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Gamma irradiation induced surface modification of silk fabrics for antibacterial application

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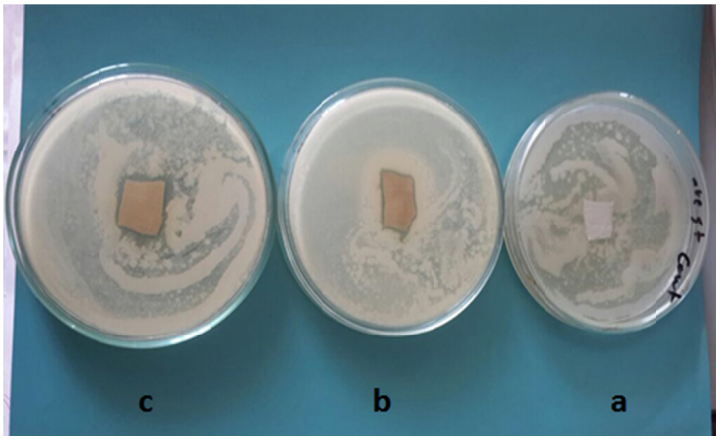
HIGHLIGHTS

- Fabrics were carried out by coating with silver nanoparticles (AgNPs) stabilized with polyvinylpyrrolidone (PVP) through γ-irradiation.
- The AgNPs-coated silk fabrics demonstrated an excellent antibacterial activity against the tested bacteria, *Escherichia coli* and *Staphylococcus aureus*.
- This work offers potentials to produce specific AgNPs-coated antimicrobial silk for various applications in the textile industry.

GRAPHICAL ABSTRACT



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ABSTRACT

Silk fabrics were modified by a treatment of silver nitrate solution ($AgNO_3$) and polyvinylpyrrolidone (PVP) as a stabilizer then exposure to γ-irradiation to create antibacterial properties. Effects of the absorbed dose on treated fabrics were investigated. The scanning electron microscopy (SEM) and X-ray diffraction (XRD) patterns were used to confirm the presence of silver nanoparticles (AgNPs) on the fabric. The treated fabrics should have enhanced thermal stability due to the presence of AgNPs. The treated silk fabric was examined for its antibacterial activity toward various types of bacteria. The AgNPs-treated silk fabrics demonstrated excellent antibacterial activity against the tested bacteria, *Escherichia coli* and *Staphylococcus aureus*. This work opens the door for production of specific AgNPs-silk as a type of textile in the antibacterial domain.

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1. Introduction

As a natural protein fiber, silk possesses a structure very similar to human skin with smooth, breathable, soft, non-itching and antistatic characteristics [1]; however, bacteria can easily adhere and grow on silk fabric causing deformation and degradation [2]. So, it is necessary to produce a silk fiber having antimicrobial activity which can be used in a wide range of applications. The antimicrobial finishing can be used for fabrics and clothes used in hospital and crowded public areas or textiles that are left wet for a long period of time between processing steps. Finally, the use of this finishing in intimate apparel, underwear and socks can prevent unpleasant odors [3].

As advances in nanotechnology have been made, numerous nanomaterials with various structures and unique properties have been fabricated [4-9]. Researchers have recently become interesting in the immobilization of fibers with nanomaterials to produce multifunctional textiles. Since the silver nanoparticle (AgNP) is a typical nanomaterial with broad-spectrum antibacterial effects on both Gram-negative and Gram-positive bacteria [10,11], it has been utilized to treat silk fibers for antimicrobial properties [12-15]. The antimicrobial properties of silver particles have been exploited for a long time in biomedical textiles as its broad-spectrum action is particularly significant in preventing polymicrobial colonization associated with hospital-acquired infections [16,17]. Silver has revealed bactericidal activity against a wide range of Gram-positive and Gram-negative bacteria, namely *Pseudomonas aeruginosa*, *S. aureus*, *Staphylococcus epidermidis*, *E. coli* and *Klebsiella pneumonia* [18]. The AgNPs interact with the bacterial membrane and are able to penetrate inside the cell. The mechanisms of interaction involve AgNPs attaching to bacterial cell membranes, which increase permeability and disturb respiration. Another advantage of AgNPs is that they are easily embedded into the fibers' polymeric matrices [19,20].

