

Synthesis, structure and properties of hybrids doped with copper ions in the silica-hydroxypropyl cellulose system

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In the present study, the formation of copper-doped hybrids and their structure were examined. The XRD analysis showed that all samples are in amorphous state. The IR spectra are characterized with typical bands for silica network (~460, 650, 795, 960, 1085, 1200 and 3480 cm⁻¹), and vibration of Cu-O bonds (460–480 cm⁻¹). The thermal stability decreased with increasing of Cu content from 15 to 25 mass%. By optical microscopy it was found that in the sample containing 5 wt.% Cu, CuSO₄·nH₂O separated from the amorphous matrix and it was not able to incorporate into the hybrid material. After heat treatment of as prepared copper-doped hybrids the XRD, IR and UV-VIS analysis were done. The amorphous state of the hybrids remains except the sample containing 5 wt.% Cu. There are three refraction peaks on the amorphous halo observed assigned to the CuO. The calculated band gap energy (E_g) values sharply decreased after heat treatment process: 3.66–3.97 eV for raw materials up to 2.54–1.30 eV for heated samples. The obtained materials were tested as antibacterial agents against *Escherichia coli* K12 used as a model microorganism.

Keywords: sol-gel method, silica hybrid materials, copper ions, antibacterial agent.

INTRODUCTION

The biocidal properties of copper, its salts and alloys have been known for centuries. It is successfully used as an antibacterial agent in the food and beverage package materials, as a wood conservation material in textile and various paints. Another field of application is in medicine where copper-containing materials are used to minimize the spread of hospital bacterial infections. In agriculture, copper compounds are used as fungicide/bactericide to control plant diseases [1–3].

An important step in the development of new materials is to provide a suitable matrix for incorporation of metal ions. In this case, the matrix must provide a homogeneous structure (without the processes of phase separation, different phase composition and morphology) in which metal particles are uniformly disintegrated [1, 3, 4]. On the other hand, it is clear that amorphous materials have good bio-

compatibility and in the last, few years have been the subject for the development of appropriate matrices for incorporation of metal ions. One of the basic methods for synthesis of biopolymer-metal oxide-metal hybrids is the sol-gel approach [5–9]. Obtained by this method the materials are classified as a new class of high efficiency materials due to the combination of both organic and inorganic properties. On the other hand, in the literature there are insufficient data available on the synthesis and properties of the hybrids in the system copper-doped silica-cellulose ether materials.

A major problem for copper nanoparticles is their strong affinity to oxidation by atmospheric oxygen and the instability of the formed oxide [2, 10]. The possibility of successful crosslinking of doped ions and their homogeneous distribution is an important part of the development and application of such materials. The antimicrobial activity of the materials depends on the difference in oxidation state of the copper as well as their size, shape, distribution and type of linking. It has also been found that CuO and Cu₂O have antimicrobial properties, but with a lower degree than copper ions [4, 10, 11].

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In our previous studies, silver-doped silica/cellulose ethers hybrid nanomaterials have been obtained and tested for antimicrobial effect and their cytotoxicity also was determined [8, 9, 12–17]. The results show that the amount of silver ions and the type of used cellulose derivative influence both the structure of the obtained materials and their biological activity. Antimicrobial behavior of SiO₂/HPC zinc doped materials, using different zinc sources, was also investigated [18, 19]. It was found that the antifungal and antibacterial activity of the hybrids depend on zinc content, type of zinc source, size and shape of formed metal particles. It was established the tendency towards of clusters formation from zinc nanoparticles with different shapes and size. Another part of our investigations included the preparation, characterization and study of antibacterial activity of copper based lignocellulosic composites using wood fibers and technically hydrolytic lignin [20, 21]. The composites based on the technical hydrolysis of lignin than the composites derived from wood fibers showed better antibacterial activity [20, 21].

The purpose of this study is to prepare the hybrids in the silica-hydroxypropyl cellulose system doped with different amount of copper ions and to clarify their structure and crystallization behavior. The presence of CuO in amorphous matrix after thermal treatment was found. The linkage between HPC and silica network is due to the interaction of OH groups of precursors and formation of H-bonds. The obtained materials were tested as antibacterial agents against *Escherichia coli* K12 used as model microorganism. It was suggested that the hybrids having the highest band gap energy value have improved antibacterial activity.

