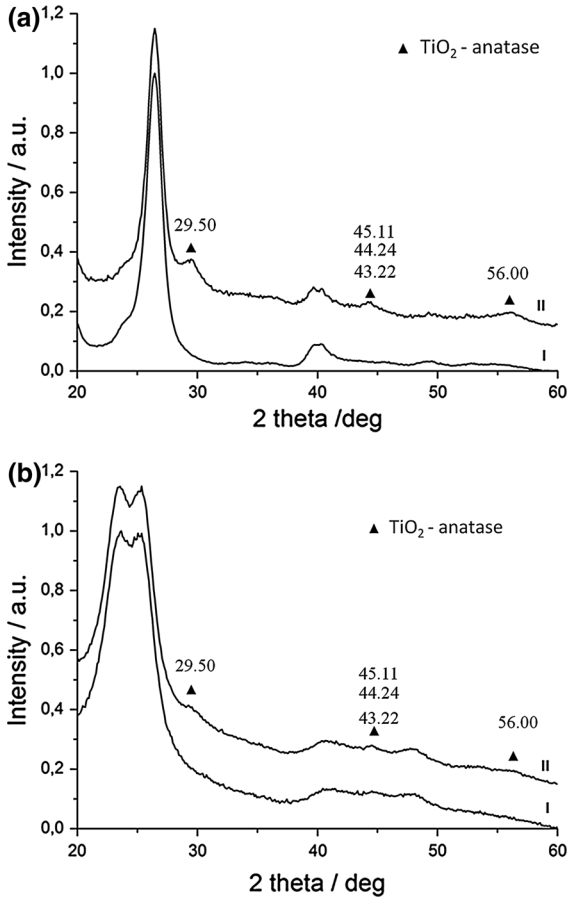

Fig. 11 XRD spectra of **a** cotton and **b** viscose I raw and II with TiO_2 after MW treatment at 650 W, 15 min

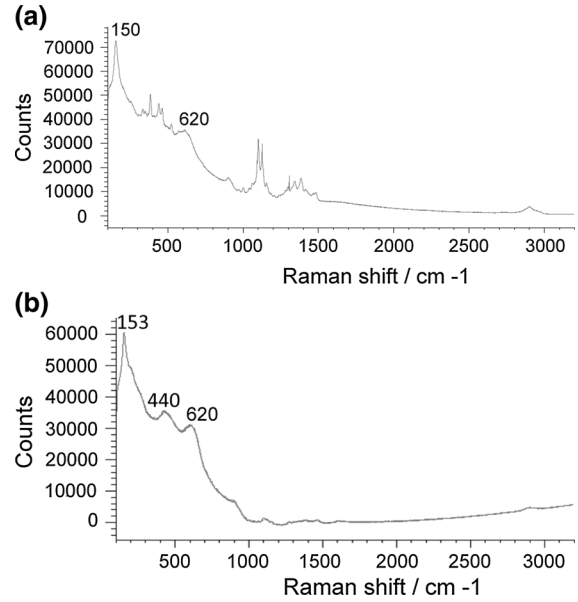

Fig. 12 Raman spectra of **a** cotton and **b** viscose fabrics with TiO_2 film after MW treatment at 500 W, 10 min

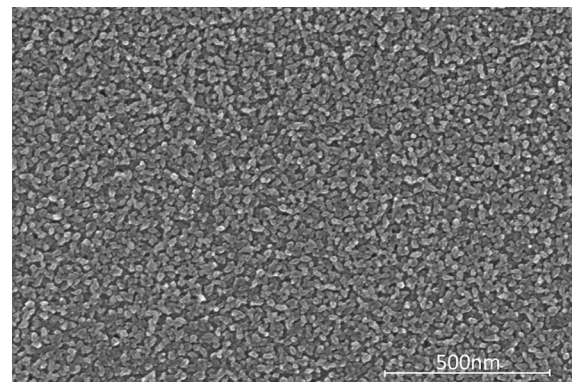

Fig. 13 SEM images of TiO_2 film on Si wafers (smooth substrate) after MW treatment at 650 W, 15 min (×120,000 magnification)

