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Antibacterial and UV protective properties of polyamide fabric impregnated with TiO₂/Ag nanoparticles

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Abstract: The possibility of *in situ* photoreduction of Ag⁺ using colloidal TiO₂ nanoparticles deposited on the surface of polyamide fabric in the presence of the amino acid alanine and methanol is discussed. The presence of TiO₂/Ag nanoparticles on the polyamide fabric was confirmed by FESEM and ICP analyses. The antibacterial activity of the fabric was tested against the Gram-negative bacterium *Escherichia coli* and the Gram-positive bacterium *Staphylococcus aureus*. The TiO₂/Ag nanoparticles fabricated on the surface of the polyamide fabric provided maximum bacterial reduction and thus, excellent antibacterial activity. In spite of silver leaching from the fabric during washing, the impregnated polyamide fabric preserved the maximum reduction of *E. coli* colonies. The antibacterial activity against *S. aureus* was slightly decreased after ten washing cycles, but still the antibacterial activity could be considered as satisfactory. In addition, the presence of TiO₂/Ag nanoparticles ensured better UV protection efficiency, which belonged to the UV protection category very good.

Keywords: TiO₂/Ag nanoparticles; polyamide; photoreduction; antibacterial activity; UV protection.

INTRODUCTION

Growing interest for the exploitation of silver nanoparticles (Ag NPs) in the production of medical and healthcare textiles due to their extraordinary antimicrobial activity has initiated broad research in this field.^{1–4} Many efforts have been made to develop simple routes for the manufacture of stable and durable antimicrobial nanocomposite textile materials with Ag NPs.⁴ Hitherto, major

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research was focused on the application of Ag NPs to cotton and polyester fibers.^{4–16} Polyamide (PA) fibers were less investigated despite their share in the production of healthcare and non-implantable medical textiles.^{10,17–24} In addition, good biocompatibility with different human cells and tissues make PA a very attractive material for implants.²⁴ Dip-coating techniques were the most commonly employed methods for the impregnation of PA materials with Ag NPs.^{10,19–23} Dubas *et al.* proposed an interesting approach based on layer-by-layer deposition whereby a thin film with antibacterial properties was formed on PA fibers by the sequential dipping of the fibers into solutions of poly(diallyldimethylammonium chloride) (PDADMAC) and Ag NPs capped with poly(methacrylic acid) (PMA).¹⁸ Sonochemical coating of Ag NPs onto PA fabrics was also reported as an alternative method for the impregnation of PA fabrics with Ag NPs.¹³ However, to the best of our knowledge, *in situ* fabrication of Ag NPs on the PA fabrics has not been reported.

The use of various reducing agents and organic compounds that control the formation, size, shape and stability of Ag NPs seems to be great disadvantage of conventional procedures for the fabrication of colloidal Ag NPs. These organic compounds can diminish or even inhibit the antimicrobial action of Ag NPs and they often have a negative environmental impact. The problematic use of strong reducing agents and stabilizers could be overcome by a previously proposed procedure.^{25,26}

Recent research indicated that *in situ* photoreduction of Ag⁺ using TiO₂ NPs deposited on the surface of polyethylene terephthalate (PET), cotton and cotton/PET fabrics in the presence of the amino acid alanine and methanol could be a viable alternative to conventional routes for the fabrication of Ag NPs.^{25,26} The proposed treatment is acceptable from the environmental point of view as it does not involve any aggressive chemicals or reducing agents. On the other hand, it provides large amounts of evenly distributed Ag NPs on the fiber surface and thus, excellent antimicrobial efficiency. The approach relies on the fact that surface modification of TiO₂ NPs smaller than 20 nm with alanine results in the replacement of hydroxyl groups on the surface of TiO₂.^{27,28} This further facilitates the coordination of surface Ti atoms with a carboxyl group and the simultaneous binding of Ag⁺.^{27,28} When TiO₂ is exposed to UV light with an energy that matches or exceeds its band gap, the formation of electron/hole pairs occurs. These charges can participate in different oxidation and reduction processes on the TiO₂ NPs surface, but their fast recombination appears as a serious limitation. In addition to improved adsorption of Ag⁺ before UV illumination, surface modification of TiO₂ NPs with amino acids results in enhanced charge separation and thus, elevated photocatalytic activity of photogenerated electrons.^{27,28} Photogenerated electrons are utilized for the photoreduction of adsorbed Ag⁺ and hence fabrication of TiO₂/Ag NPs.

