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The sol-gel synthesis of cotton/TiO_2 composites and their antibacterial properties

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Abstract

Present work is devoted to investigation of structure and functional properties of hybrid nanomaterials based on the TiO_2 -modified cellulose fibers of cotton. The titania hydrosol was successfully prepared using the titanium tetraisopropoxide as precursor and the nitric acid as peptizing agent via the low-temperature sol-gel synthesis in aqueous medium and applied to cotton fabric. For cross-linking of titania nanoparticles to cotton the 1,2,3,4-butanetetracarboxylic acid (BTCA) was used as a spacer. The morphology and composition of the surface pure and TiO_2 modified cotton fibers were investigated by the Scanning Electron Microscopy (SEM). The cotton/TiO_2 composite was characterized by the dielectric permittivity. For the estimation of total titania concentration, all samples were calcined at 650°C. The antimicrobial activity of the treated TiO_2 cotton fibers was investigated against *Escherichia coli* as a model Gram – negative bacteria after exposure to UV-irradiation for 10 minutes.

Keywords: *titania, cellulose, cross-linking agent, modification, antibacterial activity, washing durability*

1. Introduction

Titania-based coatings with high specific surface area and narrow pore size distribution proved to have great prospects for practical application in solar energy transformation [1], photocatalysis [2,3], water and air cleaning [4,5]. Potentially, they can be used as self-cleaning [6-8], photochromic [9], and superhydrophobic/hydrophilic coatings [10,11], and just recently as matrices for bioencapsulation, drug delivery [12,13], andin tissue engineering [14].

In the recent years, the attention of researchers has been drawn to the biomedical use of metallic and semiconductor nanoparticles [15-18]. Treatment by ultraviolet radiation, chlorine, or phenol-containing agents are traditional methods of disinfection and sterilization [19,20]. Unfortunately, all of them have significant drawbacks, for instance, UV-radiation is characterized by low penetration; some of chemicals are unstable since they can interact with the processed drugs [21,22]. An alternative to the existing methods is application of antimicrobial agents based on nanoparticles of different metals and oxides. Thus, silver, copper and titanium dioxide (titania) nanoparticles are widely used and they show strong biocidal effects on many pathogenic bacteria [23-27].

The nano-sized titania is the most promising antibacterial candidate for the destruction of toxic organic and inorganic compounds due to its excellent antimicrobial properties as well as non-toxicity, low cost, high chemical stability at high temperatures, and high photocatalytic properties [28,29]. As a photocatalyst TiO_2 provides an effective destruction of pathogenic bacteria even under soft ultraviolet radiation, eliminating possibility of formation of xenobiotic-products and hazardous (carcinogenic, mutagenic) compounds [30,31]. For example, O. Akhavana et al. [32] synthesized the TiO_2/multi-wall carbon nanotube heterojunction arrays based on the Si substrate possessing excellent antimicrobial properties against *E.coli* bacteria under visible light irradiation. In other work [33], the obtained graphene oxide/TiO_2 thin films were used for degradation of *E. coli* bacteria in an aqueous solution under solar light irradiation.

The bactericidal activity of cotton fabrics coated with anthraquinone-sensitized TiO_2 has been investigated under UVA and UV-free visible irradiation [34]. Ohko et al. [25] reported that the TiO_2 photocatalyst was successfully used as a coating in silicon catheters and medical tubes.

Materials based on titania have great potential for application as efficiently self-cleaning and anti-bacterial coatings [35-37]. Qi et al [38] obtained TiO_2 coated cotton textiles possessing significant photocatalytic self-cleaning properties, such as bactericidal activity, colorant stain decomposition and degradation of red wine and coffee stains. One of the areas of biomedical application of titania nanoparticle coatings is so-called "smart" textiles, which are able to purify themselves from organic matter and fungal attack, as well as to destruct bacteria under the influence of soft UV-radiation. Montazer et al [39] investigated the antifelting and antimicrobial features of TiO_2 treated wool samples against gram-negative and gram-positive bacteria. The fields of application of such materials are quite broad – from the medical staff wear and bed linen to bandaging materials. Recently, some researchers have reported the use of titania hydrosol as a modifier of textile materials [40-43]. More precisely, modification of textile fibers was performed by coating the fabric surface by a titania suspension. As a result, the TiO_2 particles have been attached to the fibers mainly by physical adsorption. Thus, such materials can give rise to aerosol of titanium dioxide nanoparticles, which enter the respiratory system and open wounds, while they do not withstand prolonged washings and lose their properties.

In our previous publication [44] we presented a new method of obtaining nanocrystalline titania sols bypassing the calcination step. The way of interaction of TiO_2 nanoparticles with the functional group of cotton fibers with the help of a cross-linking agent (1,2,3,4 – butanetetracarboxylic acid) through the formation of transverse ester bonds has been also described there. The present work is the continuation of the study of modified TiO_2 cotton fiber structure and of the special properties of produced hybrid nanomaterials. The main aim of our study was to evaluate the bactericidal properties of cotton fibers modified by nanocrystalline TiO_2 hydrosol and exposed to UV light for 10 minutes.

2. Experimental

2.1. Materials

Titanium (IV) tetraisopropoxide, nitric acid, isopropyl alcohol, 1,2,3,4-butanetetracarboxylic acid (BTCA), sodium hypophosphite (NaH_2PO_2) have been purchased from Sigma-Aldrich. The cotton fibers were 100% cotton fabrics with a density of 146 $g\cdot m^{-2}$

2.2. Synthesis of nanocrystalline TiO_2 hydrosol

Nanocrystalline titania sol [44] was obtained by low-temperature sol-gel synthesis in an aqueous medium. The scheme of synthesis is presented in Fig.1. For this purpose, 16 ml of titanium tetraisopropoxide preliminarily dissolved in 12 ml of anhydrous isopropyl alcohol was added upon constant stirring to hot (70°C) water acidified by 0.7 ml of nitric acid. The synthesis has been performed under conditions of continuous stirring at 80°C for 8 h; as a result a transparent sol was formed.

2.3. *Obtaining the cotton/TiO_2 composites*

Before the TiO_2 modification, the raw cotton was boiled in 200 ml of distilled water solution containing Na_2CO_3 (2.8 g/l) at 100°C for 2h for the removal of most of the non-cellulosic constituents. After this, the pre-treated cotton fibers were thoroughly washed withdistilled water and dried inair.

Then, the pre-treated cotton fiber samples were treated by freshly prepared saturating solution. For this, 1 g of 1,2,3,4-butanetetracarboxylic acid (BTCA) was mixed with 1 g of NaH_2PO_2 and in 50 ml of doubly distilled water, and then the cotton fibers were kept in this solution at 70 ºC during 2 h. Next, 10 ml of titania sol was added to this solution and the modification was carried out at 70 ºC during 2 h. The modified fibers were washed with doubly distilled water and dried at 60°C for 2 h for water removal. Laundry of the cotton fibers treated by the nanosized titania hydrosol was carried out according to GOST 9733.4-83. The following designations of the obtained materials (table I) were adopted. Thus, the series of the five samples was prepared and then tested for the bactericidal properties.

2.3. Bacterial inoculation of cotton/TiO_2 composites

Before testing the bactericidal properties of the TiO_2 treated samples, produced with or without cross-linking agent, they were activated by UV-irradiation using Philips TUV-W30/G30T8 Lamp during 10 minutes. Under the irradiation of $TiO_2$the reactive oxygen species (OH•, O_2•, HO_2•) are generated on the surface of TiO_2 resulting from the formation of the electron-hole pair due to transition of the electronfrom the valence to the conduction band [45]. The hydroxyl radical OH• is considered to be the most important oxidizing agent providing inactivation of bacterial cells [46-48].

For cultivation in the liquid phase the overnight culture of *E.coli* DH10B, having optical density at 600 nm (OD_{600}) equal to 0.9 was diluted 100 times by LB100 medium. The treated fibers were placed subsequently in a tube with the Escherichia coli bacterial culture within 1 minute. The tube with the fibers and the bacteria was incubated on a shaker at 37°C taking a sample every half an hour to control the OD_{600}

2.4. Characterizationof cotton/TiO_2 composites

Surface morphology and composition of pure and modified cotton fabrics were investigated by Zeiss EVO MA scanning electron microscope (SEM) equipped with the EDAX Genesis APEX 2 system for energy-dispersive X-ray microanalysis. Before the analysis the fabric samples (size of about 10x10 mm) were sputtered with thin gold layer to avoid electrostatic charging during examination.The average chemical composition was determined from a 4.87 mm x 3.61 mm area.

The size of TiO_2 particles in the sol was determined by the method of dynamic light scattering using Zeta Sizer Nano at 20°C with a 10mV He-Ne laser, 633 nm wavelength and 90° fixed scattering angle.