in their morphology and topography. Surface ablation during plasma treatment is different for the cotton fiber and viscose fibers. The cotton fiber with a bean-shaped cross section has a concentric layered structure with an outer separable cuticle layer composed of wax and pectin materials, which are removed during the pretreatment processes (scouring and bleaching). The next, primary wall is composed of cellulosic crystalline fibrils, and the secondary three-layer wall consists of closely packed parallel cellulose fibrils. The degree of polymerization of cotton is 9000–15,000, and the crystallinity of cellulose is approximately 70 %. In the viscose fiber with a skin-core structure, the skin contains numerous small crystallites with a larger total surface area than the core composed of fewer but larger crystallites. Viscose is characterized by the more than 30 times lower degree of polymerization, and its crystallinity degree is lower by almost 40 % in comparison to cotton (Duckett 1975).

The unmodified and modified cotton fabric showed higher susceptibility to nicotine sorption compared to viscose fabric. On the basis of exponential equations, the constant rate of nicotine decomposition was determined (k). The ratio of constant k for modified and unmodified cotton and viscose fabrics is 3.3 and 2.0, respectively. After application of the total irradiation dose of 405.8 kJ/m^2, the nicotine concentration decreased for unmodified and modified cotton and

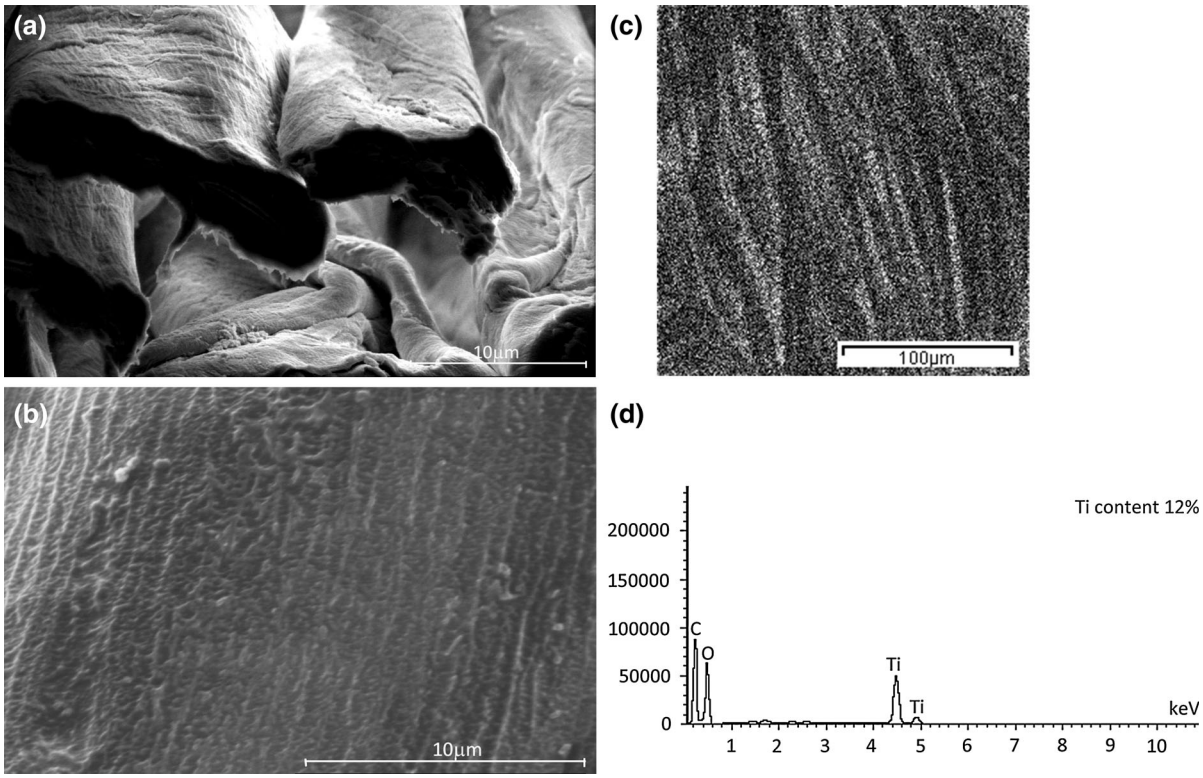

Fig. 14 SEM images of **a**, **b** TiO_2 coatings on cotton after MW treatment at 650 W, 15 min with ×6500 and ×30,000 magnifications, **c** SEM/EDS map of Ti distribution and **d** EDS spectrum of cotton textile modified with TiO_2 after MW treatment at 650 W, 15 min

viscose fabrics by about 21, 56, 45 and 64 %, respectively. A faster decrease in the nicotine concentration of modified fabrics results from their photocatalytic properties (Fig. 16).