Methanol has been exploited as an efficient hole-scavenger ($E^{\ominus}(\text{CH}_3\text{OH}/\bullet\text{CH}_2\text{OH}) = 1.2 \text{ V}$), which ultimately provides an increase in the yield of trapped electrons.²⁹ Electrochemical oxidation of methanol results in the formation of the electron-donating methanol radical ($E^{\ominus}(\bullet\text{CH}_2\text{-OH}/\text{CH}_2\text{O}) = -0.95 \text{ V}$), meaning that from one photon of absorbed light, two electrons are generated.³⁰ This phenomenon, known as a current-doubling effect, brings about an enhanced photoreduction rate of Ag⁺.³¹ The methanol radical is also able to reduce Ag⁺ ($\bullet\text{CH}_2\text{OH}$, -0.95 V).

The current study was aimed at highlighting whether the proposed method could be efficient in the impregnation of PA fabric with TiO₂/Ag NPs. The PA fabric impregnated in this manner was characterized by field emission scanning electron microscopy (FESEM) and ICP atomic emission spectroscopy analyses. The antibacterial activity of the deposited TiO₂/Ag NPs was tested against the Gram-negative bacterium *Escherichia coli* and the Gram-positive bacterium *Staphylococcus aureus*. In order to explore the stability of the fabricated nanocomposite system, washing fastness and perspiration fastness in artificial sweat under acidic and alkaline conditions were examined. The release of silver during washing and 24-h long incubation in artificial sweat was also monitored. The presence of TiO₂ NPs on the PA fabric surface was the essential motive to evaluate the UV protection efficiency of the impregnated PA fabric.

EXPERIMENTAL

Materials and methods

Desized and bleached polyamide (PA 6.6, 150 g m⁻²) fabric was cleaned in a bath containing 0.5 % the nonionic washing agent Felosan RG-N (Bezema) at a liquor-to-fabric ratio of 50:1. After 15 min of washing at 50 °C, the fabric was rinsed once with warm water (50 °C) for 3 min and three times (3 min) with cold water. The fabric was then dried at room temperature.

The colloid consisting of TiO₂ NPs was synthesized by acidic hydrolysis of TiCl₄ in a manner already described in detail in the literature.²⁸ Most of the synthesized TiO₂ NPs were single crystalline and irregularly shaped with average dimensions of 6 nm.³² The electron diffraction pattern and Raman spectroscopy measurements indicated the formation of the anatase crystal structure.³²

Impregnation of PA fabric with TiO₂ NPs (PA+TiO₂) was performed by immersion of the sample in 0.1 M TiO₂ colloid at a liquor-to-fabric ratio of 30:1 for 30 min. After squeezing at a pressure of 2 kg cm⁻², the sample was dried at room temperature. Subsequently, the sample was cured at 100 °C for 30 min, double rinsed with deionized water and dried at room temperature.

Alanine (0.1333 g) was dissolved in 40 mL of Milli-Q deionized water. PA fabric impregnated with TiO₂ NPs was immersed in this solution for 10 min. AgNO₃ solution (1.5 mL, $c = 0.015 \text{ mol L}^{-1}$) and methanol (0.4 mL) were added into 58 mL of HNO₃ solution ($1 \times 10^{-3} \text{ M}$, pH 3). This solution was added to the alanine solution and mixed. After purging with argon for 30 min, the system was illuminated with an Ultra-Vitalux lamp (300 W, Osram) for 30 min under exclusion of air. The applied lamp simulated sun-like irradiation with a spectral

radiation power distribution at wavelengths between 300–1700 nm. The PA fabric was removed from the solution, dried at room temperature, rinsed in Milli-Q deionized water for 15 min and dried at room temperature. The fabricated textile nanocomposite was denoted as PA+TiO₂/Ag.

The morphology of the PA fibers was analyzed by a Mira3 Tescan field emission scanning electron microscope (FESEM). The samples were coated with a thin layer of Au/Pd (85/15) prior to analysis.

The total content of Ag and Ti in the impregnated PA fabrics was determined using an ICP Emission Spectrometer: ICAP 6000 series (Thermo Electron Corporation). 40 mg of sample immersed in 60 mL of concentrated sulfuric acid was moderately heated for 5–10 min. Subsequently, 2 mL of nitric acid (1:1) was added and after short heating, a clear solution was obtained.