Crystal structure of the samples was determined using X-ray diffraction on a Bruker Nanostar U diffractometer (MoKα radiation, $\lambda = 0.71073$ Å) operating at 45kV voltage and 40 mA current. The crystallite size was calculated using the Scherrer equation (1):

$$D = \frac{k\lambda}{B\cos\theta} \qquad (1)$$

where k is a constant equal to 0.94, λ is the X-ray wavelength, B is the full width at half maximumof the diffraction line, and θ is the diffraction angle of the phase under investigation.

The specific surface area of samples was calculated using the BET method on a Quantachrome Nova 1200 Series-E analyzer at 77K. Using low-temperature nitrogen adsorption/desorption data the pore size distribution according to the BJH method was also calculated.

For the analysis of chemical bonds in textile fibers before and after TiO_2 treatment the IR spectroscopy was used. IR spectra were obtained using an Avatar spectrophotometer in the range of 500–4500 cm^{-1}.

For the purpose of the estimation of total titania concentration the pure and modified cotton fibers were calcined for 2 h at 650°C.

The dielectric constant of the pure and treated fibers' samples was measured by immittance meters E7-20 in a condenser-type cell with a spring pressure device in the frequency range 25-106 Hz. Before the experiment, all the samples were dried for 1 hour at 60 °C under vacuum.

3. Results and discussions

3.1. Characterization of cotton/TiO_2 composites

The surface morphologies of the pure and TiO_2 modified cotton fibers are shown in Fig.2 (a-e) together with the details of EDX analysis of a representative sample. It can be seen from Fig. 2a that the pure cotton fibers do not contain any contaminations. The cotton fibers in the CF/TiO_2 (cotton fibers/TiO_2) are unevenly covered by TiO_2 nanoparticles after modification by titania hydrosol. Fig 2(2-5) shows the quantitative EDX analysis for the modified cotton fibers and it confirms the presence of titanium dioxide.The sample CF/TiO_2-CL obtained with the use of the cross-linking agent also contains titanium dioxide particles. The visible size of TiO_2 aggregates, distinguishable due to their brightness because of the element contrast, varies from a fraction of micrometer to 50 micrometers (Fig. 2c). In this case, the particles are distributed more uniformly through fibers in comparison with the sample CF/TiO_2 obtained without BTCA. It has to be noted that the Ti peak is present even in the analyses of the darker parts, not bearing visible bright aggregates, indicating that smaller primary particles are more-or-less evenly coating the fibers and that the bright aggregates are secondary formations on the surface of the coating resulting from primary particles. The results of elemental analysis (Table I) give the quantitative evaluation of titanium content in the samples, but do not reflect the whole coating distribution over the fibers. This can be explained by the fact that titanium is detected only in the surface layers of the sample from a small area of the surface. The depth of field generation of characteristic X-ray radiation at 25 kV does not exceed 5 micrometers. The light elements C and O presented in the cotton fibers are also considered in the calculation of the elemental composition. Note that the presence of 1,2,3,4-butanetetracarboxylic acid ($C_8H_{10}O_8$) influences their concentration. Thus, the weight fraction of titanium in the CF/TiO_2 sample was found to be 11.3 wt.%, which is lower by 60% than that for the CF/TiO_2-CL sample (17.2 wt.%). As can be seen from the SEM images (Figs. 2(d,e)) the density of titanium dioxide particles decreases significantly in the samples after five cycles of washing. The EDX analysis showed that the Ti peakfor CF/TiO_2-CL-5W sample (Fig. 2(5)) is stronger than for the CF/TiO_2-5W sample (Fig. 2(4)). This means that more TiO_2 deposited on the cotton fibers modified using the cross-linking agent.The residual concentration of Ti in the CF/TiO_2-CL-5W sample was found to be 7.2 wt.%. The loss of TiO_2 on washing occurs apparently via washing-off of the bigger aggregates. Their attachment to the primary film of TiO_2 nanoparticles bound to fibers chemically via spacer is thus stronger than to non-modified fibers. EDS of the darker spots on the CF/TiO_2-CL-5W still involved distinguishable Ti-signal.

According to the EDX analysis data, only negligible amount of Na and Ca was observed in the CF/TiO_2-5W and CF/TiO_2-CL-5W samplesoriginating from the use of Na_2CO_3 during the washing process under GOST 9733.4-83. At the same time, Ca is deposited onto the cotton fibers surface during the final stage of these thoroughly washed samples first - in distilled water, and then in running cold water during 10 minutes (Fig. 2(4,5)).

3.2. Crystal structure and morphology

Crystal structure of TiO_2 on the surface of cotton fibers, was studied the XRD analysis for both pure titania and the cotton fibers modified with TiO_2 (Fig.3).The Scherrer equation is used to determine the crystallite size of the pure and TiO_2-treated samples (Fig.3).As can be seen from the XRD analysis data (Fig.3a), for a pure cotton fiber are characteristic two peaks located at $2\theta = 10.9°$ and $2\theta = 16.4°$ and relating to pure cellulose. For the pure titania quite strong peaks of anatase and brookite phases, $2\theta = 12.2°$, 17.6°, 24.7° and $2\theta = 14.3°$, 22°, respectively, were found (Fig.3b). According to the data obtained, the produced nanocrystalline titania represents an anatase-brookite modification. The crystallite size of the pure titania was 8.9 nm. DLS analysis showed a particle size distribution of the pure titania sol centered at around 12 nm for the hydrodynamic size, involving also the water in primary hydration layers (Fig.4). The particle size of TiO_2 sol by DLS was thus in good agreement with the crystallite size by XRD. After coating the titania nanocrystalline sol onto cotton fibers without using a cross-linking agent (CF/$TiO_{2)}$ the additional new peaks have been found at $2\theta = 7.2°$ and $2\theta = 12.2°$, characteristric of the anatase crystalline phase (Fig. 3c).The crystallite size in the CF/TiO_2 sample was 9.8 nm.

For CF/TiO_2-CL sample, a decrease in intensity of the peaks related to cellulose, and an increase in intensity of the anatase peak are observed at $2\theta = 12.2°$, 17.6° and the brookite peak at $2\theta = 22°$ with crystallite size of 9.1 nm (Fig. 3d). It is worth noting that the broad peaks related to titania reveal the small size of TiO_2 crystallites formed in the sol-gel synthesis process. At the same time, the use of a cross-linking agent as well as sodium hydrophosphite multiply strengthens the signals originating from crystalline anatase-brookite modification, which also reveals an increase in titania content on the surface of cotton cellulose fibers. The attachment of BTCA with SHP treatment also leads to reduction in the crystallite size in the CF/TiO_2-CL sample in comparison with TiO_2 on cotton fibers not treated with a cross-linking agent making the chains break easily.

For investigation of the porous structure of pure and processed TiO_2 cotton fibers, low-temperature nitrogen adsorption/desorption was performed. For the CF/TiO_2 sample, a decrease in the specific surface area from 57.6 to 43.5 m^2/g and in the pore volume from 0.112 to 0.092 cm^3/g in comparison to a pure cotton fiber was observed. It may be suggested that nanocrystalline titania blocks the cellulose micropores. Corresponding quantitative data are listed in Table II. In comparison to a pure cotton fiber (CF), the CF/TiO_2-CL sample has shown an increase in the specific surface area from 57.6 to 77.2 m^2/g and in the pore volume from 0.112 to 0.157 cm^3/g. This increase may be explained by a content of phosphorus compound (NaH_2PO_2) in the Sample 3, which, as has been shown elsewhere [49], in small quantities can positively affect the textural characteristics.

3.3. IR – Fourier spectroscopy

An insight into interaction of BTCA with titania nanoparticleson the surface ofcotton fibers is provided by the IR–Fourier spectroscopy (Fig.5). On the qualitative level the obtained IR-spectra are quite similar, the maximum of absorption peaks practically coincide. The adsorption peak at 1159 cm^{-1} is observed for all samples and refers to C–O–C asymmetric stretching vibrations. The peak at 1643 cm^{-1} indicates the presence of water. Several characteristic absorption bands, however, show definite differences forthe chemical structure of the TiO_2-treated cotton. Thus, the absorption peaks assigned to carboxylic groups are present in the spectra of CF/TiO_2-CL sample after TiO_2 modification with the cross-linking agent BTCA in the 1800–1600 cm$^{–1}$ region (fig.5c). The carbonyl adsorption peak at 1730 cm$^{–1}$ is attributed to C=O stretching and confirmed the formation of ester bonds in the CF/TiO_2-CL sample.