The Ti contents before and after washing were evaluated on the basis of SEM/EDS analysis (Fig. 17). After washing, the Ti content on cotton fabric decreased from 12 to 11 % and on viscose fabric from about 3 to 2.6 %. Windler et al. (2012) investigated the release of titanium dioxide from consumer products (T-shirts and pants) of different compositions, also including cotton. The results indicated that functional textiles release some TiO_2 particles, but the amount is relatively low and mostly not in the nanoparticulate range, and Ti can occur.

The average values of the breaking force and breaking elongation of both fabrics before and after applied modifications are listed in Table 3.

Slight changes of the tensile strength of cotton after each modification (plasma treatment, microwave treatment and plasma/TiO_2/microwave treatment) were observed. It can be concluded that cotton fabric retains its physical properties after modifications. Contrary to cotton fabric, the tensile strength of viscose fabric decreased after plasma treatment (about 14 %), microwave treatment (about 19 %) and the most for TiO_2-modified fabric; the breaking force dropped from 499 to 275 N (about 45 %). Breaking elongation for cotton and viscose increased after the applied modifications. The developed method of modification with TiO_2 and microwave treatment tested on two cellulose fabrics is more suitable for cotton fabric because of the significant reduction of the tensile strength of viscose fabric.

The influence of UV irradiation on raw and TiO_2–anatase-modified fabrics was evaluated (Fig. 18). The results show that raw and TiO_2-modified cotton fabrics are stable under UV irradiation. In case of raw and TiO_2-modified viscose fabrics, UV irradiation affects their tensile strength. The tensile strength of raw viscose after UV irradiation of 5184 kJ/m^2 decreased by nearly 7 %, and there were minor changes. For

