HYBRID SILICA NANOFIBERS WITH AG IONS FOR BIOMEDICAL APPLICATIONS

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Abstract

This study is focused on development of novel nanofibrous material with immobilized Ag ions. These nanofibers have a great potential for biomedical applications, especially for antimicrobial wound dressing. The hybrid silica/PVA nanofibers were prepared by electrospinning and thermally stabilized. Consequently, Ag ions were immobilized onto the surface of the nanofibers. It was proved that quantity of immobilized Ag ions depends on immobilizing process time. As SEM analysis shown, Ag ions were immobilized onto single fibers in continuous density. According to preliminary antibacterial in-vitro test, the hybrid nanofibers with Ag ions show significant antibacterial activity.

Keywords: Silica nanofibers, polyvinyl alcohol, Ag ions, antibacterial activity.

1. INTRODUCTION

Next to organic nanofibers, whose utilization is widely studied and tested in the last few years, attention is also paid to research new features possibilities of biomedical application of inorganic or combined organic-inorganic nanofibers. Our development is focused on pure and hybrid silica/polymer nanofibers and their biomedical applications. This study is aimed at development of hybrid nanofibrous material with antibacterial activity. Commercially available medical devices for wound dressing are insufficient for the treatment of superficial skin lesion, the treatment is problematic. Acute and chronic wounds type of burns or leg ulcers are often attacked by infections during long-term treatment. Problematic wound healing is often related to inappropriately combined wounds covering, which characteristics are always a compromise of ideal coverage. The novel active antibacterial nanofibrous material has a potential to be one of the ways to improve the treatment of mentioned hard-to-heal wounds.

Antibacterial modification of nanofibers is possible in two ways: immobilizing the bacterial components on the surface of the nanofibers or incorporating antibacterial component into the polymer solution for electrospinning. This research is focused on Ag ions immobilization onto the surface of hybrid silica nanofibers.

Nanosilver and Ag ions have broad spectrum of antibacterial activity and they are able to kill a wide range of bacteria including those which are resistant to antibiotics [1]. In recent years, there have been published several summaries of possible antimicrobial mechanism of nano Ag [2], but the complete mechanism of action is not fully understood. As one of the possible mechanisms, there have been shown to release silver ions from nano Ag. According to available researches, Ag ions immobilized on the surface of organic or inorganic nanofibers show significant antibacterial activity and cytocompatibility [3, 4].

1. EXPERIMENT

1.1. Material

The material used for the preparation of silica/PVA nanofibers with Ag ions include tetraethyl orthosilicate (TEOS, Sigma Aldrich), cetyltrimethylammonium bromide (CTAB, Acros Organics), ethanol (Penta),

hydrochlorid acid (HCl, Penta), (3-mercaptopropyl)trimethoxysilane (TMSPM, Sigma Aldrich), polyvinyl alcohol (PVA, Sloviol R) and silver nitrate ($AgNO_3$, Penta).

1.2. Preparation of nanofibers

The silica/PVA nanofibers were produced by needleless electrospinning from sol prepared by sol-gel method. The initial sol was prepared from TEOS by controlled hydrolysis and polycondensation in ethanol as solvent and HCl as catalyst. Finally, PVA solution was slowly dropped into the silica sol. The viscous mixture of silica sol and PVA composites was obtained. The layer of hybrid nanofibres was produce by electrospinning, the applied voltage was 43 kV. The nanofibers were consequently thermally stabilized (180 °C, 2 hours).

$AgNO_3$ was dissolved in a solution of ethanol and distilled water, the prepared nanofibers were immersed into the solution. Immobilization of Ag ions was carried out in different process times of 30 min (sample t30), 45 min (sample t45) and 60 min (sample t60) to examine effect of process time on immobilized Ag ions quantity.

1.3. Characterization

The nanofibers were inspected using FE-SEM Zeiss Ultra Plus. An InLesn secondary electron detector operated at accelerating voltage of 2 kV was used for the imaging in topographical contrast. Prior to the analysis, the samples were coated with 2 nm of Pt to achieve sustainable surface conductivity. For a local chemical analysis was used EDS detector Oxford X-MAX on SEM; applied accelerating voltage was 15 kV.

