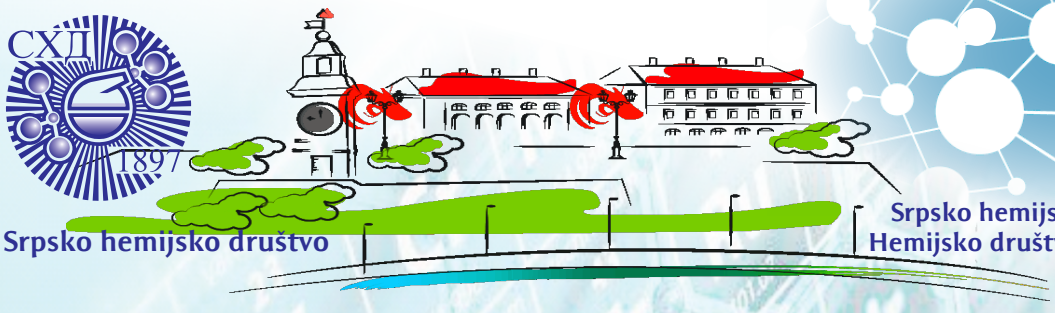

Srpsko hemijsko društvo

Srpsko hemijsko društvo
Hemijsko društvo Vojvodine

# 55. savetovanje Srpskog hemijskog društva

# KNJIGA RADOVA

## 55th Meeting of the Serbian Chemical Society

# PROCEEDINGS

Novi Sad 8. i 9. juni 2018.
Novi Sad, Serbia, June 8-9, 2018

ISBN 978-86-7132-070-2

Srpsko hemijsko društvo

Serbian Chemical Society

Srpsko hemijsko društvo
Hemijsko društvo Vojvodine

Serbian Chemical Society
Chemical Society of Vojvodina

# 55. SAVETOVANJE SRPSKOG HEMIJSKOG DRUŠTVA

# KNJIGA RADOVA

## 55th MEETING OF THE SERBIAN CHEMICAL SOCIETY

# Proceedings

**Novi Sad 8. i 9. juni 2018.**

**Novi Sad, Serbia, June 8-9, 2018**

**55. SAVETOVANJE SRPSKOG HEMIJSKOG DRUŠTVA**
*Novi Sad, 8 i 9. juni 2018.*
***KNJIGA RADOVA***

55th MEETING OF THE SERBIAN CHEMICAL SOCIETY
*Novi Sad, Serbia, June 8-9 , 2018*
*PROCEEDINGS*

***Izdaje** / Published by*
***Srpsko hemijsko društvo** / Serbian Chemical Society*
*Karnegijeva 4/III, 11000 Beograd, Srbija*
*tel./fax: +381 11 3370 467; www.shd.org.rs, E-mail: Office@shd.org.rs*

***Za izdavača** / For Publisher*
***Vesna Mišković STANKOVIĆ**, predsednik Društva*

***Urednici** / Editors*
***Janoš ČANADI***
***Sanja Panić***
***Aleksandar DEKANSKI***

***Dizajn korica, slog i kompjuterska obrada teksta***
*Cover Design, Page Making and Computer Layout*
***Aleksandar DEKANSKI***

***OnLine publikacija** / OnLine publication*

*ISBN **978-86-7132-070-2***

# The influence of 1,2,3,4-butantetracarboxylic acid on in situ synthesis of $Cu_2O$/CuO nanoparticles on the cotton fabric and its antibacterial activty

Darka Marković, Natalija Jocić*, Tim Nunney**, Christopher Deeks**, Željko Radovanović, Zoran Šaponjić***, Maja Radetić*

*Innovation Center of the Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, Belgrade*

**Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, Belgrade*

***Thermo Fisher Scientific, The Birches Industrial Estate, Imberhorne Lane, East Grinstead, West Sussex, RH19 1UB, UK*

****Institute of Nuclear Sciences "Vinča", University of Belgrade, P.O. Box 522, Belgrade*

**Introduction**

Ag nanoparticles (NPs) are widely applied as an efficient antimicrobial agent active against numerous microorganisms[1]. These NPs can be exploited for manufacturing of medical, protective and hygiene textiles. However, recently, Cu, $Cu_2O$ and CuO NPs or their mixtures became the focus of many research groups[2-4] because of cheaper precursor salts compared to Ag salts and excellent antimicrobial activity against various bacteria strains. Although dip-coating method from the Cu-based NPs colloid/dispersion can be an option, the most dominant method for cotton fabric impregnation with Cu-based NPs relies on *in situ* synthesis which comprises of three steps: the introduction of carboxyl groups to cotton fibers, the adsorption of $Cu^{2+}$-ions from salt solution and the reduction with appropriate reducing agent. In this study, cotton fabric was modified with 1,2,3,4-butantetracarboxylic acid (BTCA). The intention was to explore the influence of BTCA initial concentration on the fabrication of Cu-based NPs and antibacterial activity of textile nanocomposite against Gram-negative bacterium *E. coli* and Gram-positive bacterium *S. aureus*.