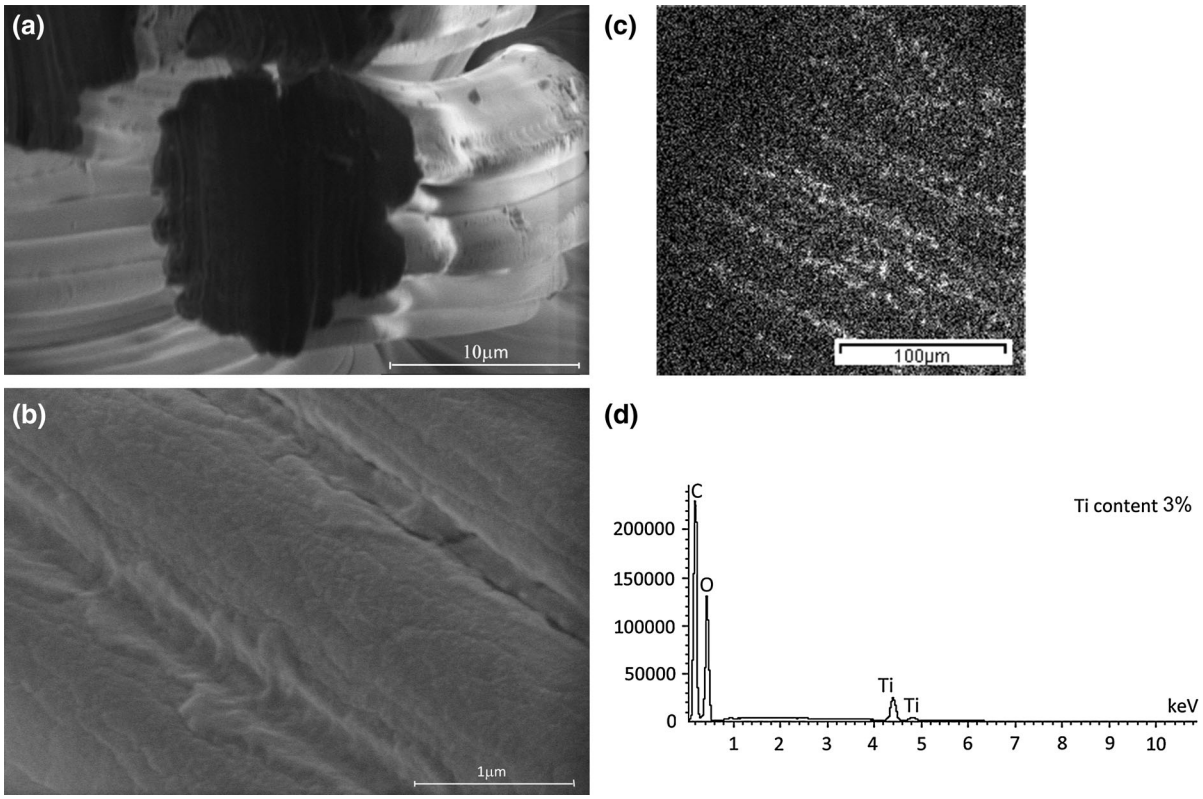

Fig. 15 SEM images of TiO_2 coatings **a**, **b** on viscose after MW treatment at 650 W, 15 min, with ×6500 and ×50,000 magnifications, **c** SEM/EDS map of Ti distribution and **d** EDS spectrum of viscose modified with TiO_2 after MW treatment at 650 W, 15 min

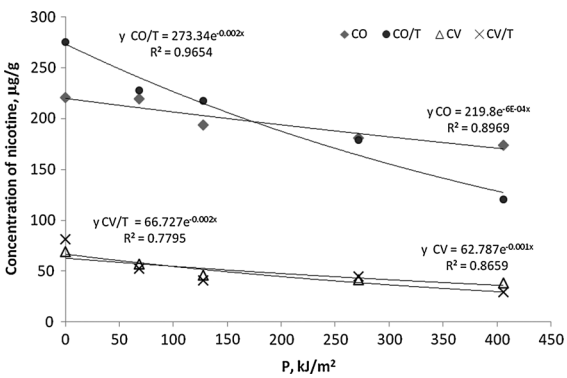

Fig. 16 The influence of the sunlight irradiation dose (*P*) on the nicotine concentration for unmodified and TiO_2 modified cotton and viscose fabrics. *CO* cotton, *CO/T* cotton modified with TiO_2, *CV* viscose, *CV/T* viscose modified with TiO_2

TiO_2-modified viscose fabric, the tensile strength decreased by about 16 % (from 275 to 232 N) (Fig. 18a). Breaking elongation for cotton and viscose fabrics increased after UV irradiation (Fig. 18b).

Conclusions

Application of microwave treatment to the formation a TiO_2–anatase layer directly on cotton and viscose fabrics was reported. In this study, two selected conditions—650 W, 15 min and 500 W, 10 min—were investigated. The microwave conditions influenced the TiO_2 form; it obtained an anatase form (650 W, 15 min, 181 °C) and a mixture of the anatase and amorphous form (500 W 10 min, 110 °C). The conversion of TiO_2 to the anatase form takes place at temperatures below 200 °C, which opens up many possibilities for modifications of different fibers with low thermal stability. The microwave step replaces the calcination process at around 500 °C and can only be used for fibers with high thermal resistance. To improve the surface properties of fibers and the TiO_2 sol application, low-temperature air plasma pretreatment was used. This resulted in better wettability of both fabrics by TiO_2 sol and significant growth in nano-roughness. The value of the root mean square