The reflectance spectra of the PA fabrics were recorded using a Datacolor SF300 spectrophotometer. The color coordinates of untreated PA fabric, PA+TiO₂ and PA+TiO₂/Ag fabric (*CIE L**, *a**, *b**) were determined under illuminant D₆₅ using a 10° standard observer. Based on the measured *CIE* color coordinates, the color difference (ΔE^*) was calculated as:

$$\Delta E^* = \sqrt{(\Delta a^*)^2 + (\Delta b^*)^2 + (\Delta L^*)^2} \quad (1)$$

where: ΔL^* is the color lightness difference between the PA+TiO₂/Ag fabric and the control PA fabric; Δa^* is the red/green difference between the PA+TiO₂/Ag fabric and the control PA fabric and Δb^* is the yellow/blue difference between the PA+TiO₂/Ag fabric and the control PA fabric.

Transmission spectra of the samples were measured using a Cary 100 Scan UV–Vis spectrophotometer (Varian). The UV protection factor (*UPF*) values were automatically calculated based on the recorded data in accordance with the Australia/New Zealand standard AS/NZS 4399:1996 using a Startek UV fabric protection application software version 3.0 (Startek Technology).

The antibacterial activity of impregnated PA fabrics was assessed against Gram-negative bacterium *E. coli* ATCC 25922 and Gram-positive bacterium *S. aureus* in accordance with the standard test method ASTM E 2149-01.³³ The percentage bacterial reduction (*R* / %) was calculated using the following equation:

$$R = 100 \frac{C_0 - C}{C_0} \quad (2)$$

where *C*₀ (CFU – colony forming units) is the number of bacterial colonies on the control PA fabric (untreated PA fabric without TiO₂/Ag NPs) and *C* (CFU) is the number of bacterial colonies on the PA fabric loaded with TiO₂/Ag NPs.

Washing fastness of impregnated PA fabrics was tested after five and ten washing cycles in Polycolor (Werner Mathis AG) laboratory beaker dyer at 45 rpm. The samples were washed in the bath containing 5 g L⁻¹ Society of Dyers & Colourists (SDC) standard detergent and 2 g L⁻¹ Na₂CO₃ at a liquor-to-fabric ratio of 80:1. After 30 min of washing at 40 °C, the fabrics were soaked twice in cold distilled water. The samples were afterwards held under the tap water for 10 min, squeezed and dried at 70 °C. The percentage of bacterial reduction after five and ten washing cycles was calculated according to Eq. (2). The concentration of silver released from the PA fabrics into washing bath after each washing cycle was measured using a Spectra AA 55 B (Varian) atomic absorption spectrometer (AAS).

The perspiration fastness of the impregnated PA fabrics was analyzed in artificial sweat. The artificial sweat at pH 5.5 and 8.0 were prepared according to ISO 105-E04:1989E.³⁴ The acidic artificial sweat (pH 5.5) contained: 0.5 g L⁻¹ of L-histidine monohydrochloride monohydrate, 5 g L⁻¹ of sodium chloride and 2.2 g L⁻¹ of sodium dihydrogen orthophosphate dihydrate. The alkaline artificial sweat (pH 8.0) contained: 0.5 g L⁻¹ of L-histidine monohydrochloride monohydrate, 5 g L⁻¹ of sodium chloride and 5 g L⁻¹ of disodium hydrogen orthophosphate dodecahydrate. The solutions were brought to pH 5.5 and 8.0 with a 0.1 M solution of sodium hydroxide. PA fabric (0.300 g) was rinsed in artificial sweat at a liquor-to-fabric ratio of 50:1. The samples were incubated in a water bath at 37 °C for 24 h. The artificial sweat was collected and the concentration of released silver was determined by AAS.

RESULTS AND DISCUSSION

The presence of Ag and Ti on the PA+TiO₂/Ag fabric was confirmed by ICP measurements. It was found that one gram of impregnated PA fabric contained 0.49±0.01 mg of Ag and 3.40±0.04 mg of Ti. These results clearly indicate that three times larger amount of Ag was detected on PA fabric than on PET fabric impregnated in the same manner.²⁵ EDX analysis of a single TiO₂/Ag nanoparticle deposited on the cotton and cotton/PET fibers in a previous study implied that metallic silver was formed exactly on the deposited TiO₂ NPs.²⁶ This was also confirmed by XPS mapping.²⁶ A thorough analysis of the FTIR spectra of pure alanine, alanine after binding to Ag⁺, after adsorption on the surface of TiO₂ NPs, and after adsorption on TiO₂ NPs and binding to Ag⁺ suggested that an interaction between TiO₂, alanine and silver was established, *i.e.*, the carboxyl group of alanine bridges the surface Ti and Ag⁺.²⁶ Therefore, this is the argument to denote the PA fabric impregnated in described manner as a PA+TiO₂/Ag fabric in the further text.