Various polymers, such as polyamide, polyvinyl-pyrrolidone, and polyacrylic acid, were employed to functionalize the silk surface [21-23] to produce a hydrophilic character to increase the adsorption amount of Ag^+, which subsequently reduced to AgNPs [11,24].

Antibacterial fabrics can be used to make bandages, gauze, bed sheets, and surgical clothes [25,26].

Mohammad Mirjalili *et al.* imparted an antimicrobial finishing to cellulose fabric using a nano silver solution [27]. The surface characteristics of these fabrics have been studied by scanning electron microscopy (SEM) which indicated silver nanoparticles were well dispersed on the fabric surface. An antibacterial test, using Gram-negative bacteria (*Escherichia coli*), was used to estimate the biological activity of the treated fabrics.

Wasif A. I. and Laga S. K. studied antimicrobial finishing on cotton woven fabric using a nano silver solution as an antimicrobial agent against Gram positive (*Staphylococcus aureus*) and Gram-negative bacteria (*Escherichia coli*), at various concentrations in the presence of polyvinylalcohol (PVOH) [28]. They found that the higher the concentration of antimicrobial agent the larger the zone of inhibition in the cases of both Gram-positive and Gram-negative bacteria. Various properties like tensile strength, bending length, crease recovery angle, and zone of inhibition were also studied.

In this study, we prepared silk fabrics treated with AgNPs via γ-ray irradiation. SEM, XRD, and TGA were used to confirm the properties of these treated fabrics. The antimicrobial finish was applied to make silk fabrics more suitable for industrial applications.

2. Experimental

2.1. Materials

Silver nitrate, crystal, and ACS, M.W. 169.87, was obtained from GAMMA, Laboratory Chemicals. Polyvinylpyrolidone (PVP), M.W. 40000, was supplied from Universal Fine Chemicals PVT. LTD, India. All the materialswere used without further purification. Silk fabric was kindly supplied by Al Khateeb Company, Akhmen, Egypt.

2.2. Treatment of silk fabric

Approximately 60 g of washed silk fabrics were irradiated in 500 ml of 3 mM $AgNO_3$ solution using the stabilizer of 1.0% Polyvinylpyrrolidone (PVP) in the dose range from 5 to 20 kGy of gamma irradiation at the National Center for Radiation Research and Technology, Cairo, Egypt.

Afterwards, samples were rinsed with water and dried at 40°C for 40 min. A similar procedure was applied for 40 repeated washes.

3. Characterizations

Samples (silk treated with AgNPs) were digested in conc. Nitric acid 69% (Anular) and H_2O_2 in a 5:1 ratio using a Microwave Digester Instrument, Milestone 1200 Miga, Italy [29]. The Ag element was estimated using an Atomic Absorption Spectrometer, Thermo Scientific E3000 series, England. Tensile (tensile strength and % elongation-at-break) properties were determined using a Mecmesin, (Model 10-1) UK, equipped with software and a crosshead speed of 50 mm/min. All mechanical parameters were directly calculated. The samples for tensile measurements were dumbbell shaped with a width of 4 mm and length of 50 mm. The surface morphology of the modified silk fabrics in comparison with unmodified silk fabrics was examined by SEM. The micrographs were taken with a JSM-5400 instrument manufactured by Joel, Japan. An XRD experiment of the samples was performed at room temperature using a Philips PW 1390 diffractometer (30 kV, 10 mA) with copper target irradiation at a scanning rate of 80/min in a 2Θ range of 400-900°C. Thermal characteristics of AgNPs treated silk fabrics were determined from the thermogravimetric analysis (TGA) data, using a TGA-30 apparatus (at Shimadzu, Kyoto, Japan), at a heating rate of 10°C/min. in air, over a temperature range from room temperature to 600°C.

4. Antibacterial activity testing

A disk diffusion test, according to the Kirby Baur method [30], was applied to identify the bacterial effect through the measurements of bacterial broth. A known quantity of bacteria was grown overnight on agar (solid growth media) plates. The samples were placed in Petri-dishes and then incubated for 24 hr at 30-32°C. The inhibition zone was then measured in cm from one side of the square sample. Both positive and negative bacteria, *Escherichia Coli* and *Staphylococcus aurous*, were tested.