EXPERIMENTAL

Hybrids preparation

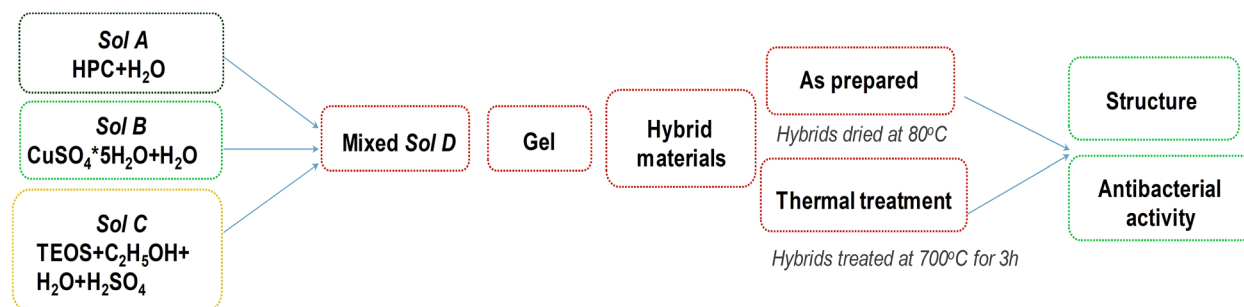
The formation of copper doped hybrids in the system SiO₂-HPC were realized via sol-gel route.

HPC (Sigma-Aldrich) was dissolved in water and the obtained sol was named as *Sol A*. The content of cellulose ether was 5 wt.% to SiO₂. *Sol B* contains different amounts of CuSO₄*5H₂O (0.5, 2.5 and 5 wt.%) dissolved in water. Tetraethoxysilane (TEOS) was used as a silica source. TEOS (Alfa Aesar) was pre-hydrolyzed with ethanol, H₂O and 0.1M H₂SO₄ (Merck) in order to obtain *Sol C*. The hydrolysis-condensation processes were performed at room temperature for an hour on magnetic stirrer.

The hybrids were obtained from mixed *sol D* after drying at 80 °C in oven. *Sol D* was derived from mixing of *Sols A, B* and *C* (Scheme 1). The hybrids were thermally treated at 700 °C for 3 h in order to convert CuSO₄ to CuO.

Hybrids characterization

The crystalline and amorphous phases were identified by XRD analysis. For the XRD measurements a Bruker D8 Advance diffractometer was used at Cu K α radiation. Structural investigation of samples was carried out by infrared (IR) spectroscopy using the KBr pellet technique by Varian 660 IR spectrometer within the range 4000–400 cm⁻¹. The optical absorption spectra in the ultraviolet and visible region were investigated by Spectrophotometer Evolution 300 in the wavelength range 190–1200 nm. The absorbance test was performed on the powdered samples. The Kubelka–Munk function (F(R ∞)) was calculated from the UV–vis diffuse reflectance spectra. The Band gap energy (E_g) was determined by plot (F(R ∞)hv)^{1/2}, for direct transition. The thermal stability of synthesized amorphous hybrids was determined by DTA/TG analysis. A Seteram Labsysis Evo 1600 instrument was used for recording of thermo diagrams over the range from room temperature up to 800 °C. The heating rate was 10°/min in air atmosphere under an air flow of 20 mL/min. Optical microscopy images were recorded on Light Microscope Zeiss Primo Star at magnification 40x.



Scheme 1. Sol-gel synthesis of copper doped hybrid materials.

Antibacterial activity

Bacterial strain used in this study included Gram-negative *Escherichia coli* K12 (obtained from the culture collection of Bulgarian National Bank of Industrial Microorganisms and Cell Cultures). The growth conditions were described in our previous studies [8, 14]. The antibacterial effect of materials onto model bacterial strain was measurement by zones of inhibition formed around the materials [8, 14, 17, 18].

RESULTS AND DISCUSSION

The thermal behavior of obtained copper doped SiO_2/HPC hybrid materials in the temperature range from 25 to 800 °C was investigated by DTA/TG analysis (Fig. 1 a and b). The DTA curves (Fig. 1a) of the hybrids showed high intensive endothermic effect with maximum at 130 °C that can be attributed with evaporation of the absorbed water. In this temperature range are the general mass losses (Fig. 1b) from the samples. The second part from the DTA curves characterized with two exo-effects with low intensity around 370 and 480 °C that can be connected with decomposition of the organic part. The last effects are difficult to distinguish from DTA curves but on the TG curves there is a mass loss around 700 °C especially for the sample containing 5 wt.% Cu and can be attributed to the decomposition of CuSO_4 to CuO. The final mass losses of the hybrids vary between 15–25% depending on the copper content in the samples. Base on DTA/TG analysis the as prepared hybrid materials have been thermally treated at 700 °C for 3 hours.