The morphology of PA fibers was analyzed by FESEM. A characteristic smooth surface of untreated PA fibers could be observed in Fig. 1a. On the other hand, Fig. 1b reveals that after the photoreduction process, the surface of the PA fibers became impregnated with TiO₂/Ag NPs. It is evident that agglomerates ranging from approximately 80 to 230 nm were randomly grouped over the surface of PA fibers (inset in Fig. 1b).

Antibacterial efficiency of PA+TiO₂/Ag fabrics was tested against *E. coli* and *S. aureus* bacteria. The results presented in Table I demonstrate that maximum bacterial reduction ($R = 99.9\%$) was obtained for both bacteria. It is well established that TiO₂ NPs exhibit antibacterial properties but only when they are exposed to UV light.^{32,35,36} Taking into account that these tests were conducted in the dark, the excellent antibacterial activity of the impregnated PA fabric are attributable only to the generated Ag NPs on the surface of the deposited TiO₂ NPs. Maximum reduction of bacteria *E. coli* was preserved after 10 washing cycles, indicating good washing fastness. In contrast, although the maximum reduction of *S. aureus* colonies remained after five washing cycles, after 10

washing cycles, bacterial reduction slightly decreased ($R = 99.5\%$). Still, the obtained antibacterial activity could be considered as satisfactory.

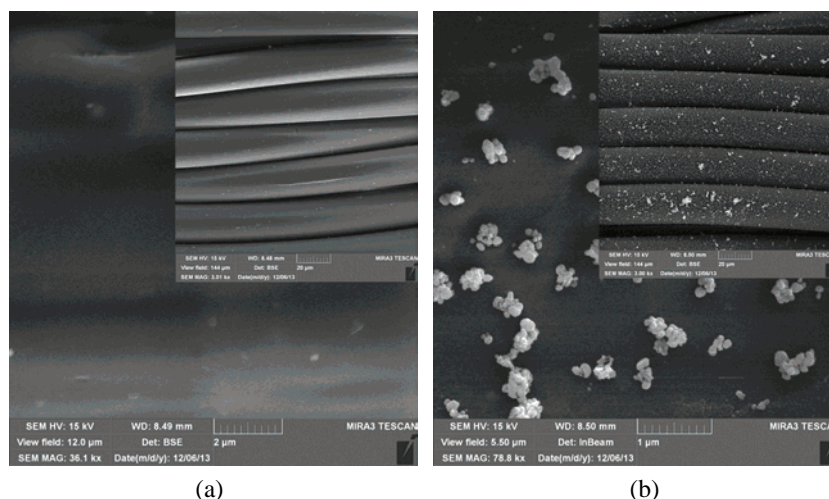


Fig. 1. FESEM images of: a) untreated PA and b) PA+ TiO₂/Ag fabrics.

TABLE I. Antibacterial activity of the PA+TiO₂/Ag fabric before and after washing

Sample	Bacterium	Number of bacterial colonies, CFU	R / %
Before washing			
Control PA	<i>E. coli</i>	1.6×10^5	99.9
PA+TiO ₂ /Ag		<10	
Control PA	<i>S. aureus</i>	2.1×10^5	99.9
PA+TiO ₂ /Ag		<10	
After 5 washing cycles			
Control PA	<i>E. coli</i>	2.5×10^5	99.9
PA+TiO ₂ /Ag		<10	
Control PA	<i>S. aureus</i>	8.0×10^3	99.9
PA+TiO ₂ /Ag		10	
After 10 washing cycles			
Control PA	<i>E. coli</i>	1.9×10^5	99.9
PA+TiO ₂ /Ag		140	
Control PA	<i>S. aureus</i>	2.1×10^5	99.5
PA+TiO ₂ /Ag		1.0×10^3	

The growth of bacterial colonies on the PA+TiO₂/Ag fabric after 10 washing cycles is suggested to be due to a decrease in Ag content after washing. AAS measurements of the Ag content in the washing bath after each washing cycle indicated that, particularly in the first four washing cycles, large amounts of silver had been released from the PA+TiO₂/Ag fabric. The results from Table II demonstrated that in each subsequent washing cycle, leaching of silver was less

pronounced. After the first washing cycle, the amount of silver was halved. However, in the last three washing cycles, the content of silver in washing bath was below the detection limit. Bearing in mind that initial silver content was around 490 $\mu\text{g g}^{-1}$ as well as that approximately 413 $\mu\text{g g}^{-1}$ of silver was released during washing, obviously sufficient amount of silver remained on the PA fabric surface to provide the desired level of antibacterial efficiency.