2. RESULTS AND DISCUSSION

SEM images of silica/PVA nanofibers spun at voltage of 43 kV and thermally stabilized are depicted in Fig. 1. The nanofibers do not break significantly after thermal stabilization; the nanofibers retained their morphology with fiber diameter of 330 nm – 650 nm.

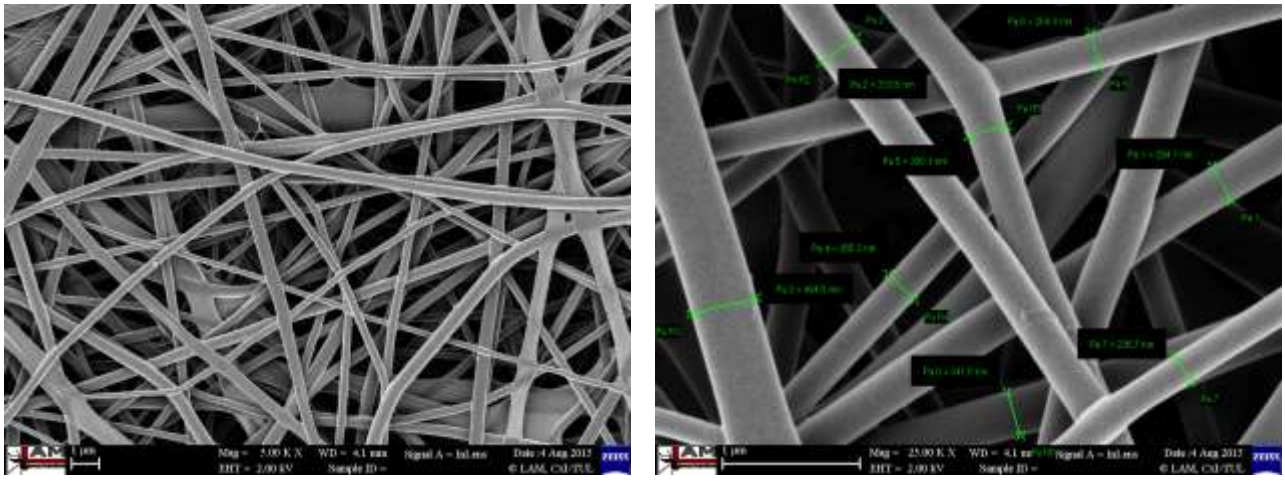

Fig. 1 SEM images of silica/PVA nanofibers after thermal stabilization. Magnification 5000x (left), 25000x (right).

Fig. 2 gave the SEM images of silica/PVA nanofibers with immobilized Ag ions – samples t30, t45 and t60. As observed, fiber mats morphologies were similar for each sample. The nanofibers structure were affected during the Ag ions immobilization process, there were evident fiber structure breaks.