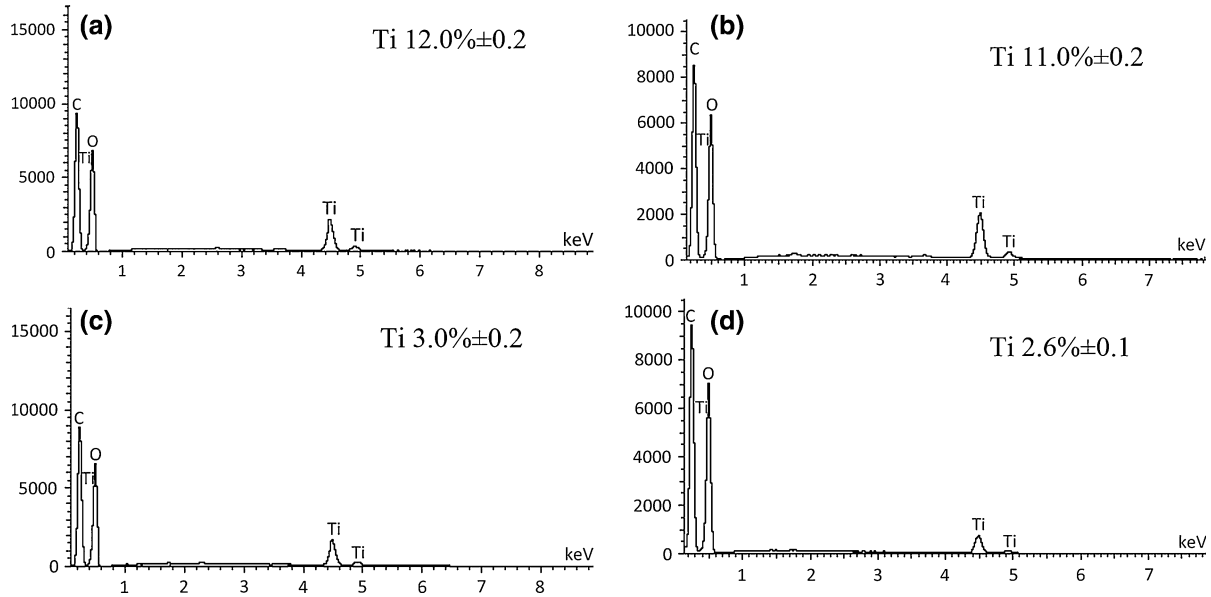

Fig. 17 Results of EDS analysis for **a** cotton fabric before washing, **b** cotton fabric after washing, **c** viscose fabric before washing and **d** viscose fabric after washing

Table 3 Results of the tensile strength of cotton and viscose fabrics before and after each step of modification

Fabric sample	Cotton		Viscose	
	Breaking force (*N*)	Breaking elongation (%)	Breaking force (*N*)	Breaking elongation (%)
Raw	422 ± 5	10.1 ± 0.1	499 ± 4	16.7 ± 0.5
Plasma treated	405 ± 7	10.7 ± 0.3	431 ± 6	17.5 ± 0.2
Microwave treated	450 ± 8	13.5 ± 0.8	404 ± 4	26.6 ± 0.9
Plasma/TiO_2/microwave treated	428 ± 5	12.6 ± 0.6	275 ± 8	21.0 ± 0.2

(RMS) increased from 44 to 166 nm (cotton) and from 9 to 112 nm (viscose). The surface free energy increased by about 26 and 23 mJ/m^2 for cotton and viscose, respectively. In the FTIR spectrum, there were new bands at 1748 and 1732 cm^{-1} corresponding to C=O stretching, which causes the increase in the hydrophilicity and adhesion properties. The final effect of modification differs for viscose and cotton fabrics. Generally, the wettability of cotton by TiO_2 sol is better, the nano-roughness and TiO_2 layer thickness are higher, and the amount of Ti is four times higher compared to viscose fabrics. TiO_2-modified cotton and viscose fabrics accelerate the decomposition of the adsorbed nicotine and thus its accumulation in fibers. The ratio of constant k for modified and unmodified cotton and viscose fabrics is 3.3 and 2.0, respectively. The nicotine concentration decreased for unmodified and modified cotton and viscose fabrics by about 21, 56, 45 and 64 %, respectively, after a UV irradiation dose of 405.8 kJ/m^2. No significant strength reduction after modifications and UV irradiation of cotton fabric was observed. For viscose, a UV dose irradiation of 5184 kJ/m^2 decreased the tensile strength by about 7 and 16 % for raw and TiO_2-modified viscose, respectively. The tensile strength of the viscose fabric after TiO_2 anatase modification reduced by about 45 %. The Ti contents after washing decreased from 12 to 11 % (cotton) and from 3 to 2.6 % (viscose). The durability of the TiO_2 film on the fabric surface was satisfactory. The developed method