TABLE II. Silver release from the PA+TiO₂/Ag fabric during washing

Number of washing cycles	Silver release, $\mu\text{g g}^{-1}$
1	254.4 \pm 22.6
2	100.8 \pm 6.8
3	33.6 \pm 3.4
4	10 \pm 1.7
5	4.4 \pm 1.7
6	6.8 \pm 2.8
7	2.8 \pm 0.6
8	Below the detection limit
9	Below the detection limit
10	Below the detection limit

The photoreduction of Ag⁺ was followed by the color change of PA fabric, which turned from white to yellowish/gray. However, the color was paler after washing due to silver leaching. The reflectance measurements in the visible region of the spectra revealed that there was no significant difference in the reflectance intensity between untreated PA fabric and PA fabric impregnated with TiO₂ NPs (Fig. 2). However, after generation of TiO₂/Ag NPs, the reflectance

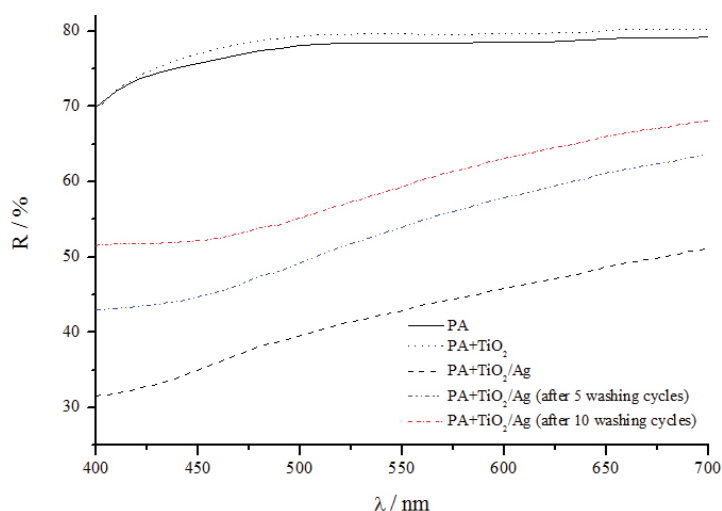


Fig. 2. Reflectance curves of the PA fabric, PA+TiO₂ fabric and PA+TiO₂/Ag fabrics before and after washing.

curve changed its shape, which was preserved after five and ten washing cycles, but the reflectance intensities decreased due to silver release. The color differences between PA fabrics impregnated with TiO₂/Ag NPs and control fabric (untreated PA fabric), expressed *via* ΔE^* , ΔL^* , Δa^* and Δb^* values, are presented in Table III. In general, the color differences (ΔE^*) greater than one can be visually detected. It is evident that after impregnation of PA with TiO₂/Ag NPs, ΔE^* drastically increased indicating a large color change, which declined after five and particularly after ten washing cycles.

TABLE III. Color change of the PA+TiO₂/Ag fabric after washing

Sample	L^*	a^*	b^*	ΔL^*	Δa^*	Δb^*	ΔE^*	Description
PA	90.91	-0.66	2.02	–	–	–	–	–
PA+TiO ₂ /Ag	71.40	1.35	9.41	-19.51	2.01	7.39	20.98	Darker, less green, yellow
PA+TiO ₂ /Ag (after 5 washing cycles)	78.34	2.27	9.23	-12.57	2.93	7.21	14.79	Darker, less green, yellow
PA+TiO ₂ /Ag (after 10 washing cycles)	81.47	2.43	6.65	-9.44	3.09	4.63	10.98	Darker, less green, yellow

The perspiration fastness of the PA+TiO₂ fabric in acidic and alkaline artificial sweat was also evaluated. The results showed that silver release occurred at both pH. Namely, 9.25 and 20.2 $\mu\text{g g}^{-1}$ of silver leached from the PA+TiO₂/Ag fabric at pH 5.5 and 8.0, respectively. Several reports revealed that silver is released to a larger extent under alkaline conditions.^{25,26,37,38}