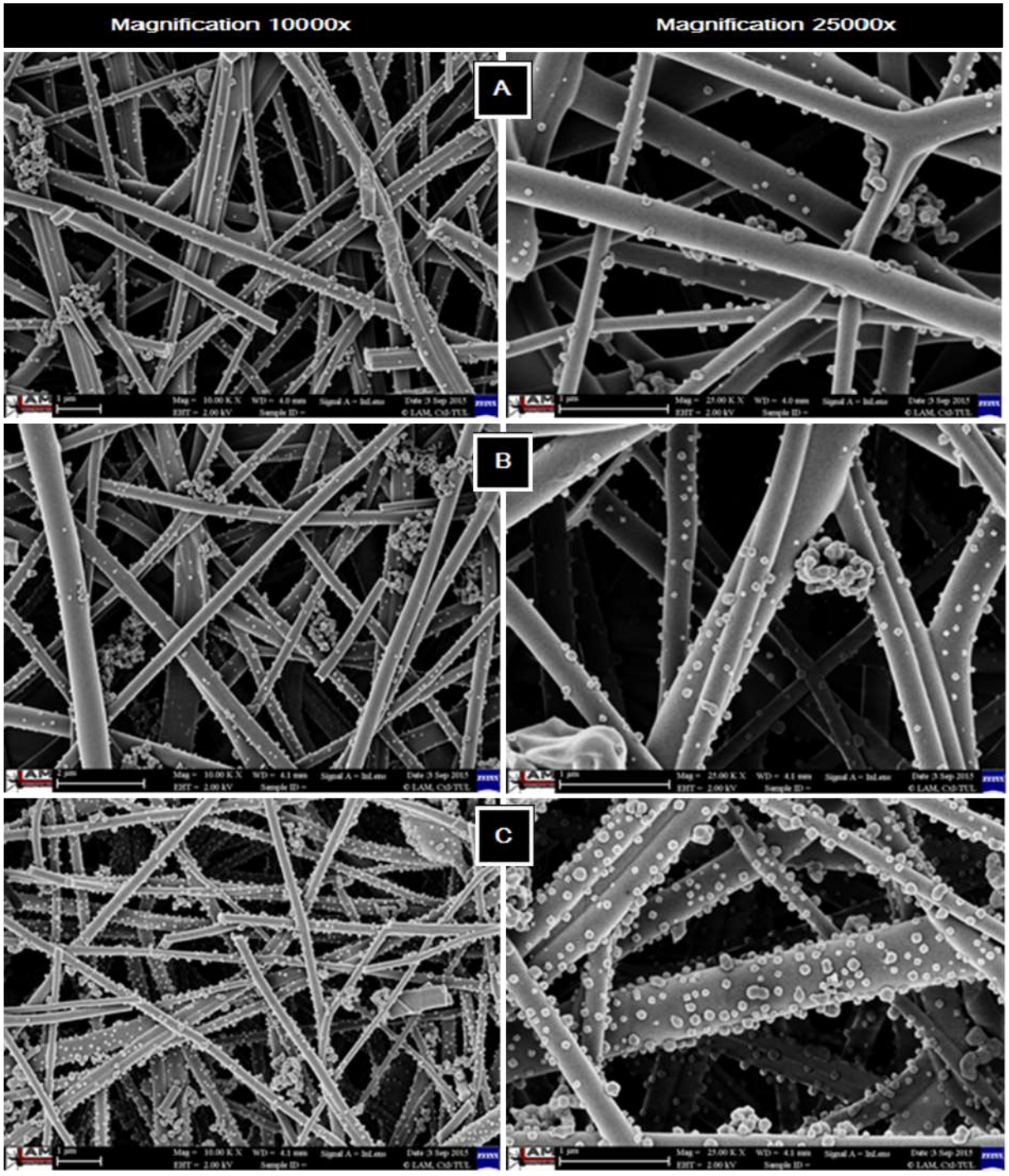

Fig. 2 SEM images of silica/PVA nanofibers with immobilized Ag ions in different magnifications. A: immobilizing process time 30 min (t30), B: immobilizing process time 45 min (t45), C: immobilizing process time 60 min (t60).

EDS analysis (Table 1) depicts elemental composition of the samples. Presence of sulfur (S) in the samples is due to using of TMSPM in preparation process. The TMSPM was used for mercapto group formation. Nanofibers functionalized with mercapto groups have a great potential to adsorb heavy metal ions. This potential was confirmed by Ag ions immobilization process.

It is shown that Ag ions immobilization onto the surface of the nanofibers was successful and that is also confirmed by EDS analysis results (Table 1, Fig. 3). It should be noted that the Ag immobilization process time significantly influences quantity of immobilized Ag ions onto the nanofibers surface. The quantity

of immobilized Ag ions onto the nanofibers surface is depends on the immobilization process time (Fig. 3). According to quantitative EDS analysis results, quantity of immobilized Ag ions for the sample t30 was 3,93 At%, for the sample t45 it was 4,44 At% and for the sample t60 the quantity of immobilized Ag ions was 5,01 At%. Compared with quantity of silicon (Si), which is the basic material of the nanofibers, quantity of Ag is relatively high, especially for sample t60. Based on this fact, we can expect intensive antibacterial activity.

As evident in SEM images on Fig. 2, Ag ions were immobilized in constant density onto the entire surface of single fibers. In the structure, there are irregularly presented clusters of Ag ions. This finding is valid for each sample t30, t45 and t60. Ag ions were immobilized not only on the fibers in the surface layer of the sample, but also on the fibers inside the bulk of samples. That is very important factor for long-term antibacterial activity of the samples corresponding with the nanofibers degradation and gradual releasing of Ag ions.

Table 1 Quantitative EDS analysis results for silica/PVA nanofibers with immobilized Ag ions for the samples t30, t45 and t60.