**Experimental**

Desized and bleached cotton (Co) woven fabric (117.5 g/m$^2$, 52 picks/cm, 27 ends/cm, thickness of 0.26 mm) has been studied. Co fabrics were cleaned in the bath containing 0.1 % nonionic washing agent Felosan RG-N (Bezema) at liquor-to-fabric ratio of 50:1. After 15 min of washing at 50 $^oC$, the fabric was rinsed first with warm water (50 $^oC$) and then thoroughly with cold water. The samples were dried at room temperature.

One hour long treatment of Co fabrics with 1,2,3,4-butantetracarboxylic acid (BTCA) was conducted by immersion of 0.50 g of the sample in 20 mL of the acid aqueous solutions of 4, 6 and 10 w/v% in the presence of 0.82, 1.24 and 2.06 g of the catalyst sodium hypophosphite (SHP), respectively. After drying at 80 $^oC$ for 3 min the samples were cured at 170 $^oC$ for 3 min. The samples were then rinsed in distilled water and dried at room temperature. Modified samples are marked as Co+BTCA4, Co+BTCA6 and Co+BTCA10.

Afterwards, 0.50 g of Co+BTCA4, Co+BTCA6 and Co+BTCA10 fabrics were soaked in 25 mL of 10 mM solution of $CuSO_4$ for 2 h. In order to eliminate the excessive $Cu^{2+}$-ions, the samples were rinsed three times (1 min) with deionized water. 0.050 g of sodium borohydride ($NaBH_4$) was dissolved in 25 mL of 0.1 mM NaOH solution and the samples were immediately dipped into the solution where the reduction process took place in the following 30 min at room temperature. The samples were thoroughly rinsed with deionized

water and left to dry at room temperature. These samples are marked as Co+BTCA4+Cu, Co+BTCA6+Cu and Co+BTCA10+Cu.

Fourier transform infrared (FTIR) spectra of the control Co fabric, Co fabric treated with BTCA and Co fabric treated with BTCA after immersion in 0.1 M NaOH solution were recorded in the ATR mode using a Nicolet 6700 FTIR Spectrometer (Thermo Scientific) at 2 $cm^{-1}$ resolution, in the wavenumber range 500–4000 $cm^{-1}$.

The morphology of Co fibers impregnated with NPs was studied by field emission scanning electron microscopy (FESEM, Tescan Mira3 FEG). The samples were coated with a thin layer of Au prior to analysis.

The amounts of adsorbed $Cu^{2+}$-ions on the Co+BTCA4, Co+BTCA6 and Co+BTCA10 fabrics from $CuSO_4$ solution were calculated on the basis of the concentration of residual $Cu^{2+}$-ions in the solution which was measured using a Spectra AA 55 B (Varian) atomic absorption spectrometer (AAS). AAS was also used for the measurement of the total Cu content in the Co fabrics after reduction process. Dry impregnated Co fabrics were dissolved in the 1:1 $HNO_3$ solution.

X-ray photoelectron spectroscopy (XPS) measurements were performed in order to evaluate the chemistry of the control Co and the Co+BTCA10+Cu fabric. The XPS analysis was carried out using a K-Alpha spectrometer (Thermo Scientific, UK) utilizing a monochromated Al Kα ($h\nu$ = 1486.6 eV) X-ray source.

The XRD powder patterns were acquired using a Philips PW 1050 powder diffractometer with Ni-filtered Cu-Kλ radiation ($\lambda$=1.5418 Å). The diffraction intensity was measured by the scanning technique (a step size of 0.05° and a counting time of 50 s per step).