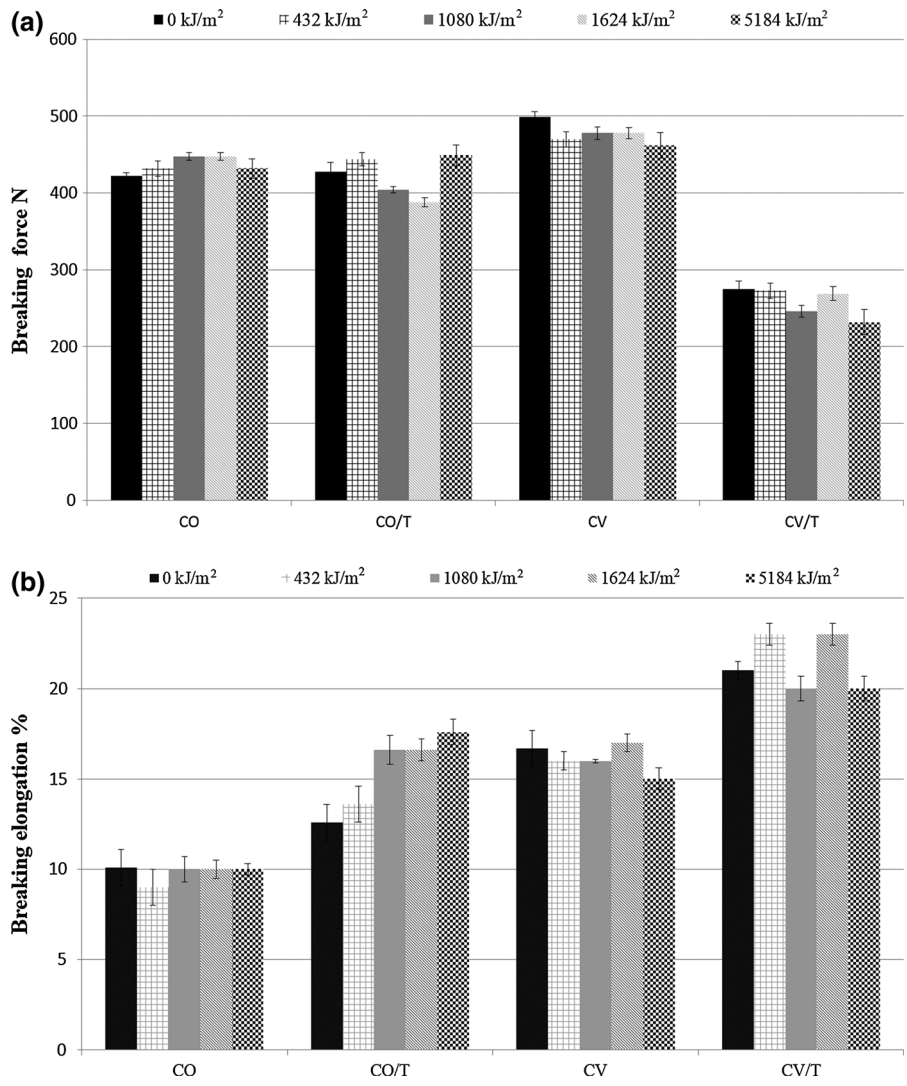

Fig. 18 Results of **a** breaking force and **b** breaking elongation for cotton and viscose fabrics before and after UV irradiation. *CO* cotton, *CO/T* cotton modified with TiO_2, *CV* viscose, *CV/T* viscose modified with TiO_2

of modifying cotton and viscose with TiO_2 to obtain the anatase form directly on the cellulose fabric surface is more effective for cotton fabric because of the reduction of the tensile strength of viscose fabric.

Acknowledgments This study was carried out within the Key Project—POIG.01.03.01-00-004/08 Functional nano- and micro textile materials—NANOMITEX co-financed by the European Union with the financial resources of the European Regional Development Fund and the National Centre for Research and Development within the framework of the Innovative Economy Operational Programme, 2007–2013, Priority 1; research and development of modern technologies, activity 1.3; supporting R&D projects for enterprises undertaken by science establishments, subactivity 1.3.1. Development projects.