5. Results and discussions

5.1. Measurement of silver content on the treated silk fabrics

The amount of silver content on the treated silk fabrics was calculated. Figure 1 shows the relationship between the absorbed dose and silver content. The results obtained from this figure indicate that the content of AgNPs on the silk fabrics increases as the absorbed dose increases up to 10 kGy then tends to level off. A maximal value of the AgNPs content on fabrics was found to be 177 ppm for the silk fabrics in a 3 mM $AgNO_3$ solution irradiated with an absorbed dose of 10 kGy.

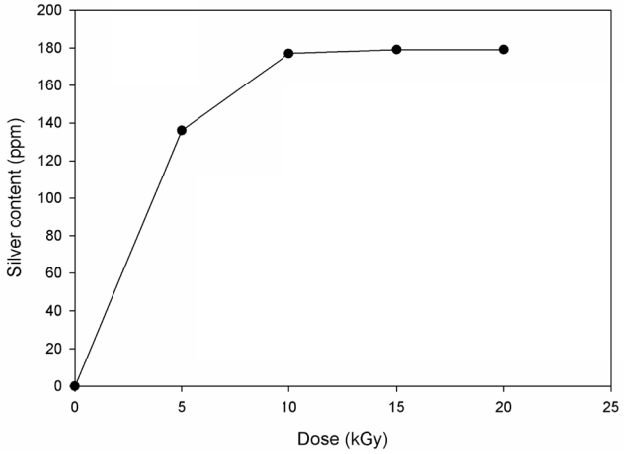

Fig. 1. Relationship between the content of AgNPs on the silk fabrics and irradiation dose.

The formation of Ag^+ ions was a result of silk fabrics treated with the $AgNO_3$ solution. These Ag^+ ions were reduced to Ag atoms and simultaneously deposited on the silk fabrics. The interaction between fibers and metallic AgNPs stabilized by PVP polymer caused the formation of a chemical bond between the silver and alcoholic groups of silk and resulted in the physical adsorption of AgNPs on the fabric surface [31].

5.2. Mechanical properties

Mechanical properties of the treated silk fabrics in terms of tensile strength (TS) and elongation (E,%) in the dose range from 0 to 20 kGy were plotted in Figures 2 and 3. The results show that tensile strength and elongation at break (%) of the AgNPs treated silk fabrics are slightly affected at the doses (5-20 kGy) in comparison with the control silk fabrics. The results showed that tensile strength (TS) of the AgNPs treated silk fabrics irradiated with 5 kGy exhibit slightly lower tensile strength than the control silk fabric as shown in Figure 2. Whereas, the strain value of the treated fabric at the same dose was more than that of the untreated fabric as shown in Figure 3. The results obtained from this figure indicate that the treatment process did not alter the mechanical properties of the silk fabric.

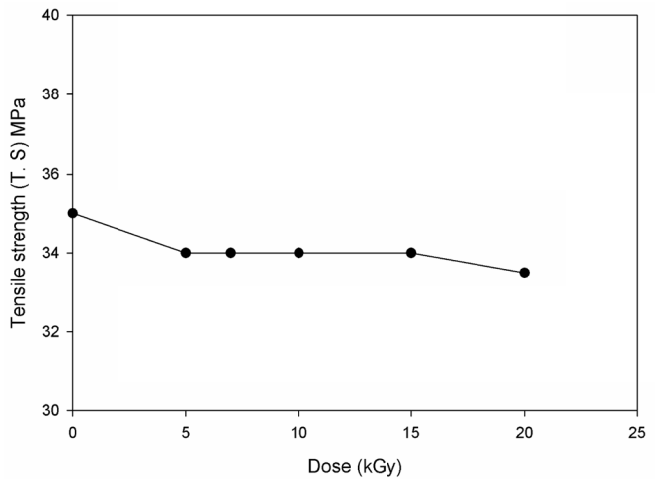

Fig. 2. Effect of different irradiation dose on the tensile strength at break of untreated silk fabric and AgNPs-treated ones with different gamma irradiation doses.