The antibacterial activity of Co fabrics was tested against Gram-negative bacteria *E. coli* ATCC 25922 and Gram-positive bacteria *S. aureus* ATCC 25923 using a standard test method for the determining the antimicrobial activity of immobilized antimicrobial agents under dynamic contact conditions ASTM E 2149-01 (2001). The percentage of bacterial reduction ($R$, %) was calculated by the following equation:

$$R = \frac{C_0 - C}{C_0} \cdot 100$$

where $C_0$ (CFU – colony forming units) is the number of bacteria colonies on the control fabric and $C$ (CFU) is the number of bacteria colonies on the fabric with NPs.

**Results and discussion**

Chemical changes induced by modification of Co fabric with BTCA were evaluated by FTIR spectroscopy. FTIR spectra of the control Co fabric, the Co+BTCA10 sample and the Co+BTCA10 sample which was immersed in 0.1 M NaOH solution are shown in Fig. 1. The bands specific for cellulose can be clearly seen in all spectra. The band with a peak centered at 1720 $cm^{-1}$ in the spectrum of the Co+BTCA10 fabric indicated the establishing of ester bonds between hydroxyl groups of cellulose and carboxyl groups of BTCA[5,6]. An immersion of the Co+BTCA10 sample into NaOH solution brought about the deprotonation of free carboxyl groups. The carboxylate groups were proved by appearance of the band at 1565 $cm^{-1}$. The presence of both bands at 1720 $cm^{-1}$ and 1565 $cm^{-1}$ in shown spectra pointed out that BTCA was efficiently bound to cellulose by ester bonds, while a certain number of carboxyl groups retained free.

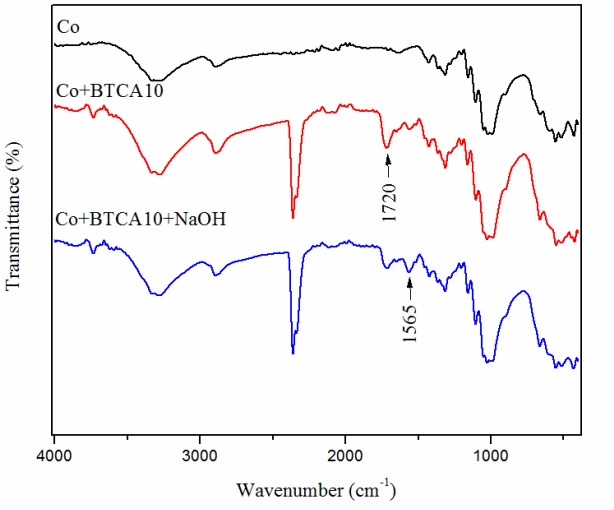


***Figure 1.*** *FTIR spectra of the control sample, the Co+BTCA10+Cu sample and the Co+BTCA10+Cu sample which was immersed in 0.1 M NaOH solution*

Free carboxyl groups were exploited for adsorption of $Cu^{2+}$-ions from $CuSO_4$ aqueous solution. The values of $Cu^{2+}$-ions uptakes after 2 h long adsorption are given in Table 1. Obviously, the higher the concentration of applied BTCA solution, the larger the $Cu^{2+}$-ions uptake and consequently, the higher the content of Cu after reduction (Table 1). Cu content in the Co+BTCA6+Cu and the Co+BTCA10+Cu samples increased by 75 % and 174 % compared to the Co+BTCA4+Cu sample, respectively. In other words, the largest amounts of NPs were generated on the Co+BTCA10+Cu fiber surface. This can be attributed to an increase in the content of free carboxyl groups.

The form and distribution of NPs over the fiber surfaces are illustrated by FESEM images (Fig. 2). It can be noticed that larger amounts of single and agglomerated NPs were present on the surface of the Co+BTCA10+Cu sample. The size of the single NP was approximately 40 nm. The application of BTCA of lower concentrations (4 w/v%) resulted in synthesis of smaller amounts of NPs. Additionally, agglomeration was less prominent in this sample. Uneven distribution of NPs over the fiber surface is common for all studied Co fibers.