References

Abidi N, Cabrales L, Hequet E (2009) Functionalization of a cotton fabric surface with titania nanosols: applications for self-cleaning and UV-protection properties. ACS Appl Mater Interfaces 1:2141–2146

Behzadnia A, Montazer M, Rashidi A, Mahmoudi Rad M (2014a) Rapid Sonosynthesis of N-Doped Nano TiO_2 on wool fabric at low temperature: introducing self-cleaning, hydrophilicity, antibacterial/antifungal properties with low alkali solubility, yellowness and cytotoxicity. Photochem Photobiol 90:1224–1233

Behzadnia A, Montazer M, Rashidi A, Rad MM (2014b) Sonosynthesis of nano TiO_2 on wool using titanium isopropoxide or butoxide in acidic media producing multifunctional fabric. Ultrason Sonochem 21:1815–1826

Calvimontes A, Mauersberger P, Nitschke M, Dutschk V, Simon F (2011) Effects of oxygen plasma on cellulose surface. Cellulose 18:803–809

Caschera D, Mezzi A, Cerri L, Caro T, Riccucci C, Ingo GM, Padeletti G, Biasiucci M, Gigli G, Cortese B (2014) Effects of plasma treatments for improving extreme wettability behavior of cotton fabrics. Cellulose 21:741–756

Cieslak M, Schmidt H, Swiercz R, Wasowicz W (2009) TiO_2/Ag modified carpet fibres for the reduction of nicotine exposure. Fibres Text East Eur 17:59–65

Cieslak M, Puchowicz D, Schmidt H (2012) Evaluation of the possibility of using surface free energy study to design protective fabrics. Text Res J 82:1177–1189

Cieslak M, Schmidt H, Swiercz R, Wasowicz W (2014) Fibers susceptibility to contamination by environmental tobacco smoke markers. Text Res J 84:840–853

Cieslak M, Celichowski G, Giesz P, Nejman A, Puchowicz D, Grobelny J (2015) Formation of nanostructured TiO_2-anatase films on the basalt fiber suraface. Surf Coat Tech 276:686–695

Duckett KE (1975) Surface properties of cotton fibers, fiber science series. In: Schick MJ (ed) Surface characteristics of fibers and textiles, part I. Marcel Dekker, New York and Basel, pp 64–70

Dupre A (1869) Theorie Mecanique de La Chaleur. Gauthier-Villan, Paris

Ibrahim NA, Refaie R, Ahmed AF (2010) Novel approach for attaining cotton fabric with multi-functional properties. J Ind Text 40:65–83

Ibrahim NA, Eid BM, Youssef MA, El-Sayedb SA, Salah AM (2012) Functionalization of cellulose-containing fabrics by plasma and subsequent metal salt treatments. Carbohyd Polym 90:908–914

Kadziola K, Piwonski I, Kisielewska A, Szczukocki D, Krawczyk B, Lisowska K, Sielski J (2014) The photoactivity of titanium dioxide coatings with silver nanoparticles prepared by sol–gel and reactive magnetron sputtering methods—comparative studies. Appl Surf Sci 288:503–512

Karahan HA, Özdoan E (2008) Improvements of surface functionality of cotton fibers by atmospheric plasma treatment. Fib and Polym 9:21–26

Karimi L, Mirjalili M, Yazdanshenas ME, Nazari A (2010) Effect of Nano TiO_2 on self-cleaning property of cross-linking cotton fabric with succinic acid under UV irradiation. Photochem Photobiol 86:1030–1037

Karimi L, Yazdanshenas ME, Khajavi R, Rashidi A, Mirjalili M (2014) Using graphene/TiO_2 nanocomposite as a new route for preparation of electroconductive, self-cleaning, antibacterial and antifungal cotton fabric without toxicity. Cellulose 21:3813–3827

Kavkler K, Demšar A (2011) Examination of cellulose textile fibres in historical objects by micro-Raman spectroscopy. Spectrochim Acta A Mol Biomol Spectrosc 78:740–746

Kiwi J, Pulgarin C (2010) Innovative self-cleaning and bactericide textiles. Catal Today 151:2–7