Bearing in mind the ever-increasing warning on ozone layer depletion and potential health risks, much more attention has recently been paid on UV protective finishing of textile goods. Although many organic finishing agents have been conventionally used for UV protection of textiles, lately TiO₂ NPs appeared as a very attractive alternative since a small amount of TiO₂ NPs efficiently imparts the desired levels of UV protection.^{32,35,36,39,40} The present study also confirmed that TiO₂/Ag NPs could significantly enhance the UV protective properties of PA fabric. The UPF values and UPF ratings of untreated and impregnated PA fabric before and after washing are given in Table IV. As expected, the PA fabric exhibited poor UV protection with a UPF rating of only 10. The deposition of TiO₂ NPs on the PA fabric led to an increase in the UPF value from 12.76 to 28.13. Consequently, the UPF rating of the PA+TiO₂ fabric rose to 25, indicating very good UV protection. The presence of silver on the surface of TiO₂ NPs and corresponding color change of the PA fabric into yellowish brought about a further elevation of the UPF rating to 30. However, after washing, UPF rating decreased to 25, very likely due to silver release. There was no significant difference between UPF values of the PA+TiO₂/Ag fabric after five and ten washing cycles. The UPF values measured after washing were almost

equivalent to the one corresponding to the PA+TiO₂ fabric. These results are in a good correlation with a fact that approximately 85 % of silver had been released after ten washing cycles.

TABLE IV. UV protection properties of the PA fabric, PA+TiO₂ fabric and PA+TiO₂/Ag fabrics before and after washing

Sample	UPF	UPF rating
PA	12.76	10
PA+TiO ₂	28.13	25
PA+TiO ₂ /Ag	38.24	30
PA+TiO ₂ /Ag (after 5 washing cycles)	28.22	25
PA+TiO ₂ /Ag (after 10 washing cycles)	27.59	25

CONCLUSIONS

The results of this study indicated that colloidal TiO₂ nanoparticles deposited on PA fabric could be efficiently exploited for the photoreduction of Ag⁺ ions in the presence of the amino acid alanine and methanol. The fabricated TiO₂/Ag nanoparticles could be utilized for imparting antibacterial and UV protective properties to PA fabric. PA fabric impregnated with TiO₂/Ag nanoparticles provided the maximum reduction of *E. coli* and *S. aureus* bacterial colonies. Maximum bacterial reduction was preserved after ten washing cycles in the case of *E. coli*, whereas the antibacterial activity of the fabric slightly decreased against *S. aureus*. This was suggested to be due to leaching of silver during washing and thus, a smaller amount of retained silver on the surface of the fabric. The leaching of silver occurred to a much smaller extent in artificial sweat, particularly under alkaline conditions. In addition, the impregnated PA fabric had a UPF rating of 30, which could be classified as very good UV protection.

Excellent antibacterial activity and good washing fastness of PA impregnated with TiO₂/Ag nanoparticles could be utilized in the production of medical and protective textiles, which show an ever-increasing demand.

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ИЗВОД
АНТИБАКТЕРИЈСКА И UV-ЗАШТИТНА СВОЈСТВА ПОЛИАМИДНЕ ТКАНИНЕ
ИМПРЕГНИРАНЕ НАНОЧЕСТИЦАМА TiO₂/Ag

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У овом раду је дискутована могућност *in situ* фоторедукције Ag⁺ помоћу колоидних наночестица TiO₂ депонованих на површину полиамидне тканине у присуству аминокиселине аланина и метил-алкохола. Присуство наночестица TiO₂/Ag на полиамидној тканини потврђено је FESEM и ICP анализама. Антибактеријска активност тканине је тестирана према грам-негативној бактерији *Escherichia coli* и грам-позитивној бактерији *Staphylococcus aureus*. Генерисане наночестице TiO₂/Ag на површини полиамидне тканине обезбеђују максималну бактеријску редукцију и тиме одличну антибактеријску активност. Упркос ослобађању сребра са тканине током прања, импрегнирана полиамидна тканина је очувала максималну редукцију колонија *E. coli*. Антибактеријска активност према бактерији *S. aureus* је смањена након десет циклуса прања, али се још увек може сматрати задовољавајућом. Присуство наночестица TiO₂/Ag такође обезбеђује бољу ефикасност UV заштите која се може класификовати као врло добра.

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