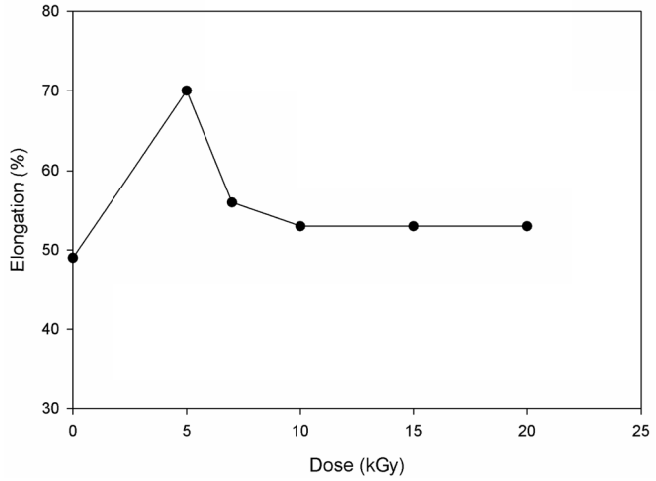

Fig. 3. Effect of different irradiation dose on the elongation (%) at break of untreated silk fabric and AgNPs-treated silk fabrics with different gamma irradiation doses.

5.3. Scanning electron microscopy (SEM) of untreated and treated silk fabrics

The surface morphology of untreated and treated silk fabrics irradiated to different doses (5 and 10 kGy) was investigated by SEM (Figure 4 a, b, and c). (a) shows the surface morphology of untreated fabric, which appeared smooth and homogeneous. Figure 4 (b, and c) illustrates the surface morphology of silk fabric treated with silver NPs, which appeared rough and full of particle aggregates due to the imbedding of AgNPs. It was noted that after irradiation to 5 kGy in $AgNO_3$ solution, some of the AgNPs were agglomerated and therefore caused the formation of large nanoparticles dispersed on the fabric surface. As the irradiation dose increased from 5 kGy to 10 kGy, the aggregation of the AgNPs increases [32]. To limit the side effects of AgNPs aggregation, a

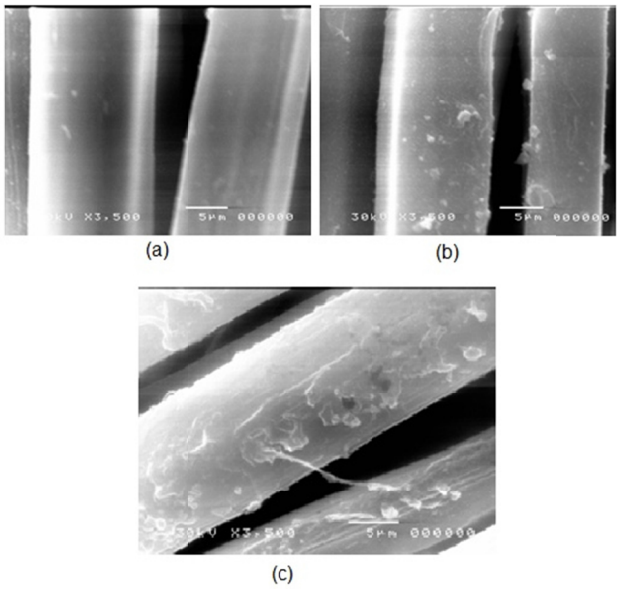

Fig. 4. SEM of untreated and AgNPs-treated silk fabrics with different gamma irradiation doses, a) Original silk fabric, b) 5 kGy, c) 10 kGy.

low irradiation dose with efficient AgNPs production is preferred for obtaining homogeneously dispersed AgNPs on the surface.

5.4. XRD of untreated and treated silk fabrics

XRD patterns of untreated and treated silk fabrics with AgNPs are shown in Figure 5 (a, b and c). The silk fabrics had a crystalline peak located at $2\Theta=20.28^{o}$ [33]. Figure (5a) shows there is no significant change in this peak after the treatment; this suggests that the gamma irradiation and AgNPs attachment do not alter the structure of the silk fibers. (Figure 5b and c) shows four new peaks at 2Θ values of $38.4^{o}C$, $44.6^{o}C$, $64.7^{o}C$ and $77.5^{o}C$ were detected, which were attributed to the diffraction peaks of the (111), (200), (220) and (311) planes of silver NPs, respectively [34]. The XRD pattern clearly indicates that AgNPs were deposited directly on the silk surface and the silk fabrics treated with AgNPs were successfully prepared using silver nitrate by radiation.