On the basis of observed morphology, it is possible to assume that TiO_2 nanoparticles are cross-linked to the surface of a cotton fiber by formation of transverse ester bonds with BTCA (Fig.6). The cellulose macromolecule is composed of glucose units linked together. The hydroxyl –OH groups emerging from the macromolecular chain provide a strong cross-linkage to the functional groups of BTCA. An active five-membered cyclicanhydride is formedfrom 1,2,3,4-butanetetracarboxylic acid containing four functional carboxylic groups –COOH. The esterification reaction between cellulose and BTCA proceeds in three steps (Scheme 1): at first there is formation of cyclic anhydride by dehydration of two carboxylic groups (Step I), then the intermediate reacts with functional groups of cellulose to form transverse ester bonds (Step II). On the other side, the two other free carboxylic groups of BTCA are linked to titania nanocrystalline sol by a strong electrostatic interaction (Step III). Sodium hypophosphite, in this case, acts as a catalyst of the reaction, increasing the rate of cross-linking of cellulose macromolecules to BTCA and TiO_2. It was revealed that NaH_2PO_2 weakens hydrogen bonds between carboxylic acid functional groups in BTCA, promoting the accelerated formation of cyclic anhydride at low temperatures.

Calcination procedure was used as an independent technique for the estimation of total titania concentration in the samples. As can be seen from Table II for the CF/TiO_2 sample, the nanocrystalline TiO_2 content is 9 wt%, which is almost twice lower than that in the sample obtained with BTCA (17 wt %). This fact may be explained by the action of the cross-linking agent, which allows tocross-link covalently crystalline TiO_2 with the functional groups of cellulose by the formation of transverse ester bonds (Fig. 6). Furthermore, according to the X-ray diffraction analysis the cross-linking agent allows to increase the degree of crystallinity of the CF/TiO_2-CL sample compared to the cotton fibers treated by nanocrystalline titania only. In the case of using the cross-linking agent, the mechanism of fixing of the titania nanoparticles includes two stages: first, chemical bonding (Fig.6) and then – the adsorption of nanoparticles on the fiber surface. The effect of this mechanism can be seen in our materials obtained with a high content of fibers deposited on the surface of titanium dioxide [44]. As can be seen from Table II, the TiO_2 content in the CF/TiO_2sample decreases practically twofold after 5 cycles of washing compared to the CF/TiO_2-CL sample. So, the use of the spacer in the samples CF/TiO_2-CL and CF/TiO_2-CL-5W allows bonding the titania to the functional groups of cellulose 52% more effectively than without it. Also it can be concluded that onlyunfixed adsorbed titanium dioxide is washed off during laundry both from the CF/TiO_2 and CF/TiO_2-CL samples.

3.4. Dielectric permittivity

In the previous research high photocatalytic activity of titania chemically bonded to the cotton fibers was shown in the reaction of decomposition of the Rhodamine B as model dye applied on the material [44]. The photocatalytic properties are caused by generation radical forms of oxygen and hydroxide on the surface of titania nanoparticles under the influence of irradiation. Obviously, while bonding titania nanoparticles with the fibers via polar spacers, an additional charge separation in the hybrid nanomaterial takes place. It can be explained by difference in the output energy of the electrons in the titanium dioxide and in the fiber, in other words, due to the effects of interfacial polarization. Such kind of charge separation leads to the increase in dielectric permittivity and of the loss tangent of the modified fabric compared to the pure one. In this case the larger charge separation and polarization should be accompanied by the increase in the corresponding electrophysical characteristics.

The results of dielectric permittivity measurements demonstrate highest conductivity for cotton fibers modified by titania and cross-linking agent (Figs.7,8). Thus, the application of BTCA as the cross-linking agent leads to the growth of polarization in the material caused by the additional effect of charge transfer between the polar groups and titanium dioxide, while for the fabric with adsorbed TiO_2 nanoparticles the main contribution is made by Maxwell-Wagner interfacial polarization. That is why the CF/TiO_2-CL sample accumulates and retains charges and has the highest photocatalytic and antibacterial properties.

3.5. Antibacterial properties of cotton/TiO_2 composites

At present, a large number of works are devoted to the investigation of bactericidal properties of nanocrystalline titania under uninterrupted UV-radiation exposure [10,50,51]. In our experiments titania modified samples were continuously exposed to UV light for 10 minutes only.It is well known that bactericidal activity of the samples is closely related to its photocatalytic properties and crystalline structure of synthesized titania [52]. As a result of TiO_2 UV-irradiation reactive oxygen species (OH•, O_2•, HO_2•) are generated on its surface. Among them OH• hydroxyl radical is considered to be the most important oxidizing agent providing inactivation of bacterial cell (Fig.9) [46-48]. Previously, in our research work [44] the high photocatalytic activity of the cotton fabric, modified with titania and chemically bonded titania with the usage of the cross-linking agent (1,2,3,4 – butanetetracarboxylic acid) was investigated in the reaction of decomposition of the Rhodamine B as a model dye applied on the material. According to the obtained data, the maximum of amount of active oxygen forms and hydroxideradicals is accumulated during this UV-irradiation, which is sufficient for long-term inactivation of Escherichia coli bacterial culture. We have been considering these properties only after 10 minutes UV light exposure of titania.

The investigation of dynamics of the gram-negative bacteria growth on the modified cotton fibers was carried out by means of optical density (OD) measurement. The OD_{600} curves as a function of time are depicted in Fig.10.

The conducted investigations have shown that the cotton fabrics treated by nanocrystalline titania with or without the cross-linking agent decrease the survival of microorganisms E. coli in comparison with the control sample (D = 1.18). It is known, that *E. coli* have a cell wall of gram-negative type: there is a lipopolysaccharide on the surface, which forms insurmountable outer membrane. Due to such structure, the interaction of titania nanoparticles with the surface of the cell is quite complicated. To kill *E. coli* completely, the direct attack of hydroxyl radicals is necessary [53]. It can be seen from Fig. 10 that the relative density of the culture after 5 hours of contact is decreased by more than 70% for the CF/TiO_2 and CF/TiO_2-CL samples compared to the control one (0.43 and 0.34, respectively) (Table III). Thus, titanium dioxide demonstrates high bacteriostatic effect. Although the lifetime of active oxygen and hydroxyl radicals OH•, resulting after TiO_2 photocatalytic activation on the surface of cotton fibers was insufficient to penetrate the cell and cause its complete destruction. The bacteriostatic activity of titanium dioxide for the CF/TiO_2-CL sample is 20% as low in comparison with the CF/TiO_2 sample. This fact may be explained by the acidic character of the cross-linking agent. The minimum pH for E. coli growth is 4.0–4.5. In response to increase in the acidity, *E. coli* bacteria reacts by the synthesis of aminoacid decarboxylase. As a result of such reaction the forming amines alkalize the solution and thereby the bacteriostatic effect of the CF/TiO_2-CL sample slightly decreases. It is worth noting that the deviation from monotony of the growth curves in Fig.10, first of all, is connected to the non-uniform distribution of the titania hydrosol coating on the cotton fibers. Our further investigations will be directed at the elimination of this irregularity in coating

The bactericidal properties of the samples were also tested after five washing cycles. As it was mentioned above, during laundry the amount of TiO_2 and correspondingly the number of its reactive centers on the surface of modified cotton fibers reduces by 50% on average. The presence of titania covalently bonded with the cotton fibers leads to inhibition of the bacteria growth even after numerous washing cycles. The relative optical density of the CF/TiO_2-5W sample is equal to 0.83. On the other hand, with the spacer usage the same parameter OD_{600} of the CF/TiO_2-CL-5W sample goes down to 0.53. It can be explained by the fact that the TiO_2 nanoparticles are cross-linked with the cotton fibers by covalent bonds which preserves the reactive centers. In this case, the bactericidal activity of the fabric with unfixed titania reduces by a factor of 2.5 in a result of mechanical action (laundry) in comparison with CF/TiO_2 sample. Thus, the application of 1,2,3,4-butanetetracarboxylic acid as cross-linking agent allows to maintain the bactericidal effect of the modified fibers at approximately half of the level of CF/TiO_2-CL-5W sample after 5 washing cycles.

4. Conclusions

In the present work, the cotton fibers were modified by the nanocryslalline titania hydrosol with and without use of 1,2,3,4-butanetetracarboxylic acid (BTCA) as cross-linking agent. The titania nanoparticles have been successfully synthesized by means of the low temperature sol-gel method in an aqueous medium. According to SEM and FTIR and the results of calcination process the bonding mechanism of titania with cotton fibers includes both the chemical bonding and the physical adsorption of the nanoparticles to the fiber surface. The use of the cross-linking agent allows bonding the titania to the functional groups of cellulose 52% more effectively than without it. It has been found that during laundry 50 wt. % of unfixed titanium dioxide on average is lost from the fiber surface as in the TiO_2 modified sample, so in the sample modified by TiO_2 in the presence of BTCA.

