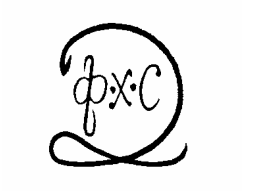

PHYSICAL CHEMISTRY 2016

13th International Conference on
Fundamental and Applied Aspects of
Physical Chemistry

Proceedings
Volume I

B E L G R A D E
September 26 - 30, 2016

ISBN 978-86-82475-34-7
Title: Physical Chemistry 2016 (Proceedings)
Editors: Željko Čupić and Slobodan Anić
Published by: Society of Physical Chemists of Serbia, Studentski trg 12-16, 11158, Belgrade, Serbia.
Publisher: Society of Physical Chemists if Serbia
For Publisher: S. Anić, President of Society of Physical Chemists of Serbia
Printed by: "Jovan", Printing and Publishing Company; 200 Copies.
Number of pages: 6+502; Format B5; printing finished in September 2016

Text and Layout: "Jovan"

200 - *Copy printing*

PHYSICAL CHEMISTRY 2016

13th International Conference on
Fundamental and Applied Aspects of
Physical Chemistry

Organized by

The Society of Physical Chemists of
Serbia

in co-operation with

Institute of Catalysis Bulgarian Academy of Sciences

and

Boreskov Institute of Catalysis Siberian Branch of
Russian Academy of Sciences

and

University of Belgrade, Serbia:

Faculty of Physical Chemistry
Institute of Chemistry, Technology and Metallurgy
Vinča Institute of Nuclear Sciences
Faculty of Pharmacy
Institute of General and Physical Chemistry, Belgrade, Serbia

International Organizing Committee

Chairman:	S. Anić (Serbia)
Vice-chairman:	M. Gabrovska (Bulgaria) A. A. Vedyagin (Russia) S. N. Blagojević (Serbia)
Members:	N. Cvjetićanin (Serbia), S. M. Blagojević (Serbia), M. Daković (Serbia), J. Dimitrić-Marković (Serbia), T. Grozdić (Serbia), Lj. Ignjatović (Serbia), D. Jovanović (Serbia), J. Jovanović (Serbia), M. Kuzmanović (Serbia), D. Marković (Serbia), B. Milosavljević (USA), M. Mojović (Serbia), N. Ostrovski (Serbia), N. Pejić (Serbia), M. Petković (Serbia), A. Popović-Bjelić (Serbia), B. Simonović (Serbia), D. Stanisavljev (Serbia), M. Stanković (Serbia), Z. Šaponjić (Serbia), B. Šljukić (Serbia) , G. Tasić (Serbia), N. Vukelić (Serbia), V. Vukojević (Sweden)

International Scientific Committee

Chairman:	Ž. Čupić (Serbia)
Vice-chairmans:	V. N. Parmon (Russia) S. Rakovsky (Bulgaria) B. Adnađević (Serbia)
Members:	S. Anić (Serbia), A. Antić-Jovanović (Serbia), G. Bačić (Serbia), R. Cervellati (Italy), G. Ćirić-Marjanović (Serbia), A. Cricenti (Italy), V. Dondur (Serbia), S. D. Furrow (USA), L. Gábor (Hungary), Vilmos Gáspár (Hungary), K. Hedrih (Serbia), M. Jeremić (Serbia), E. Kiš (Serbia), Lj. Kolar-Anić (Serbia), U. Kortz (Germany), T. Kowalska (Poland), V. Kuntić (Serbia), Z. Marković (Serbia), S. Mentus (Serbia), K. Novaković (UK), B. Novakovski (Poland), T. Parac Vogt (Belgium), M. Perić (Serbia), M. Plavšić (Serbia), G. Schmitz (Belgium), I. Schreiber (Czech Republic), P. Ševčik (Slovakia), N. Stepanov (Russia), M. Trtica (Serbia), V. Vasić (Serbia), D. Veselinović (Serbia), Á. Tóth (Hungary)