5.5. Thermogravimetric analysis (TGA) of untreated and treated silk fabrics

Thermal behavior of untreated and treated silk fabrics in a temperature range from room temperature to $600^{o}C$ at all gamma irradiation doses (5-20 kGy) are shown in Figure 6. It can be seen that the thermal decomposition

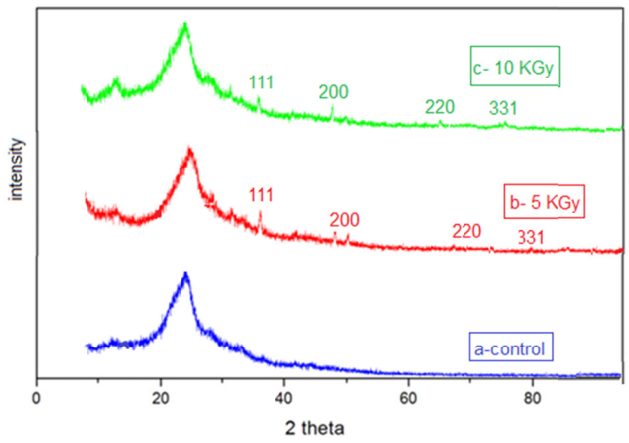

Fig. 5. XRD patterns of untreated (a) and AgNPs-treated silk fabric with different gamma irradiation doses (b and c).

of both the untreated and treated silk fabrics passes through three stages upon heating from room temperature to 600°C. All the curves show an initial stage of weight loss below 100°C, which can be ascribed to the elimination of adsorbed water from the fabrics. In the second stage at temperatures from 100-290°C, all samples again show weight loss, which may be attributed to the degradation of side chain groups of silk fibroin proteins [35]. The third stage of weight loss from 300 to 600°C may be caused by the breakdown of the main chains of silk fibers [35]. Moreover, it was found that thermal stability increases as the irradiation dose increases up to 10 kGy. For example, at a constant temperature of 350°C weight loss % is 30% and 19% at an irradiation dose of 5 and 10 kGy, respectively. Since carboxyl groups on the side chains of silk proteins are expected to be the binding sites of AgNPs, its attachment may possibly protect the side chains from thermal degradation [36-38].

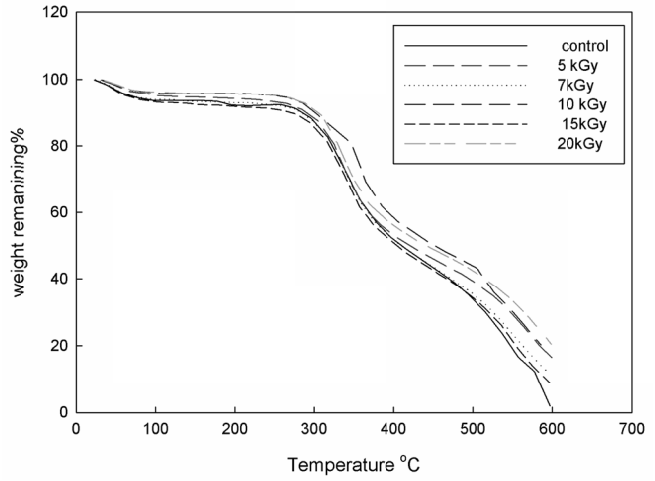

Fig. 6. TGA curves of untreated and AgNPs-treated silk fabric with different gamma irradiation doses.

5.6. Antibacterial activity testing

Figures 7 and 8 show the antibacterial effects of untreated and Ag NPs-treated silk fabrics (5 and 10 kGy) on *E.coli* (A) Gram-negative and *S. aureus* (B) Gram-positive bacteria. *E. coli* and *S. aureuswere* selected as model bacteria to explore the antimicrobial effects of the modified silk fabric in the zone of inhibition test since they are typical Gram-negative and Gram-positive bacteria, respectively. In this study [39], no clear zone occurs on either the *E. coli* and *S. aureus* agar plates for the untreated silk fabric. In contrast, all AgNPs-treated fabrics have obvious inhibition zones. The results obtained from these figures signified the following features: (a) the untreated silk fabric (control) exhibited no inhibition zone indicating no antibacterial activity; (b) treatment of a constant concentration of silver nitrate (3 mM) irradiated to 5 and 10 kGy rendered the fabric antibacterial irrespective of the bacteria used, (c) resistance of the modified fabric to *E.coli* (A) Gram-negative bacteria is greater than that for the *S. aureus* (B) Gram-positive bacteria as evidenced by comparing the inhibition zone for all used bacteria. These results strongly prove that AgNPs-treated silk fabrics possess the capability to kill both Gram-negative and Gram-positive bacteria.