The results on dielectric permittivity have shown that cotton fibers modified by titania and the cross-linking agent possess the highest conductivity. It has been shown that composite fibers demonstrate high bacteriostatic effect against gram-negative E. coli bacteria and reduce bacteria survival by 70%. Moreover, the application of BTCA provides chemical bonding of nanocrystalline titania with the functional groups of cellulose fibers and maintains the bactericidal effect of the modified fibers after 5 cycles of washing at approximately half of the level of unlaundered composite.

Thus, the long-term effect of preservation of antibacterial properties (more than 3.5 hours long) even after 5 cycles of washing followed by short UV activation has been observed in the cotton fibers modified by titania and BTCA. This fact has a great importance in the development of perspective antimicrobial systems.

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References:

[1]W. Ching, M. Leung, D.Y.C. Leung, Solar photocatalytic degradation of gaseous formaldehyde by sol–gel TiO_2 thin film for enhancement of indoor air quality, Solar Energy. 77(2) (2004) 129–135.

[2]A. Fujishima, T. Ra, D. Tryk, Titanium dioxide photocatalysis, J PhotochemPhotobiol C: Photochem Rev. 1 (2000) 1–21.

[3]L. Lopez, W. Daoud, D. Dutta, Preparation of large scale photocatalytic TiO_2 films by the sol-gel process, Surf. Coat. Technol. 205 (2012) 251–257.

[4]M. Lazar, S. Varghese, S. Nair, Photocatalytic Water Treatment by Titanium Dioxide: Recent Updates, Catalysts. 2 (2012) 572-601.

[5]T.Ochiaia, A. Fujishimaa, Photoelectrochemical properties of TiO_2photocatalyst and its applications for environmental purification, J PhotochemPhotobiol C: Photochem Rev. 13 (2012) 247–262.

[6]T. Kamegawa, Y. Shimizu, H. Yamashita, Superhydrophobic Surfaces with Photocatalytic Self-Cleaning Properties by Nanocomposite Coating of TiO_2 and Polytetrafluoroethylene,Adv Mater. 24 (2012) 3697-3700.

[7]E.Pakdel, W. Daoud, Self-cleaning Cotton Functionalized with TiO_2/SiO_2: Focus on the Role of Silica. J. Colloid Interface Sci. 401(2013) 1-7.

[8] K.T.Meilert, D.Laub, J. Kiwi, Photocatalytic self-cleaning of modified cotton textiles by TiO_2 clusters attached by chemical spacers. J. Mol. Catal. A: Chem. 237(2005) 101-108.

[9]Y. Djaoued, S. Balaji, N. Beaudoin, Sol–gel synthesis of mesoporous WO_3–TiO_2 composite thin films for photochromic devices,J Sol-Gel Sci Technol.65 (2013)374–383.

[10]Y.K. Lai, Y.X. Tang, J.J. Gong, D.G. Gong, L.F. Chi, C.G. Lin, Z. Chen, Transparent superhydrophobic/superhydrophilic TiO_2-based coatings for self-cleaning and anti-fogging, J Mater Chem. 22 (2012) 7420-7426

[11]X.T. Zhang, M. Jin, Z.Y. Liu, D.A.Tryk, S.Nishimoto, T. Murakami, A. Fujishima, Superhydrophobic TiO_2 Surfaces: Preparation, Photocatalytic Wettability Conversion, and Superhydrophobic−Superhydrophilic Patterning, J PhtsChem C. 111 (2007) 14521-14529**.**

[12]V.G. Kessler, G.A. Seisenbaeva, S. Håkansson, M.Unell, Chemically triggered biodelivery using metal-organic sol-gel synthesis. AngewChem, 47(2008) 8506-8509.

[13]M. Vallet-Regi, F. Balas, D. Arcos, Mesoporous materials for drug delivery, AngewChemInt Ed. 46 (2007) 7548–7558.

[14]O.Akhavan, E. Ghaderi, Differentiation of human neural stem cells into neural networks on graphenenanogrids. J. Mater. Chem. B. 1 (2013) 6291-6301.

[15]M.C. Gutierrez, M.L. Ferrer, P.Tartaj, F. Monte, Biomedical applications of organic–inorganic hybrid nanoparticles, Hybrid NanocompositesNanotechnol, 2009, pp.707–768.

[16]V.A. Nadtochenko, M.A. Radzig, I.A. Khmel, Antibacterial action of metal and semiconductor nanoparticles, Nanotechnologies in Russia. 5 (2010) 37-46.

[17]N. Thanha, L. Green, Functionalisation of nanoparticles for biomedical applications, Nano Today 5(2010) 213–230.

[18]C. Xu, S. Sun, New forms of superparamagnetic nanoparticles for biomedical applications. Adv Drug Deliv Rev. 65 (2013) 732-43.

[19]S.S. Block, Disinfection, sterilization, and preservation, Philadelphia: Lippincott Williams & Wilkins, 2001.

[20]W.A. Rutala, S.L. Barbee, N.C.Aguiar et al., Antimicrobial activity of home disinfectants and natural products against potential human pathogens, Infect. Control Hosp. Epidemiol. 21(2000) 33-38.

[21]S.A. Ulasevich, E.V. Skorb et al., Bactericidal properties of thin-film photocatalysts based on nanostructured titanium dioxide. (2008) http://elib.bsu.by/handle/123456789/20747

[22]M.H. Wilcox, W.N. Fawley, N. Wigglesworth, Comparison of the effect of detergent versus hypochlorite cleaning on environmental contamination and incidence of Clostridium difficile infection, J. Hosp. Infect. 54 (2003) 109-14.

[23]J. Hardes, C.vonEiff, A. Streitbuerger, M. Balke, T.Budny, M.P.Henrichs, G. Hauschild, H.Ahrens, Reduction of periprosthetic infection with silver-coated megaprostheses in patients with bone sarcoma, J SurgOncol. 101 (2010) 389–395.

[24]Y. Inoue, M. Hoshino, H. Takahashi, Bactericidal activity of Ag–zeolite mediated by reactive oxygen species under aerated condition, J InorgBiochem. 92 (2002) 37–42.

[25]Y. Ohko, Y. Utsumi, C. Niwa, Tatsuma T, K. Kobayakawa, Y. Satoh, Y. Kubota, A.Fujishima, Self-sterilizing and self-cleaning of silicone catheters coated with TiO_2 photocatalyst thin films: a preclinical work, J Biomed Mater Res. 58 (2001) 97–101.

[26]K.M. Tarquinio, N.K. Kothurkar, D.Y. Goswami, R.C.Jr Sanders,A.L.Zaritsky,A.M. LeVine, Bactericidal effects of silver plus titanium dioxide-coated endotracheal tubes on Pseudomonas aeruginosa and Staphylococcus aureus,Int J Nanomedicine. 5 (2010) 177–18.

[27]H. Wang, T. Huang, J.Jing, J. Jin, P. Wang, M. Yang,W. Cui,Y. Zheng, H. Shen, Effectiveness of different central venous catheters for catheter-related infections: a network meta-analysis. J Hosp Infect, 76(2010) 1–11.

[28]A.M. Azad, S. Dolan, S.A. Akbar, Development of agile titania sensors via high-temperature reductive etching process (HiTREP): 1. Structural reorganization, Int J Appl Ceram Tech. 5 (2008) 480-489.

[29]A.M. Azad, R. Hershey, A. Aboelzahab, V. Goel, Infection mitigation efficacy of photoactive titania on orthopedic implant materials, AdvOrthop. (2011) 571652.

[30]H. Koseki, K. Shiraishi, T.Tsurumoto, Bactericidal performance of photocatalytic titanium dioxide particle mixture under ultraviolet and fluorescent light: An in vitro study, Surf Interface Anal. 41 (2009) 771-774.

[31]K.P. Kuhn, I.F. Chabernya,K. Massholderb, M. Stickler, Disinfection of surfaces by photocatalytic oxidation with titanium dioxide and UVA light, Chemosphere. 53 (2003) 71-77.

[32]O. Akhavan, M Abdolahad, Y Abdi, S Mohajerzadeh, Synthesis of titania/carbon nanotube heterojunction arrays for photoinactivation of E. coli in visible light irradiation, Carbon. 47 (2009) 3280-3287

[33]O. Akhavan, E. Ghaderi, Photocatalytic Reduction of Graphene Oxide Nanosheets on TiO_2 Thin Film for Photoinactivation of Bacteria in Solar Light Irradiation, J. Phys. Chem. C. 113 (2009) 20214–20220

[34]R. Rahal, M. Le Becheca, R. Guyoneauda et al., Bactericidal activity under UV and visible light of cotton fabrics coated with anthraquinone-sensitized TiO_2, Catalysis Today 209 (2013) 134-139

[35]C.Maneerat, Y. Hayata, Antifungal activity of TiO_2 photocatalysis against Penicilliumexpansum in vitro and in fruit tests,Int J Food Microbiol. 107 (2006) 99-103.