Local Executive Committee

Chairman:	S. N. Blagojević
Vice-chairmans:	A. Ivanović-Šašić A. Stoiljković
Members:	M. Ajduković, P. Banković, N. Bošnjaković, I. N. Bubanja, D. Dimić, A. Dobrota, J. Dostanić, A. Ignjatović, S. Jovanović, Z. Jovanović, A. Jović, N. Jović-Jovičić, D. Lončarević, M. Kragović, J. Krstić, S. Maćešić, J. Maksimović, V. Marković, D. Milenković, M. Milovanović, B. Nedić-Vasiljević, M. Pagnacco, A. Pavićević, N. Potkonjak, D. Ranković, M. Ristić, B. Stanković, A. Stanojević

ANTIMICROBIAL ACTIVITY OF COPPER-POLYANILINE NANOCOMPOSITE

U. Bogdanović[1], V. Vodnik[1], M. Mitrić[1], S. Dimitrijević[2], S. D. Škapin[3], V. Žunič[3], M. Budimir[1] and M. Stoiljković[1]

[1]*Vinča Institute of Nuclear Sciences, University of Belgrade, P. O. Box 522, 11001 Belgrade, Serbia(una.bogdanovic@gmail.com)*
[2]*Department of Bioengineering and Biotechnology, Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia*
[3]*Jožef Stefan Institute, Department of Advanced Materials, Jamova 39, 1000 Ljubljana, Slovenia*

ABSTRACT

By combining copper nanoparticles (CuNPs) as a good antimicrobial agent with polyaniline (PANI), which also shows some degree of antimicrobial activity, we were able to synthesize a novel promising antimicrobial material – copper-polyaniline (Cu-PANI) nanocomposite. It was prepared by simple *in situ* polymerization method, when thepolymer and metal nanoparticles (d_{av}= 6 nm)are produced simultaneously.Quantitative (antimicrobial assay) and qualitative (atomic force microscopy – AFM) analyses showed that synergestic effect of CuNPs and PANI against bacteria*E. coli* and*S. aureus*,and fungus*C. albicans*, provides its faster andhigher antimicrobial activity than any component acting alone.This makes it a great candidate for fast waste water treatment.

INTRODUCTION

Microbial contamination of water presents a major threat to public health. With the emergence of strains resistant to multiple antimicrobial agents, there is increased demand for novel antimicrobial materials with superior performance for disinfection applications. Nanocomposites based on metal nanoparticles such asCuNPs and conductivePANI,that expose some antimicrobial effect, represent one of these materials[1,2]. Antimicrobial activity of metal NPs is inversely proportional to their average size as a result of large number of the low-coordinate atoms on their surface available to interact with microbial membranes or to release metal ions, while PANI chains generate electrostatic interaction with microbial functional groups, altering their function [1,2]. Combining these two components, these effects become intense making Cu-PANI nanocomposite very effective antimicrobial agent [2]. Here, we present a cheapCu-PANI nanocomposite

materialwith improved antimicrobial action, comparing to CuNPs and PANI components alone.

EXPERIMENTAL

Cu-PANI nanocomposite was synthesized by a simple process of oxidative polymerizationof aniline, in methanol as a medium[2]. Copper salt ($CuCl_2 \cdot 2H_2O$, 0.12 M) dissolved in methanol with adjusted pH < 4 by 1 M HCl, was first added in a round bottom flaskequipped with a magnetic stirrer. Then, aniline (0.04 M) in molar relation to Cu salt [aniline]/[$CuCl_2$] = 1/3, was added.The mixture was stirred for 20 h at room temperature. The initial fluorescent green color of copper salt almost immediately turns dark red-brown and then to brownish-green as Cu-PANI nanostructures form. The final solution was evaporated by rotary evaporator to remove methanoland soluble oligomers. The precipitate was then washed with 5 mM HCl and dried at 30 °C. After collecting the powder, the amount of the Cu in the nanocomposite determined by ICP-AES wasfound to be 14.25 wt%. For comparison of antimicrobial activity, pure PANI sample without CuNPs was synthesized using the procedure described in our previous report [3]. Antimicrobial activity of synthesized samples was determined according to our previous work [2], for Cu-PANI and pure PANI, concentrations of 1, 2, 5, 10 and 20 ppm, and incubation time of 1h.