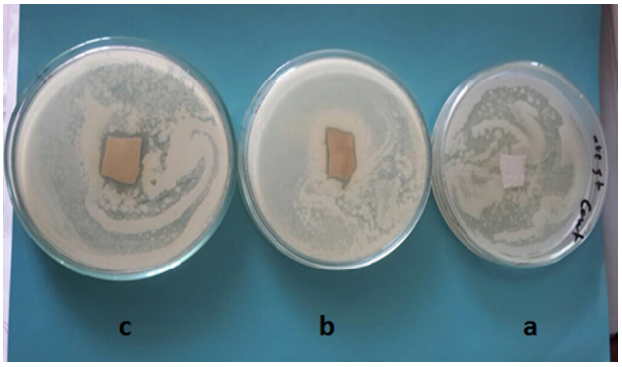

Fig. 7. Antibacterial effects of the untreated and AgNPs-treated silk fabrics on *E.coli* (A) Gram-negative bacteria.

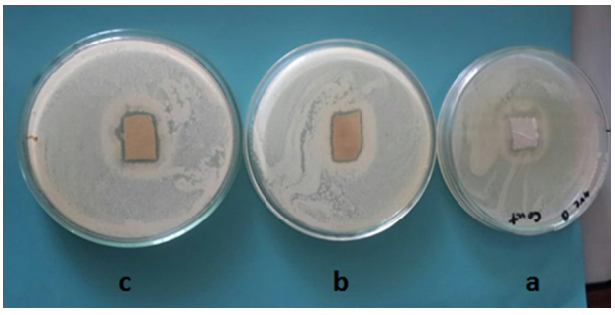

Fig. 8. Antibacterial effects of the untreated and AgNPs-treated silk fabrics on *S. aureus* (B) Gram-positive bacteria.

6. Conclusions

The preparation of the treated fabric depends on the gamma irradiation doses in the presence of PVP polymer and silver ions. Gamma irradiation doses cause significant aggregation of AgNPs on the fabric. A good distribution of AgNPs on the silk fabric surface, exhibited in SEM images, proves the existing of AgNPs on the silk fabrics. The XRD data reveal that the synthesized treated fabric possess good crystalline structures. The presence of AgNPs greatly changed the pattern of the TGA curve, and may be due to the attached AgNPs protecting the silk fibers from degradation. The residue weight observed in the TGA experiment further proves the successful synthesis of AgNPs on the fiber surface. The antimicrobial activity including bacterial growth inhibition and bactericidal effects of the AgNPs-coated silk is demonstrated in the zone of inhibition. Based on the data, it can be concluded that AgNPs-coated silk, which possesses excellent antibacterial activity, is directly fabricated with a gamma irradiated-assisted in situ synthesis approach using degummed silk fibers and a $AgNO_3$ solution as raw materials. This work offers the potential to produce treated antimicrobial silk for applications including clothing and industrial textiles.

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References

[1] D.M. Phillips, L.F. Drummy, D.G. Conrady, D.M. Fox, R.R. Naik, M.O. Stone, P.C. Trulove, H.C. De Long, R.A. Mantz, Dissolution and regeneration Bombyx mori Silk fibroin using ionic liquids, J. Am. Chem. Soc. 126 (2004) 14350-14351.

[2] H.J. Jin, J. Park, R. Cebe, P. Valluzzi, D.L. Kaplan, Biomaterial films of Bom-byx mori silk fibroin with poly(ethylene oxide), Biomacromolecules 5 (2004) 711-717.

[3] G. Arai, G.M. Colonna, E. Scotti, A. Boschi, R. Murakami, M.T. Tsukada, Absorption of metal cations by modified *B. mori* silk and preparation of fabrics with antimicrobial activity, J. Appl. Polym. Sci. 80 (2001) 297-303.