The XRD analysis (Fig. 2) of as prepared hybrids showed that the all samples are amorphous due to the silica network. The existence of diffraction peaks in the sample containing 5% copper was connected with the presence of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$ (JPDS: No 98-016-6102 and JPDS: No 98-006-0059). After thermal treatment at 700 °C the all hybrids are still in amorphous state. The sample containing 5 wt.% Cu displayed well-defined diffraction peaks characteristic of crystalline CuO (JPDS: No 01-080-1916).

Figure 3a and b shows the IR spectra of synthesized hybrid materials before and after thermal treatment. The absorption bands at 1079, 797, and 450 cm^{-1} can be assigned to valence asymmetric, symmetric and deformation vibrations of Si–O–Si bonds [8,9,12, 22–24]. The shoulder at 1192 cm^{-1} is due to Si–O–Si linkage [25, 26]. The characteristic vibrations of silanol group at 940 and 570 cm^{-1} can be found. The band at 1634 cm^{-1} is characteristic for adsorbed water on the sample surface. In the range 3670–3440 cm^{-1} the OH stretching vibrations of H-bonded water and/or intra H-bonding in the hybrids between Si–OH and hydroxyl groups from HPC can be found. The hypothesis for successful cross-linking between organic and inorganic components was described in details in our previous work using mathematical approach [9, 24]. The asymmetric shape of the band in this area, and theoretical existence of the vibration above 3500 cm^{-1} give as the opportunity to propose the successful bonding between silica network and cellulose ether via H-bonds [9, 12, 24]. After thermal treatment of the samples (Fig. 3b) the disappearance of the peaks characteristic of the Si–OH groups is observed. The bands at 940 cm^{-1} completely disap-

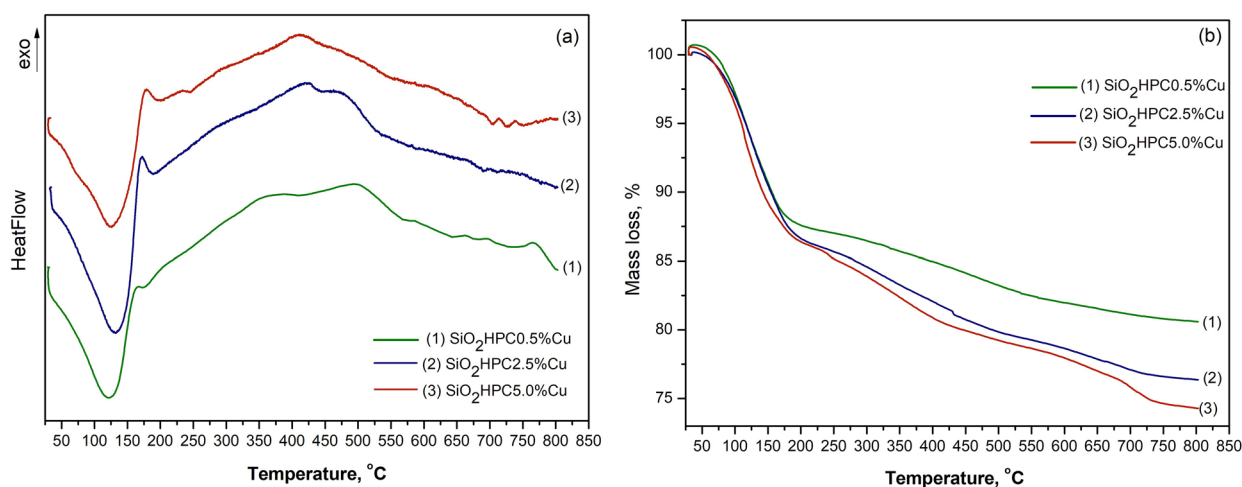


Fig. 1. DTA (a) and TG (b) curves of Cu doped SiO_2/HPC hybrid materials.