RESULTS AND DISCUSSION

Since the only reactants in this synthetic route are Cu^{2+} ions as an oxidizing agent and aniline as a reductant, the nucleation and growth of CuNPs, and polymerization of aniline takes place simultaneously. The formation of Cu-PANI nanocomposite was first confirmed by the UV-Vis spectrum (Fig 1a, Inset), with CuNPs absorption band at 550 nm due to collective oscillations

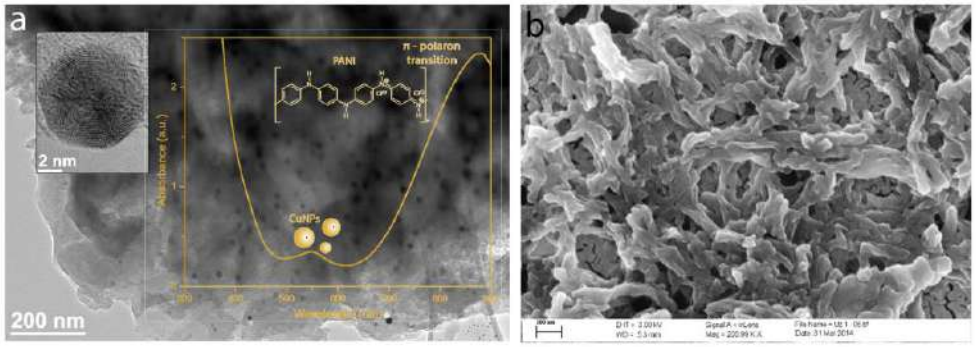

Figure 1. a) TEM image with UV-Vis spectrum and b) FESEM image of Cu-PANI nanocomposite.

of a surface Cu electrons and characteristic peak of PANI protonated by HCl visible at 880 nm (π-polaron transition) [3]. During the polimerization of aniline, spherical CuNPs with mean diameter of about 6.0 ± 3.3 nm were formed. Theyare well separated and homogeneously dispersed throughout the polymer matrix (Fig. 1a). FESEM image of Cu-PANI (Fig. 1b) indicated that PANI chains form coral-like dendritic nanofibers in a large quantity and good uniformity with pores between the branches nanofibers. Such nanostructure offer great effective surface area of Cu-PANI composite.
The results of quantitative antimicrobial efficiency of the Cu-PANI nanocomposite of different concentrations over 1 h incubation time with the microbesare shematically represented in Fig. 2. The stronger antimicrobial effect is achieved for the higher Cu-PANI or pure PANI concentrations.

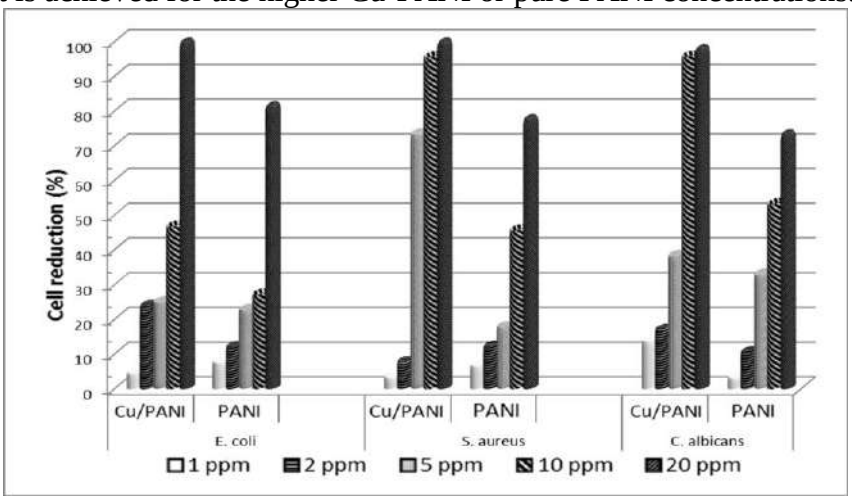

Figure 2. Concentration-dependent reduction ability of the Cu-PANI and PANI on *E. coli*, *S. aureus* and *C. albicans*, over 1 h incubation time

After 1 h, the number of strains is significantly reduced with increasing the Cu-PANI concentration, and almost complete growth inhibition was achieved (99.9 % microbial reduction) against *E. coli* and *S. aureus*, but slightly smaller fungal reduction (97.9 %) at highest composite concentration of 20 ppm. These results are much better than for pure PANI, which reduced ≤ 81.5 % of all tested strains for the same incubation time and concentrations, as well as CuNPs for higher concentrations and longer incubation time (2h), presented in the previous work [1].