[36]T. Nonami, H. Hase, K. Funakoshi, Apatite-coated titanium dioxide photocatalyst for air purification,Catal Today 96 (2004) 113-118.

[37]K. Sunada, Y. Kikuchi, K. Hashimoto, A. Fujishima, Bactericidal and detoxification effect of TiO_2 thin film photocatalysts, Environ Sci Technol.32 (1998) 726-728.

[38]K. Qi, W.A. Daoud, J.H. Xin et al., Self-cleaning cotton. J. Mater. Chem. 16 (2006) 4567-4574.

[39]M.Montazer, E. Pakdel, A. Behzadnia, Novel feature of nano-titanium dioxide on textiles: Antifelting and antibacterial wool. J. Appl. Polym. Sci. 121 (2011) 3407-3413.

[40]Y. Gao, R. Cranston, Recent advances in antimicrobial treatments of textiles, Text Res J. 78 (2008) 60–72.

[41]M. Montazer, E. Pakdel, Reducing photoyellowing of wool using nano TiO_2. PhotochemPhotobiol. 86 (2010) 255–260.

[42]A.P.S. Sawhney, B. Condon, K.V. Singh et al., Modern applications of nanotechnology in textiles, Text Res J. 78 (2008) 731-739

[43]T. Yuranova, D.Laub,J. Kiwi, Synthesis, activity and characterization of textiles showing self-cleaning activity under daylight irradiation,Catal Today. 122 (2007) 109–117

[44]O.L. Galkina, V.V. Vinogradov VV et al., Development of the low temperature sol-gel synthesis of TiO_2 to provide self-cleaning effect on the textile materials, Nanotechnologies in Russia. 7 (2012) 604–614.

[45]A.Fujishima, K. Hashimoto, T. Watanabe, TiO_2 Photocatalysis: Fundamentals andApplications, BKC, Tokyo, 1999.

[46]W.A. Daoud, J.H.Xin, Y.H. Zhang, Surface functionalization of cellulose fibers with titanium dioxide nanoparticles and their combined bactericidal activities, Surface Science. 599 (2005) 69–75.

[47] W.Kangwansupamonkon, V. Lauruengtana et al., Antibacterial effect of apatite-coated titanium dioxide for textiles applications, Nanomed Nanotech Biol Med. 5 (2009) 240–249.

[48]K. Sunada, T. Watanabe, K. Hashimoto, Studies on photokilling of bacteria on TiO_2 thin film, J Photochem. Photobiol A–Chem. 156 (2003) 227–233.

[49]L.Korosi, I. Dekany, Preparation and investigation of structural and photocatalytic properties of phosphate modified titanium dioxide, Colloids Surfaces A. 280 (2006) 146–154.

[50]B. Seentrakoona, B.Junhasavasdikul et al., Enhanced UV-protection and antibacterial properties of natural rubber/rutile-TiO_2nanocomposites, PolymDegradStabil. 98 (2013) 566-578.

[51]A.Morawski, E. Kusiak-Nejman, J. Przepiórski et al., Cellulose-TiO_2nanocomposite with enhanced UV–Vis light absorption, Cellulose 20 (2013) 1293–1300.

[52]Y. Cai, M.Strømme, K. Welch, Photocatalytic Antibacterial Effects Are Maintained on Resin-Based TiO_2 Nanocomposites after Cessation of UV Irradiation, PLoS ONE. 8 (2013)10 pg e75929.

[53]K. Ishibashi, Generation and deactivation processes of superoxide formedon TiO_2 film illuminated by very weak UV light in air or water, J PhysChem B. 104 (2000) 4934-4938

Tables

Table I Average elemental compositions of pure and TiO_2 modified fabrics based on EDS spectra acquired from a 4.87 x 3.61 mm area

Samples	**Weight fraction, %**						**Atomic fraction, %**					
	(C)	***(O)***	***(Ti)***	***(Ca)***	***(Mg)***	***(Na)***	***(C)***	***(O)***	***(Ti)***	***(Ca)***	***(Mg)***	***(Na)***
CF	52.8	47.1	--	--	--	--	59.9	40.1	--	--	--	--
CF/TiO_2	40.8	47.8	11.3	--	--	--	51.3	45.1	3.5	--	--	--
CF/TiO_2-CL	36.7	46.0	17.2	--	--	--	48.5	45.7	5.7	--	--	--
CF/TiO_2-5W	51.7	45.8	2.1	0.2	--	0.3	59.6	39.6	0.6	0.1	--	0.2
CF/TiO_2-CL-5W	47.9	44.3	7.2	0.3	--	0.2	57.6	39.9	2.2	0.1	--	0.1

Table II Weight fractions of titania in TiO_2 modified fabrics after calcination at 650 °C

Samples	**Weight fraction of TiO_2, %**
CF	0
CF/TiO_2	9
CF/TiO_2-CL	17
CF/TiO_2-5W	4
CF/TiO_2-CL-5W	8

Table II. Textural characteristics of the pure cotton fibers and cotton/TiO_2 composites

Sample	**V_p(cm^3/g)**	**S_{BET},m^2/g**	**D_p (nm)**
CF	0.112	57.6	2.8
CF/TiO_2	0.092	43.5	4.2
CF/TiO_2-CL	0.157	77.2	3.5

Table III. Antibacterial test of the pure cotton fibers and cotton/TiO_2 composites against *E.coli*

Sample	***Escherichia coli (OD_{600})***									
	0.5 h	***1 h***	***1.5h***	***2 h***	***2.5h***	***3 h***	***3.5 h***	***4 h***	***4.5h***	***5h***
CF	0.01	0.03	0.07	0.17	0.26	0.36	0.61	0.96	1.05	1.18
CF/TiO_2	0.05	0.07	0.04	0.04	0.09	0.10	0.13	0.14	0.34	0.43
CF/TiO_2-CL	0.02	0.03	0.03	0.05	0.07	0.06	0.11	0.08	0.24	0.34
CF/TiO_2-5W	0.02	0.01	0.02	0.03	0.09	0.11	0.25	0.64	0.72	0.83
CF/TiO_2-CL-5W	0.06	0.04	0.04	0.04	0.09	0.10	0.13	0.34	0.41	0.53

Figure captions:

Fig.1 The scheme of synthesis of composite based on cotton fibers and titania hydrosol

Fig.2 The SEM micrographs and EDX analysis: CF (a,1), CF/TiO_2 (b,2), CF/TiO_2-CL (c,3), and the same composite samples after 5 cycles of washing CF/TiO_2-5W (d,4) and CF/TiO_2-CL-5W(e,5).

Fig.3 X-ray diffraction patterns: (a) CF; (b) pure TiO_2; (c) CF/TiO_2; (d) CF/TiO_2-CL.

Fig.4 Particle size distribution of TiO_2 sol using DLS method

Fig.5 FTIR spectra of (a) CF, (b) CF/$TiO_{2,}$(c) CF/TiO_2-CL.

Fig.6 The mechanism of interaction of cotton fibers with BTCA and TiO_2

Fig.7 The value of the dielectric constant of samples

Fig.8 The dependence of the dielectric loss tangent of samples

Fig.9 Possible acting mechanism of composite cotton/titania fabric, produced using cross-linking agent, on tested pathogenic strains

Fig.10 Dependencies of optical density OD_{600} of the gram-negative bacteria E. coli solution on the time of contact with the samples showing the antibacterial effect

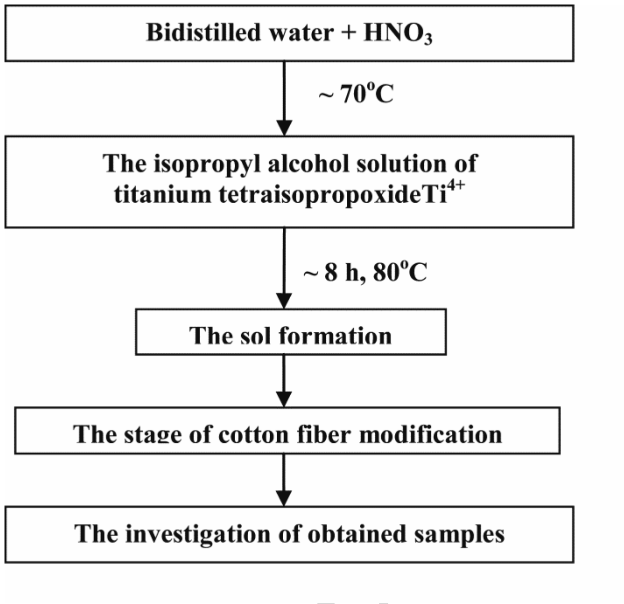
Bidistilled water + HNO3
~ 70°C
The isopropyl alcohol solution of titanium tetraisopropoxideTi4+
~ 8 h, 80°C
The sol formation
The stage of cotton fiber modification
The investigation of obtained samples