[4] V. Scognamiglio, Nanotechnology in glucose monitoring: advances and challenges in the last 10 years, Biosens. Bioelectron. 47 (2013) 12-25.

[5] Z.S. Lu, C.X. Guo, H.B. Yang, Y. Qiao, J. Guo, C.M. Li, One-step aqueous synthesis of graphene-CdTe quantum dot-composed nanosheet and its enhanced photoresponses, J. Colloid Interf. Sci. 353 (2011) 588-592.

[6] Z.S. Lu, W.H. Hu, H.F. Bao, Y. Qiao, C.M. Li, Interaction mechanisms of CdTe quantum dots with proteins possessing different isoelectric points, Med. Chem. Commun. 2 (2011) 283286.

[7] Z.S. Lu, C.M. Li, Quantum dot-based nanocomposites for biomedical applications, Curr. Med. Chem. 18 (2011) 3516-3528.

[8] Z.S. Lu, C.M. Li, H.F. Bao, Y. Qiao, Q.L. Bao, Photophysical mechanism for quantum dots- induced bacterial growth inhibition, J. Nanosci. Nanotechnol. 9 (2009) 3252-3255.

[9] Z.S. Lu, C.M. Li, H.F. Bao, Y. Qiao, Y. Toh, X. Yang, Mechanism of antimicrobial activity of CdTe quantum dots, Langmuir 24 (2008) 5445-5452.

[10] E. Amato, Y.A. Diaz-Fernandez, A. Taglietti, P. Pallavicini, L. Pasotti, L. Cucca, C. Milanese, P. Grisoli, C. Dacarro, J.M. Fernandez-Hechavarria, Synthesis, characterization and antibacterial activity against Gram positive and Gram negative bacteria of biomimetically coated silver nanoparticles, Langmuir 27 (2011) 9165-9173.

[11] L.Y. Guo, W.Y. Yuan, S. Lu, C.M. Li, Polymer/nanosilver composite coatings for antibacterial applications, Colloid Surface A 439 (2013) 69-83.

[12] W.D. Yu, T. Kuzuya, S. Hirai, Y. Tamada, K. Sawada, T. Iwasa, Preparation of Ag nanoparticle dispersed silk fibroin compact, Appl. Surf. Sci. 262 (2012) 212-217.

[13] L. He, S.Y. Gao, H. Wu, X.P. Liao, Q. He, B. Shi, Antibacterial activity of silver nanoparticles stabilized on tannin grafted collagen fiber, Mater. Sci. Eng. C 32 (2012) 1050-1056.

[14] J.J. Wu, G.J. Lee, Y.S. Chen, T.L. Hu, The synthesis of nano silver/polypropylene plastics for antibacterial application, Curr. Appl. Phys. 12 (2012) S89-S95.

[15] R. Bhattacharya, P. Mukherjee, Biological properties of "naked" metal nanoparticles, Adv. Drug

Deliver. Rev. 60 (2008) 1289-1306.

[16] S. Shahidi and J. Wiener, Antimicrobial Agents-Chapter 19: Antibacterial Agents in Textile Industry; InTech: Rijeka, Crotia, 2012, pp. 387-406.

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

[18] J. Hasan, R.J. Crawford, E.P. Ivanova, Antibacterial surfaces: The quest for a new generation of biomaterials, Trends Biotechnol. 31 (2013) 295-304.

[19] B. Simoncic, B. Tomsic, Structures of novel antimicrobial agents for textiles-A review, Text. Res. J. 80 (2010) 1721-1737.

[20] H. Palza, Antimicrobial polymers with metal nanoparticles, Int. J. Mol. Sci. 16 (2015) 2099-2116.

[21] D. Zhang, G.W. Toh, H. Lin, Y.Y. Chen, In situ synthesis of silver nanoparticles on silk fabric with PNP for antibacterial finishing, J. Mater. Sci. 47 (2012) 5721-5728.

[22] S. Tangbunsuk, G.R. Whittell, M.G. Ryadnov, G.W.M. Vandermeulen, D.N. Woolfson, I. Manners, Metallopolymer-peptide hybrid materials: Synthesis and Self-Assembly of Functional, Poly ferrocenylsilane-Tetrapeptide Conjugates, Chem.-Eur. J. 18 (2012) 2524-2535.