At %	C	O	Si	S	Ag
t30	36.90	40.05	15.13	2.84	**3.93**
t45	35.78	40.22	15.57	2.93	**4.44**
t60	36.07	38.86	14.95	2.88	**5.01**

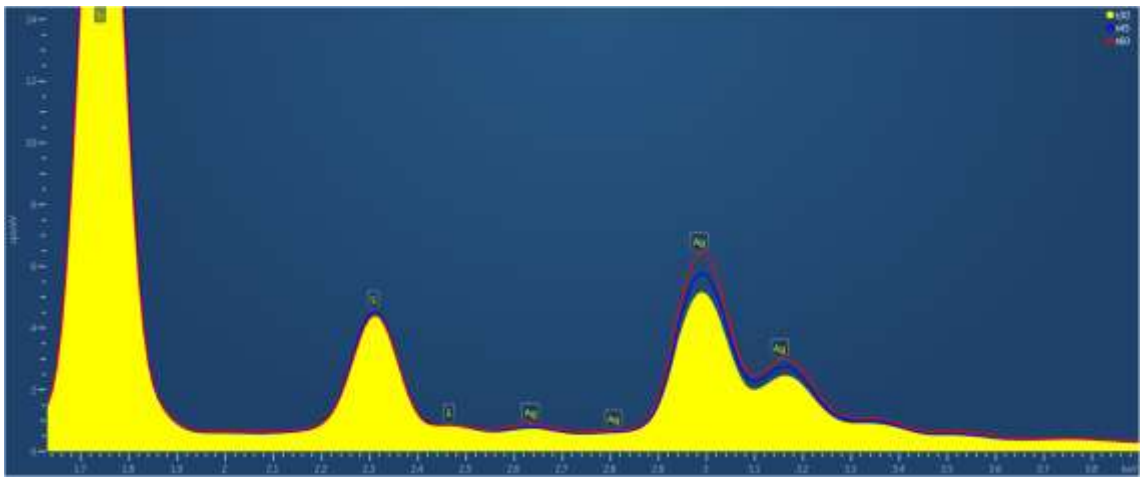

Fig. 3 EDS analysis of silica/PVA nanofibers with immobilized Ag ions. Samples t30 – yellow line, t45 – blue line, t60 – red line.

3. CONCLUSION

Fiber mats of silica/PVA composite were prepared by electrospinning and consequently different quantity of Ag ions was successfully immobilized onto the surface of the nanofibers. In the study, we demonstrate preparation of hybrid organic-inorganic nanofibrous mats functionalized with mercapto groups. These nanofiber mats are able to adsorb Ag ions on the nanofibers surface thorough the nanofiber mats bulk. The quantity of immobilized Ag ions onto the nanofibers surface depends on the immobilization process time. These hybrid silica/PVA nanofibers have a great potential for antibacterial applications, what was confirmed by preliminary *in-vitro* tests.

4. FUTURE WORKS

Based on the results reported here, antibacterial activity of the material will be tested *in-vitro* for a broad spectrum of bacterial strains. The tests of cytotoxicity for different cell types of the developed nanofibrous material *in-vitro* will be done as well. Mechanical properties of material are also very important for the intended application, therefore the further development will be focused on their improvement.

REFERENCES

[1] MAUTER M. S., WANG Y. Antifouling Ultrafiltration Membranes via Post-Fabrication Grafting of Biocidal Nanomaterials. ACS Applied Materials, Vol. 3, No. 8, 2011, pp. 2861-2868.

[2] CHALOUPKA K., MALAM Y., SEIFALIAN A. M. Nanosilver as a new generation of nanoproduct in biomedical applications. Trends in Biotechnology, Vol. 28, No. 11, 2010, pp. 580-588.

[3] CHUN Ja Y., KANG K.H. Epidermal cellular response to poly(vinyl alcohol) nanofibers containing silver nanoparticles. Colloids and Surfaces B: Biointerfaces, Vol. 78, No. 2, 2010, pp. 334-342.

[4] MA Z., JI H. Silver nanoparticles decorated, flexible SiO2 nanofibers with long-term antibacterial effect as reusable wound cover. Colloids and Surfaces A: Physicochemical and Engineering Aspects, Vol. 387, No. 1-3, 2011, pp. 57-64.