Figure 1

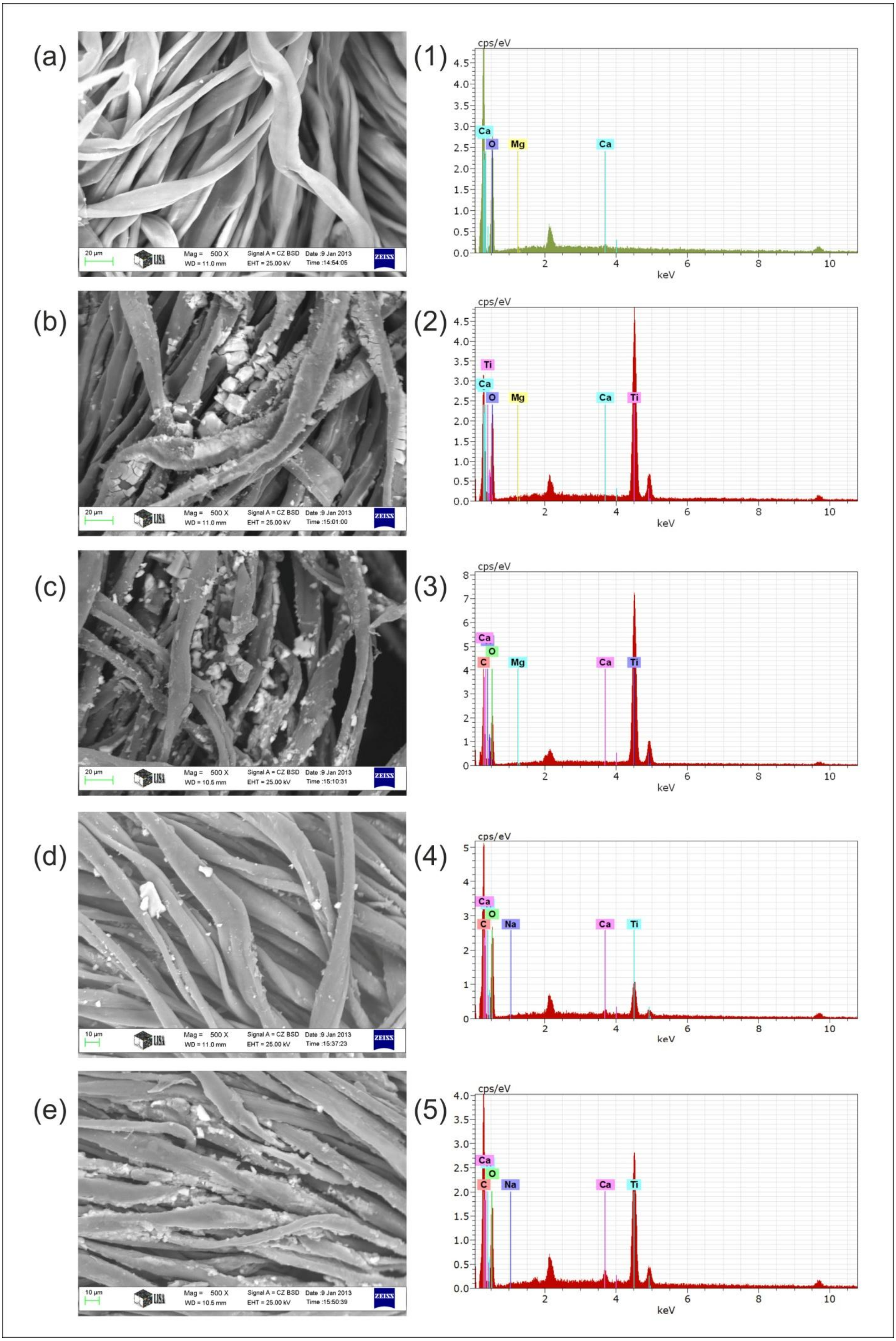
(a)
20 µm
Mag = 500 X
WD = 11.0 mm
Signal A = CZ BSD
EHT = 25.00 kV
Date :9 Jan 2013
Time :14:54:05
(1)
cps/eV
Ca
O
Mg
Ca
keV
(b)
20 µm
Mag = 500 X
WD = 11.0 mm
Signal A = CZ BSD
EHT = 25.00 kV
Date :9 Jan 2013
Time :15:01:00
(2)
cps/eV
Ti
Ca
O
Mg
Ca
Ti
keV
(c)
20 µm
Mag = 500 X
WD = 10.5 mm
Signal A = CZ BSD
EHT = 25.00 kV
Date :9 Jan 2013
Time :15:10:31
(3)
cps/eV
Ca
O
C
Mg
Ca
Ti
keV
(d)
10 µm
Mag = 500 X
WD = 11.0 mm
Signal A = CZ BSD
EHT = 25.00 kV
Date :9 Jan 2013
Time :15:37:23
(4)
cps/eV
Ca
O
C
Na
Ca
Ti
keV
(e)
10 µm
Mag = 500 X
WD = 10.5 mm
Signal A = CZ BSD
EHT = 25.00 kV
Date :9 Jan 2013
Time :15:50:39
(5)
cps/eV
Ca
O
C
Na
Ca
Ti
keV
2
4
6
8
10

Figure 2

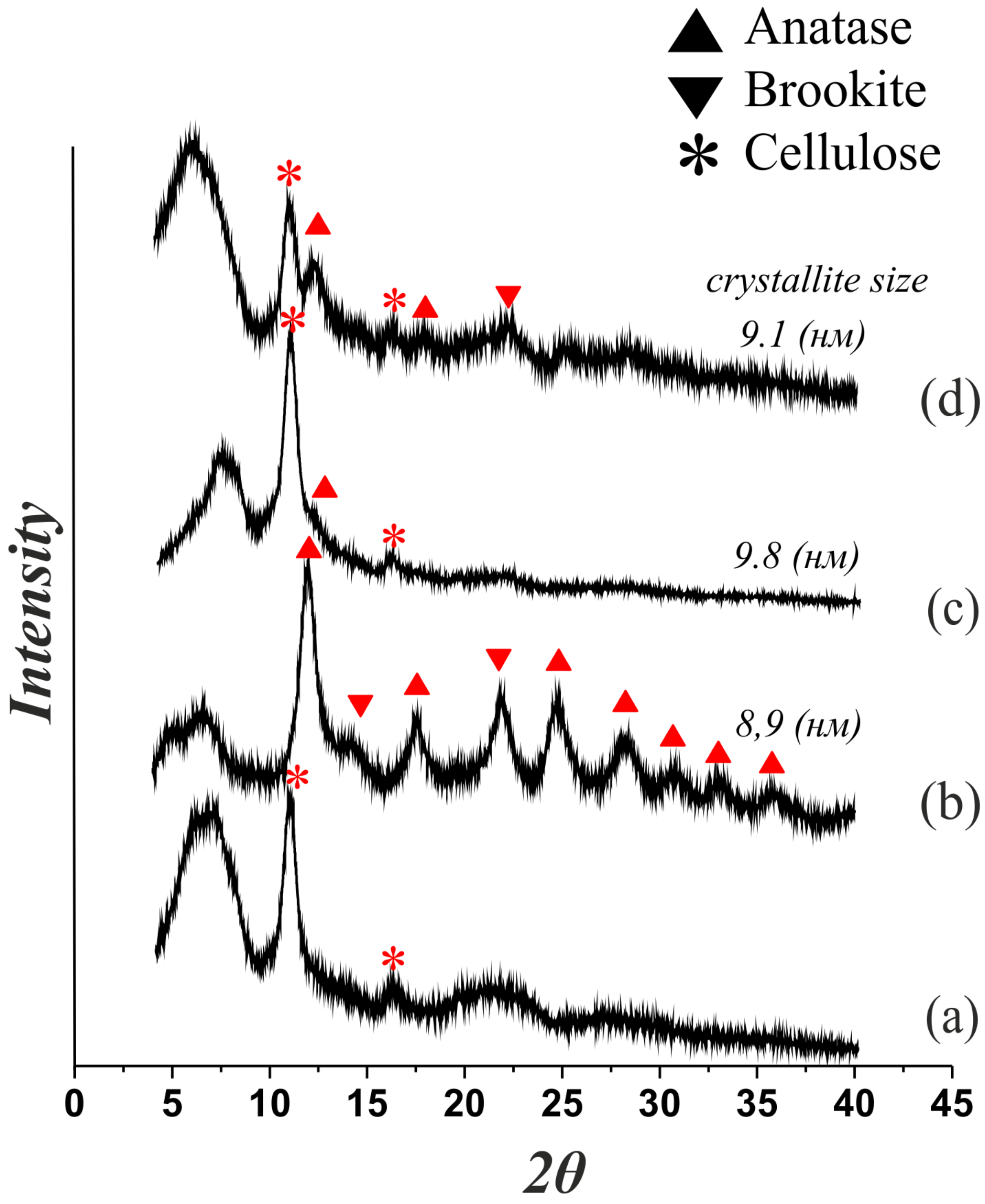
▲ Anatase
▼ Brookite
✱ Cellulose
crystallite size
9.1 (нм)
9.8 (нм)
8,9 (нм)
(d)
(c)
(b)
(a)
Intensity
2θ
0
5
10
15
20
25
30
35
40
45