***Table 1.*** *$Cu^{2+}$-ions uptake and total content of Cu after $Cu^{2+}$-ions reduction in Co fabrics modified with BTCA*

| Sample | $Cu^{2+}$-ions uptake (μmol/g) | Total content of Cu after reduction, μmol/g |
|---|---|---|
| Co+BTCA4 | 55.8±6.4 | 50.8±1.4 |
| Co+BTCA6 | 101.1±6.1 | 89.0±3.4 |
| Co+BTCA10 | 145.0±7.0 | 139.0±4.1 |

XPS analysis was utilized for detection of the copper oxidation state in fabricated NPs. A high resolution scans of the Co+BTCA10+Cu sample were accomplished in the C1s, O1s and Cu2p regions and they are shown in Fig. 3a, 3b and 3c, respectively. Deconvolution of the C1s spectrum (Fig. 3a) revealed the presence of three components corresponding to C-O-, O-C-O and C-O-C groups of cellulose. Additional peak assigned to C-C/C-H groups is likely the contribution of residual waxes[7].

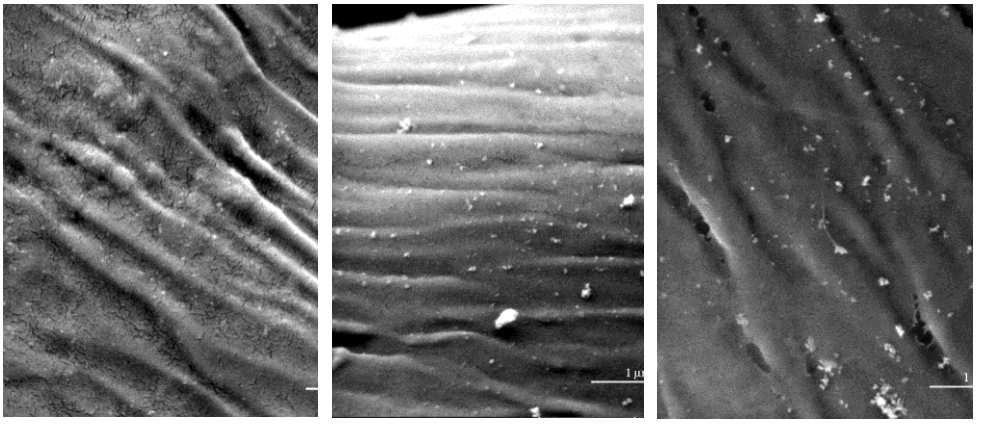

***Figure 2.*** *The FESEM images of the Co+BTCA4+Cu (a), Co+BTCA6+Cu (b) and Co+BTCA10+Cu (c) fibers*

The O1s spectrum (Fig. 3b) was deconvoluted into two components attributed to organic O1s from cellulose and copper oxides. Two main peaks corresponding to $Cu2p_{3/2}$ and $Cu2p_{1/2}$ followed by shakeup satellites can be seen in the Cu2p spectrum (Fig. 3c). Asymmetric $Cu2p_{3/2}$ peak can be deconvoluted into two components: the peak associated to metallic Cu or $Cu_2O$ and the peak ascribed to CuO. The presence of shakeup satellites proves the appearance of copper in the form of CuO. The shakeup satellites are specific for the materials which have a $d^9$ configuration like in a $Cu^{2+}$[8]. However, XPS measurements were not helpful for differentiation between metallic Cu and $Cu_2O$ since the binding energies of the $Cu2p_{3/2}$ signal for these two forms differs by only 0.1 eV (932.6 and 932.7 eV for Cu and $Cu_2O$, respectively). Broader $Cu2p_{3/2}$ main peak and corresponding satellite in the Co+BTCA10+Cu sample may indicate larger amounts of CuO.

The Co+BTCA10+Cu fabric was also mapped and fitted to determine the atomic concentrations across its surface and to detect the uniformity of the surface. The results of the mapping of C1s, O1s and Cu2p signals are demonstrated in Fig. 4. It is obvious that the intensity of Cu2p signal varies over the sample. However, the mapping revealed relatively uniform distribution of Cu-based structures across the surface of the fabric.

Stronger evidence of NPs composition came from the XRD measurements. The XRD patterns of the control Co and Co+BTCA10+Cu samples are shown in Fig. 5. The cotton fabric has the characteristic cellulose $I_\beta$ diffraction pattern. Shoulders (marked with rectangles) at $2\theta$~35.5° and 38.7° in difractogram of the Co+BTCA10+Cu composite indicated the formation of (-111) and (111) crystal planes of base centered monoclinic crystal phase of CuO (ICDD 01-089-5899). On the other hand, low intensity peak at $2\theta$~37.2° could be attributed to shifted peak characteristic for (111) crystal plane of cubic $Cu_2O$ (ICDD 01-077-0199). Therefore, according to XPS and XRD measurements, it can be suggested that NPs are present on the Co fiber surface as a $Cu_2O$/CuO mixture.