[23] X.M. Wang, W.R. Gao, S.P. Xu, W.Q. Xu, Luminescent fibers: in situ synthesis of silver nanoclusters on silk via ultraviolet light-induced reduction and their anti-bacterial activity, Chem. Eng. J. 210 (2012) 585-589.

[24] A.R. Abbasi, A. Morsali, Influence of various reduction reagents on the morphological properties of Ag nanoparticles@silk fiber prepared using sonochemical method, J. Inorg. Organomet. P. 21 (2011) 369-375.

[25] S.T. Dubas, P. Kimlangdudsana, P. Potiyaraj, Layer-by-layer deposition of antimicrobial silver nanoparticles on textile fibers, Colloid. Surface. A 289 (2006) 105-109.

[26] P. Gupta, M. Bajpai, S.K. Bajpai, Investigation of antibacterial properties of silver nanoparticle-loaded poly (acrylamide-co-itaconic acid)-grafted cotton fabric, J. Cotton Sci. 12 (2008) 280-286.

[27] M. Mirjalili, N. Yaghmaei1, M. Mirjalili, Antibacterial properties of nano silver finish cellulose fabric, J. Nanostruct. Chem. 3 (2013) 43.

[28] A.I. Wasif, S.K. Laga, Use of nano silver as an antimicrobial agent for cotton, AUTEX Res. J. 9 (2009) 5-13.

[29] IAEA: Elemental analysis of biological materials. International Atomic Energy Agency (IAEA), Veinna, Technical Reports Series No. 197 (1980) 379.

[30] Clinical and Laboratory Standards Institute, Performance Standards for Antimicrobial Disk Susceptibility Tests; Approved Standard-Ninth Edition, Clinical and Laboratory Standards Institute document M2-A9 (ISBN 1-56238-586-0), 940 West Valley Road, Suite 1400, Wayne, Pennsylvania 19087-1898 USA, 2006.

[31] I. Perelshtein, G. Applerot, N. Perkas, Sonochemical coating of silver nanoparticles on textile fabrics (nylon, polyester and cotton) and their antibacterial activity and their antibacterial activity, Nanotechnology 19 (2008) 245705.

[32] B. Liu, W.Z. Chen, S.W. Jin, Synthesis, structural characterization, and luminescence of new silver aggregates containing short Ag-Ag contacts stabilized by functionalized bis (N-heterocyclic carbene) ligands, Organometallics 26 (2007) 3660-3667.

[33] Q. Lu, X. Hu, X.Q. Wang, J.A. Kluge, S.Z. Lu, P. Cebe, D.L. Kaplan, Water-insoluble silk films with silk I structure, Acta Biomater., 6 (2010) 1380-1387.

[34] X. Zou, E. Ying, S. Dong, Preparation of novel silver gold bimetallic nanostructures by seeding with silver nanoplates and application in surface enhanced Raman scattering, J. Colloid Interf. Sci. 306 (2007) 307-315.

[35] X.X. Feng, L.L. Zhang, J.Y. Chen, Y.H. Guo, H.P. Zhang, C.I. Jia, Preparation and characterization of novel nanocomposite films formed from silk fibroin and nano-TiO_2, Int. J. Biol. Macromol. 40 (2007) 105-111.

[36] L. Piao, K.H. Lee, B.K. Min, W. Kim, Y.R. Do, S. Yoon, A facile synthetic method of silver nanoparticles with a continuous size range from sub-10 nm to 40 nm, Bull. Korean Chem. Soc. 32 (2011) 117-121.

[37] F. Chen, Y. Liu, R.E. Wasylishen, Z.H. Kuznicki, Solid-state NMR and TGA studies of silver reduction in chabazite, J. Nanosci. Nanotechno. 12 (2012) 1988-1993.

[38] M.A.M. Khan, S. Kumar, M. Ahamed, S.A. Alrokayan, M.S. AlSalhi, Structural and thermal studies of silver nanoparticles and electrical transport study of their thin film, Nanoscale Res. Lett. 6 (2011) 434.

[39] S.A. Khan, A. Ahmad, M.I. Khan, M. Yusuf, M. Shahid, N. Manzoor, F. Mohammad, Antimicrobial activity of wool yarn dyed with *Rheum emodi* L. (Indian Rhubarb), Dyes Pigments 95 (2012) 206-214.