Figure 3

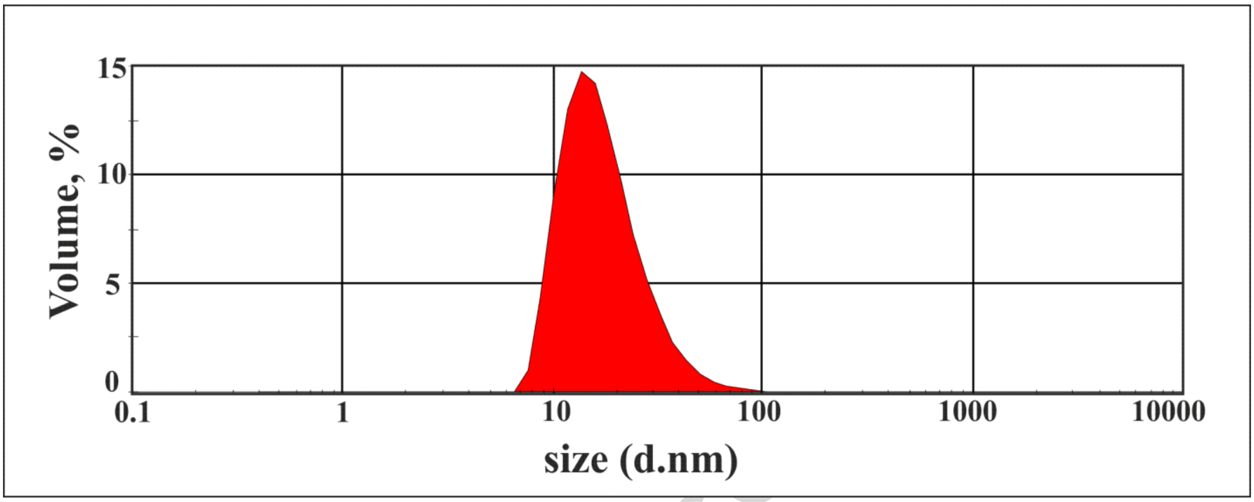

Figure 4

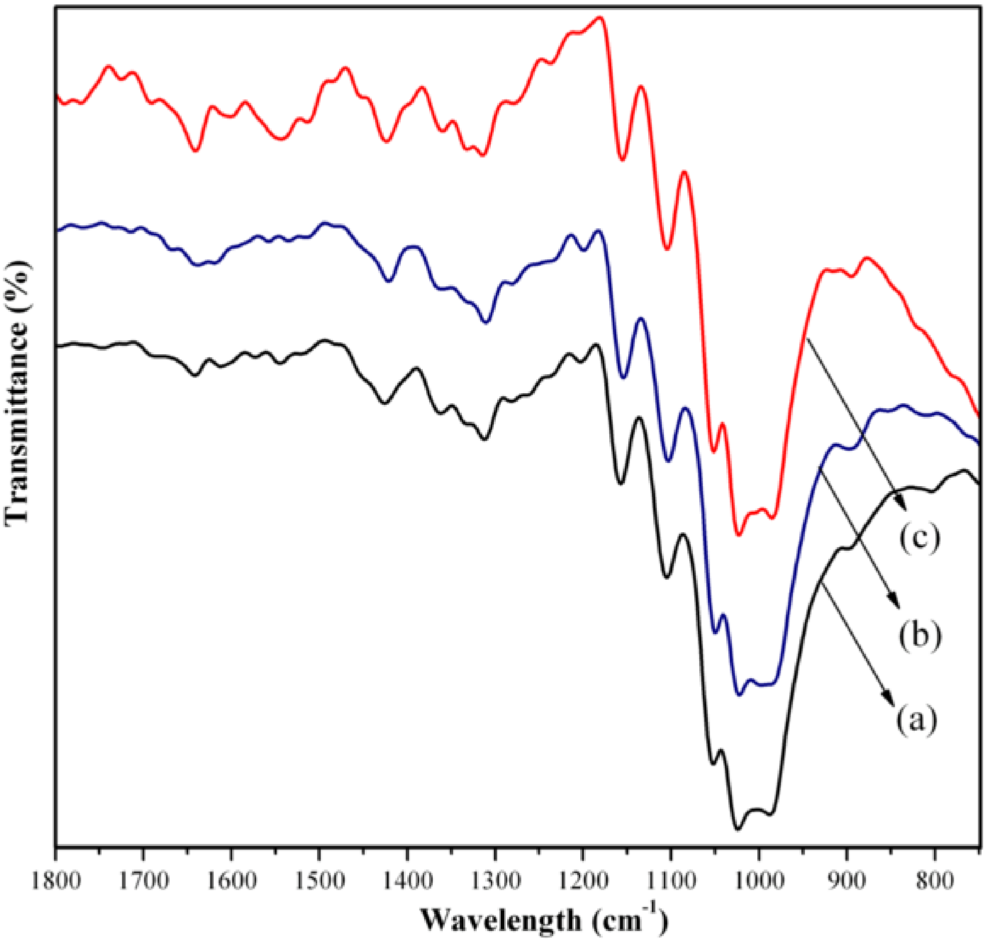

Figure5

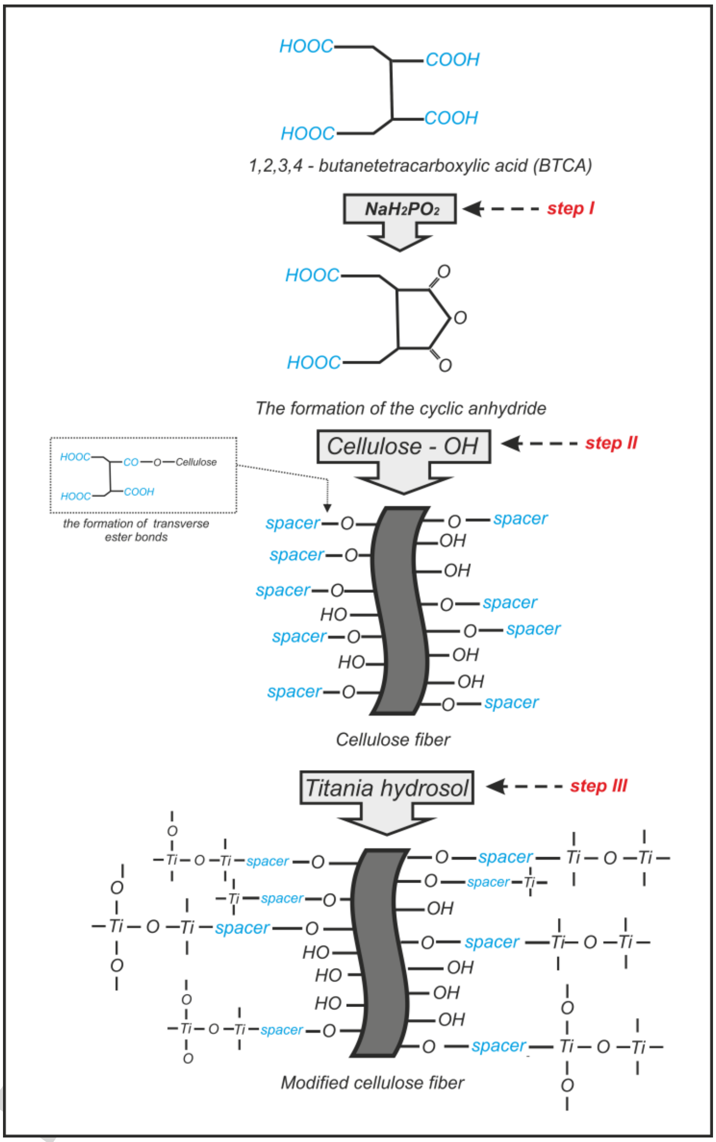
HOOC
COOH
HOOC
COOH
1,2,3,4 - butanetetracarboxylic acid (BTCA)
NaH2PO2
step I
HOOC
O
O
O
HOOC
The formation of the cyclic anhydride
Cellulose - OH
step II
HOOC
CO—O—Cellulose
HOOC
COOH
the formation of transverse ester bonds
spacer—O
O—spacer
OH
HO
Cellulose fiber
Titania hydrosol
step III
Ti
O
spacer
OH
HO
Modified cellulose fiber