The antibacterial activity of the Co fabrics was tested against Gram-negative bacterium *E. coli* and Gram-positive *S. aureus*. The samples modified with BTCA alone did not show any antibacterial activity. The results summarized in Table 2 reveal that the antibacterial activity depends on the Cu content in the samples. The Co+BTCA6+Cu and the Co+BTCA10+Cu samples provided 99.9 % bacterial reduction of both bacteria strains. However, the

Co+BTCA4+Cu sample ensured 99.9% reduction of *E. coli* colonies while the reduction of *S. aureus* was slightly lower (99.4%). Apparently, the amount of fabricated $Cu_2O$/CuO NPs was not sufficient for obtaining the maximum reduction of bacteria *S. aureus.*

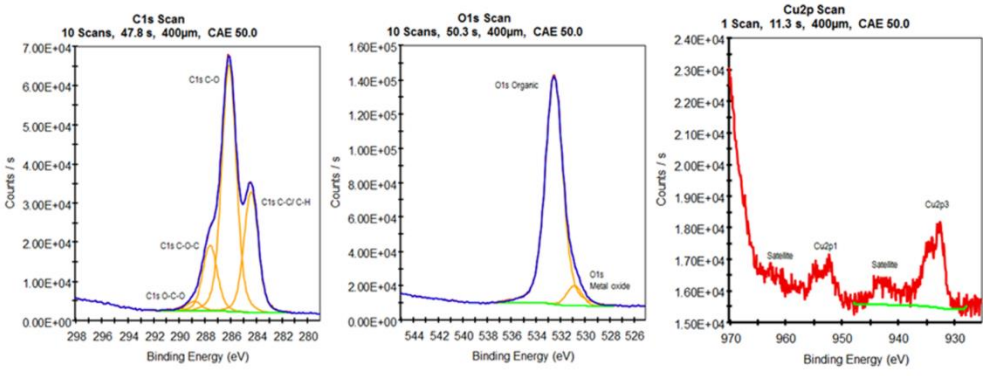


***Figure 3.*** *XPS high resolution spectra of the Co+BTCA10+Cu in the* C1s, O1s, and *Cu2p regions*

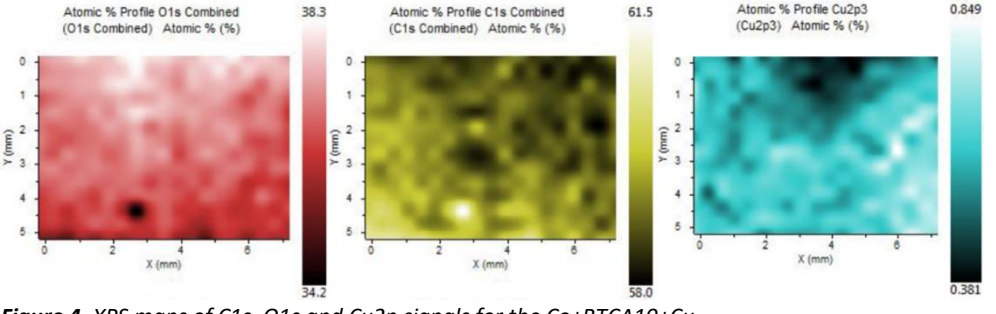


***Figure 4.*** *XPS maps of C1s, O1s and Cu2p signals for the Co+BTCA10+Cu*

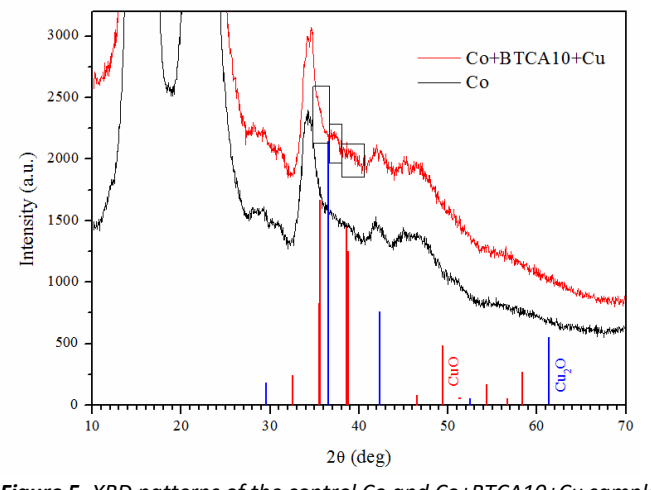


***Figure 5.*** *XRD patterns of the control Co and Co+BTCA10+Cu samples*

***Table 2*** *Antibacterial activity of the Co fabrics impregnated with $Cu_2O$/CuO NPs*

| Sample | Number of bacterial colonies, CFU | R, % | Number of bacterial colonies, CFU | R, % |
|---|---|---|---|---|
| | *E. coli* | | *S. aureus* | |
| Control Co | $1.5\times10^5$ | | $6.6\times10^4$ | |
| Co+BTCA4+Cu | 65 | 99.9 | 730 | 99.4 |
| Co+BTCA6+Cu | <10 | 99.9 | <10 | 99.9 |
| Co+BTCA10+Cu | <10 | 99.9 | <10 | 99.9 |

**Conclusions**

Treatment of cotton fabrics with BTCA imparted the free carboxyl groups necessary for uptake of $Cu^{2+}$-ions. The application of higher concentration BTCA brought about larger uptake of $Cu^{2+}$-ions and fabrication of larger amounts of nanoparticles which were detected by FESEM analysis. XPS and XRD analyses revealed that nanoparticles existed as a mixture of $Cu_2O$ and CuO. The amounts of $Cu_2O$/CuO nanoparticles on all studied cotton fabrics was sufficient to secure 99.9% reduction of Gram-negative bacteria *E. coli* and Gram-positive bacteria *S. aureus*, except in the case of the fabric modified with 4 w/v% of BTCA which exhibited slightly lower activity against *S. aureus*.