Lam YL, Kan CW, Yuen CW (2011) Physical and chemical analysis of plasma-treated cotton fabric subjected to wrinkle-resistant finishing. Cellulose 8:493–503

Li X, Wang L, Lu X (2010) Preparation of silver-modified TiO_2 via microwave-assisted metod and its photocatalytic activity for toluene degradation. J Hazard Mater 177:639–647

Liu Y, Yang S, Hong J, Sun C (2007) Low-temperature preparation and microwave photocatalytic activity study of TiO_2-mounted activated carbon. J Hazard Mater 142:208–215

Liuxue Z, Xiulian W, Peng L, Zhixing S (2007) Photocatalytic activity of anatase thin films coated cotton fibers prepared via a microwave assisted liquid phase deposition process. Surf Coat Tech 201:7607–7614

Mihailović D, Šaponjić Z, Radoičić M, Lazović S, Baily CJ, Jovančić P, Nedeljkovic J, Radetić M (2011) Functionalization of cotton fabrics with corona/air RF plasma and colloidal TiO_2 nanoparticles. Cellulose 18:811–825

Mirjalili M, Karimi L, Bararitari A (2015) Investigating the effect of corona treatment on self-cleaning property of finished cotton fabric with nano titanium dioxide. J Text I 106:621–628

Morawski AW, Kusiak-Nejman E, Przepiorski J, Kordala R, Pernak J (2013) Cellulose-TiO_2 nanocomposite with enhanced UV–Vis light absorption. Cellulose 20:1293–1300

Navaneetha Pandiyaraj K, Selvarajan V (2008) Non-thermal plasma treatment for hydrophilicity improvement of grey cotton fabrics. J Mater Process Tech 199:130–139

Ohsaka T, Izumi F, Fujiki Y (1978) Raman spectrum of anatase TiO_2. J Raman Spectrosc 7:321–324

Owens DK, Wendt RC (1969) Estimation of the surface free energy of polymers. J Appl Polym Sci 13:1741–1747

Peiro AM, Peral J, Domingo C, Domenech X, Ayllon JA (2001) Low-temperature deposition of TiO_2 thin films with photocatalytic activity from colloidal anatase aqueous solutions. Chem Mater 13:2567–2573

Prysiazhnyi V, Kramar A, Dojcinovic B, Zekic A, Obradovic BM, Kuraica MM, Kostic M (2013) Silver incorporation on viscose and cotton fibers after air, nitrogen and oxygen DBD plasma pretreatment. Cellulose 20:315–325

Qi K, Daoud WA, Xin JH, Mak CL, Tang W, Cheung WE (2006) Self-cleaning cotton. J Mater Chem 16:4567–4574

Radetic M (2013) Functionalization of textile materials with TiO_2 nanoparticles. J Photochem Photobiol C 16:62–76

Shishoo R (2007) Plasma technologies for textiles. Woodhead Publishing Ltd, Cambridge. ISBN 978-1-84569-073-1

Tung WS, Daoud WA (2011) Self-cleaning fibers via nanotechnology: a virtual reality. J Mater Chem 21:7858–7869

Vigil E, Ayllon JA, Peiro AM, Rodriguez-Clemente R, Domenech X, Peral J (2001) TiO_2 layers grown from flowing precursor solutions using microwave heating. Langmuir 17:891–896

Wilson JG, Will GD, Frost RL, Montgomery SA (2002) Efficient microwave hydrothermal preparation of nanocrystalline anatase TiO_2 colloids. J Mater Chem 12:1787–1791

Windler W, Lorenz C, Goetz N, Hungerbuhler K, Amberg M, Heuberger M, Nowack B (2012) Release of titanium dioxide from textiles during washing. Environ Sci Technol 46:8181–8188

Zhang YH, Chan CK, Porter JF, Guo W (1998) Micro-Raman spectroscopic characterization of nanosized TiO_2 powders prepared by vapor hydrolysis. J Mater Res 13:2602–2609

Zhang H, Zhu H, Sun R (2012) Fabrication of photocatalytic TiO_2 nanoparticle film on PET fabric by hydrothermal method. Text Res J 82:747–754