Figure 6

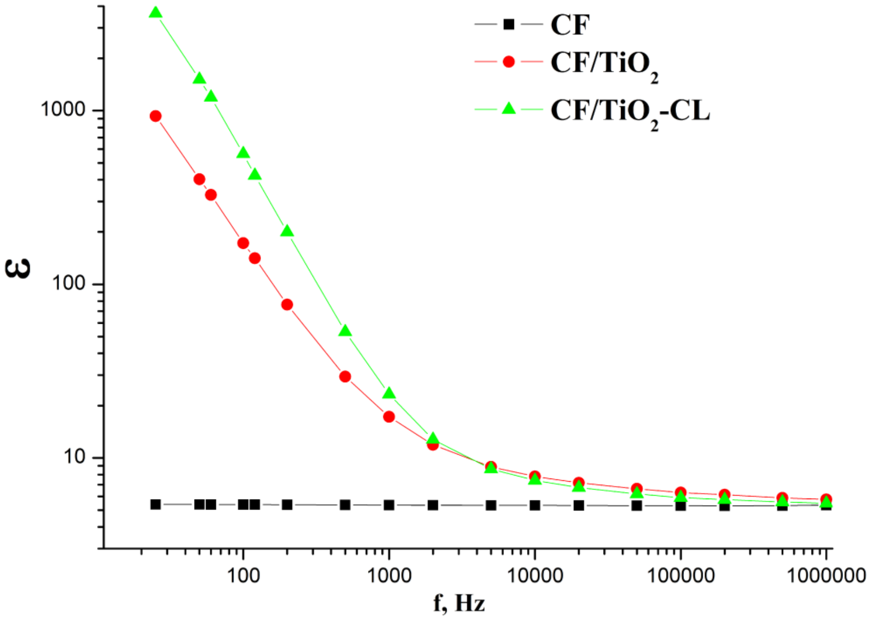

Figure 7

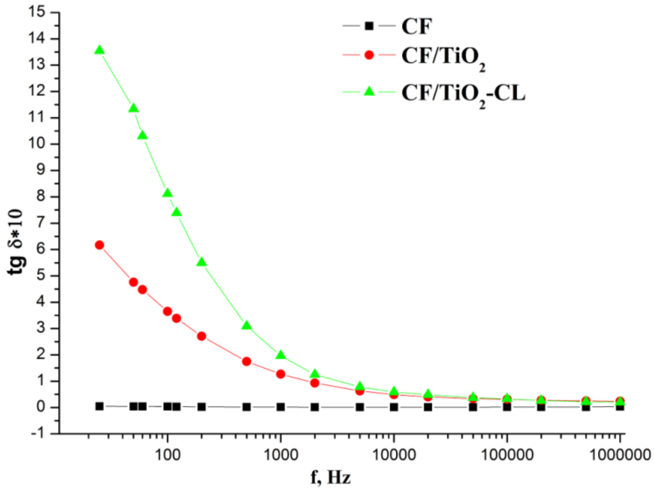

Figure 8

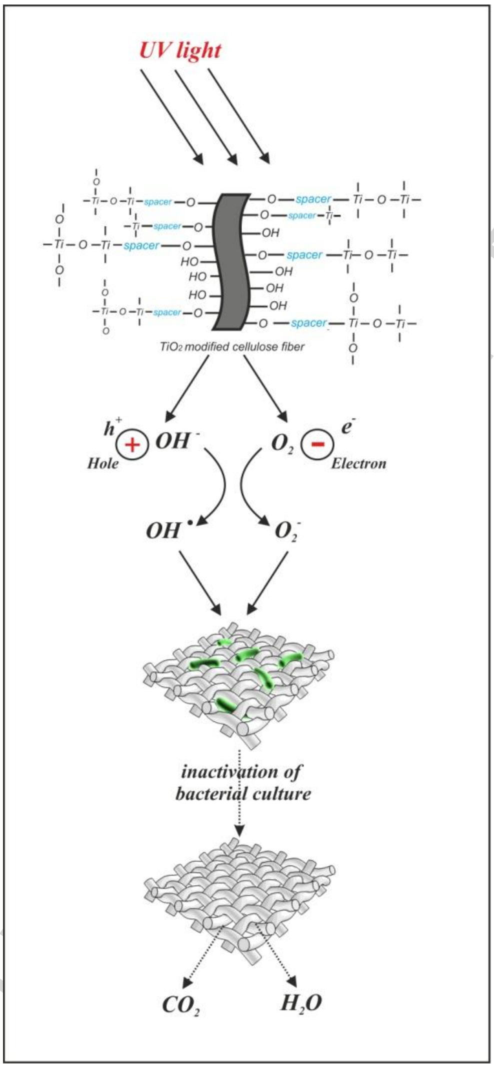
UV light
spacer
TiO2 modified cellulose fiber
h+
Hole
OH-
O2
e-
Electron
OH•
O2-
inactivation of bacterial culture
CO2
H2O

Figure 9

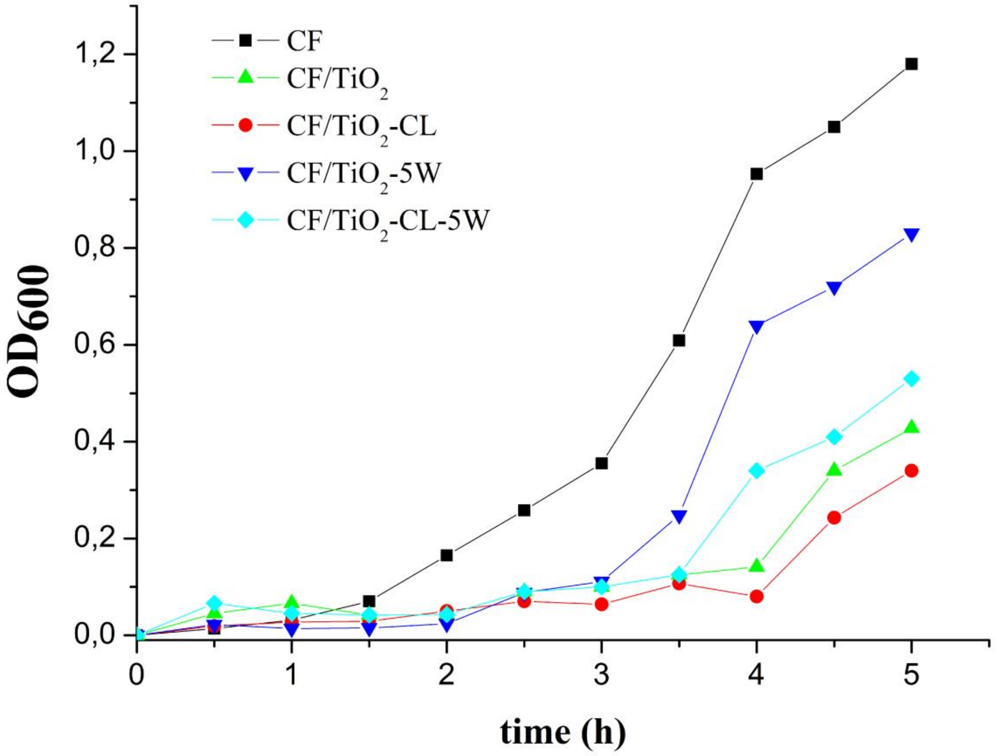
CF
CF/TiO2
CF/TiO2-CL
CF/TiO2-5W
CF/TiO2-CL-5W
OD600
1,2
1,0
0,8
0,6
0,4
0,2
0,0
0
1
2
3
4
5
time (h)

Figure 10

Highlights

1. The titania hydrosol was prepared by the low-temperature sol-gel synthesis;
2. The antimicrobial activity was investigated after exposure to UV-irradiation for 10 minutes;
3. Cotton fibers modified by titania and the cross-linking agent possess the highest conductivity;
4. Cotton/TiO_2 composites demonstrate high bacteriostatic effect against E. coli;
5. CF/TiO_2-CL shows the long-term effect of preservation of antibacterial properties.