Antimicrobial activity of Cu-PANI nanocomposite was also visually confirmed by AFM analysis (Fig. 3). It can clearly be seen that morphology of all tested strains is drastically changed. Smooth and compact surface of all tested strains, after 1 h contact with Cu-PANI, becomes rough, with a lot

of indentations on the cell wall, indicated by arrows. As can be seen, the effect of Cu-PANI to cells' morphology, is more intense in the case of *E. coli* (Fig. 3a) than for two other cells (Fig. 3b,c), because of the intrinsic difference in the cell wall structure. These results are in agreement with the results of antimicrobial assays. Beside synergistic effect of CuNPs and PANI in the composite, important role in the antimicrobial activity of the Cu-PANI has PANI dendrite morphology, which provides great surface area in contact with microbes, preventing the nutrient-uptake process of the microbes from the surroundings. This allows increasing of the interaction between CuNPs, cycling redoxCu^{2+}/Cu^{+}reactions at the surface of the cells and their electrostatic interactions with microbes' peptidoglycans and lipids. These interactions lead to conformational changes of biomolecules, altering their biological function and finally causing cells death.

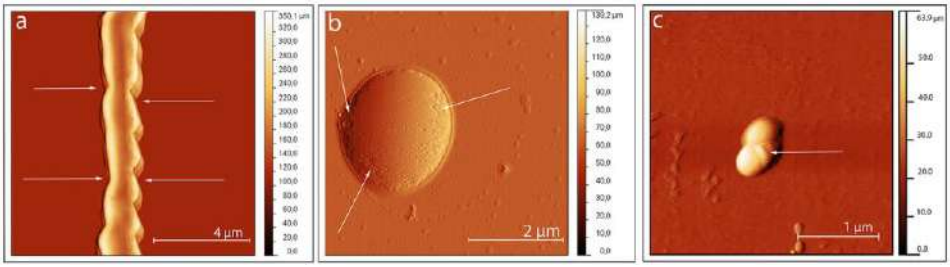

Figure 3. AFM images of treated cells *E. coli* (a), *S. aureus* (b) and *C. albicans* (c) after 1 h incubation with Cu-PANI nanocomposite

CONCLUSION

The presented Cu-PANI nanocomposite has shown excellent antimicrobial activity as a result of CuNPs and PANI synergy, after only 1 h of the strains exposure. This composite can serve as a template for the development of novel antimicrobial agent for fast control microbial infections and waste water treatment.

Acknowledgement

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (grants 172056 and TR 31035).

REFERENCES

[1] U. Bogdanović, V. Lazić, V. Vodnik, M. Budimir, Z. Marković, S. Dimitrijević, Materials Letters, 2014, **128,** 75–78.

[2] U. Bogdanović, V. Vodnik, M. Mitrić, S. Dimitrijević, S. Škapin, V. Žunič, M. Budimir, M. Stoiljković, ACS Applied Materials & Interfaces, 2015, **7,** 1955–1966.

[3] U. Bogdanović, V. Vodnik, S. Ahrenkiel, M. Stoiljković, G. Ćirić-Marjanović, J. Nedeljković, Synthetic Metals, 2014, **195,** 122–131.

CIP - Каталогизација у публикацији - Народна библиотека Србије, Београд

544(082)
66.017/.018(082)
502/504(082)
663/664:658.56(082)
615.31:547(082)

INTERNATIONAL Conference on Fundamental and Applied Aspects of Physical Chemistry (13 ; 2016 ; Beograd)
Physical Chemistry 2016 : proceedings. Vol. 2 / 13th International Conference on Fundamental and Applied Aspects of Physical Chemistry, Belgrade, 26-30 September 2016 ; [editors Željko Čupić and Slobodan Anić]. - Belgrade : Society of Physical Chemists of Serbia, 2016 (Belgrade : Jovan). - IV, 507-930 str. : ilustr. ; 24 cm

Tiraž 200. - Bibliografija uz svaki rad.

ISBN 978-86-82475-33-0

1. Society of Physical Chemists of Serbia (Beograd)
a) Физичка хемија - Зборници b) Наука о материјалима - Зборници c) Животна средина - Заштита - Зборници d) Животне намирнице - Контрола квалитета - Зборници e) Фармацеутска хемија - Зборници
COBISS.SR-ID 225802508