***Acknowledgement:*** *The financial support for this study was provided by the Ministry of Education, Science and Technological Development of Republic of Serbia (projects no. 172056 and 45020).*

## Uticaj koncentracije 1,2,3,4-butantetrakarboksilne kiseline na *in situ* sintezu nanočestica $Cu_2O$/CuO na pamučnoj tkanini i njenu antibakterijsku aktivnost

*U ovom radu je ispitana mogućnost in situ sinteze nanočestica $Cu_2O$/CuO na pamučnoj tkanini prethodno modifikovanoj 1,2,3,4-butantetrakarboksilnom kiselinom (BTCA) različitih koncentracija sa ciljem postizanja antibakterijske zaštite. Utvrđeno je da se većom koncentracijom BTCA postiže bolja sorpcija $Cu^{2+}$-jona iz rastvora $CuSO_4$ i veći sadržaj nanočestica nakon redukcije. Prisustvo nanočestica na pamučnoj tkanini dokazano je FESEM analizom. XPS i XRD analizama je ustanovljeno da sintetisane nanočestice predstavljaju smešu $Cu_2O$ i CuO. Dobijeni tekstilni nanokompoziti obezbeđuju odličnu antibakterijsku zaštitu prema Gram-negativnoj bakteriji E. coli i Gram-pozitivnoj bakteriji S. aureus koja zavisi od količine sintetisanih nanočestica $Cu_2O$/CuO.*

**References**

1. M. Radetić, *Journal of Materials Science*, **48** (2013) 95.
2. N.C. Cady, J.L. Behnke, A.D. Strickland AD, *Advanced Functinal Materials*, **21** (2011) 2506.
3. A. Errokh, A.M. Ferraria, D.S. Conceição, L.F. Vieira Ferreira, A.M. Botelho de Rego, M. Rei Vilar, S. Boufi, *Carbohydrate Polymers*, **141**(2016) 229.
4. D. Marković, M. Korica, M. Kostić, Ž. Radovanović, Z. Šaponjić, M. Mitrić, M. Radetić, *Cellulose*, **25** (2018) 829.
5. O. Šauperl, K. Stana-Kleinschek, V. Ribitsch, *Textile Research Journal*, **79** (2009) 780.
6. R. Khajavi, A. Berendjchi, *ACS Applied Materials & Interfaces*, **6** (2014) 18795.
7. D. Mihailović, Z. Šaponjić, M. Radoičić, S. Lazović, C. Baily, P. Jovančić, J. Nedeljković, M. Radetić,*Cellulose*, **18** (2011) 811.
8. C.K. Wu, M. Yin, S. O' Brien, T. Koberstein, *Chemistry of Materials*, **18** (2006) 6054.