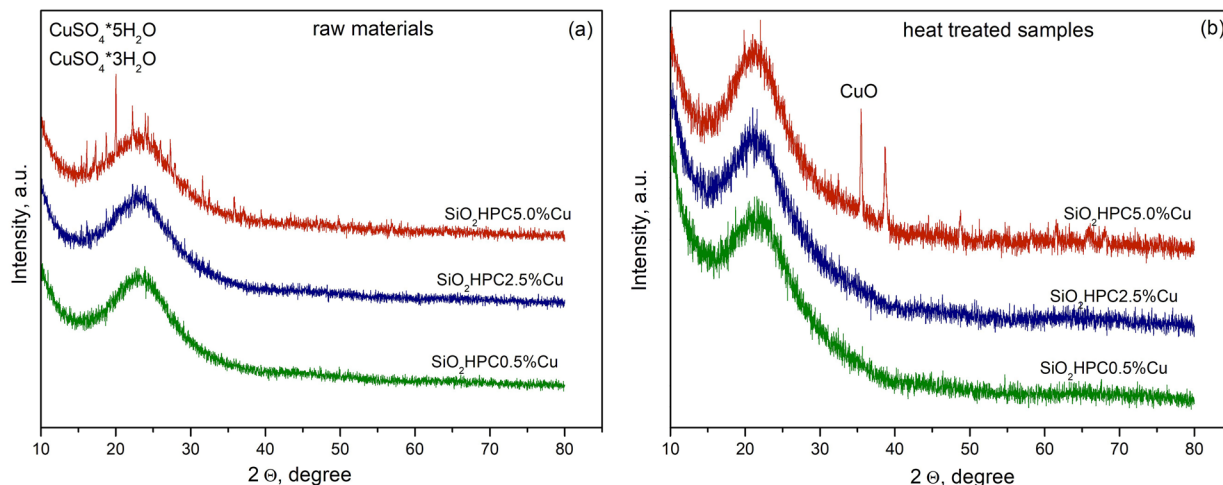


Fig. 2. XRD patterns of Cu doped SiO_2/HPC hybrid materials before (a) and after thermal treatment (b).

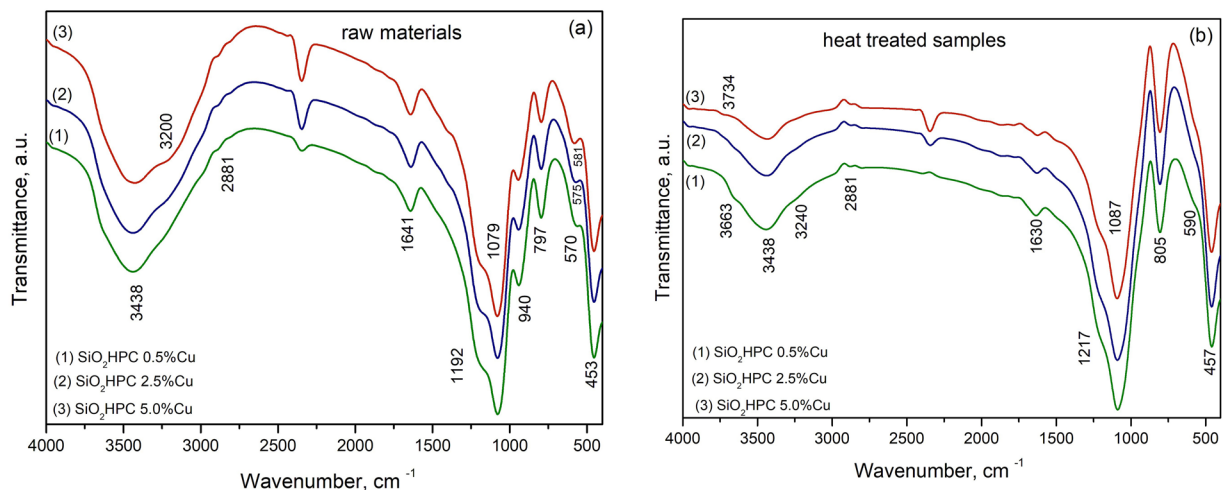


Fig. 3. IR spectra of Cu doped SiO_2/HPC hybrid materials before (a) and after thermal treatment (b).

pears and a shoulder at 590 cm^{-1} is observed. These facts could be assigned to the structural rearrangement in the obtained hybrids [7, 22, 23]. The bands in the range $3670\text{--}3440\text{ cm}^{-1}$ also undergo changes, their intensity decreases, and they are broaden. The band at 3730 cm^{-1} is due to free OH groups [22–24]. Must be mentioned that the Me–O (Cu–O) vibration bands are situated around 460 cm^{-1} and overlapped with Si–O–Si bridging linkage and in our case is difficult to distinguish [22, 23, 27].

The optical absorption spectra of as prepared and thermally treated hybrids are shown on Fig. 4, a and b. The absorption bands around 248 and 253 nm in the spectra of as prepared hybrids can be attributed to the specific different structural characteris-

tics approach from the precursors. As can be seen with increase in copper content the absorption band around 800 nm also increases. This bands can be related with the presence of copper in the divalent state in the hybrids. The band is characteristic to the ${}^2\text{E}_g \rightarrow {}^2\text{T}_g$ transition of Cu^{2+} ions coordinated octahedrally with oxygen ions [28, 29]. By Tauc's plot method the Band gap energy (E_g) for indirect electronic transition of Cu doped SiO_2/HPC hybrid materials before and after thermal treatment was calculated and presented on Fig. 4, c and d. The band gap energy for as prepared hybrids (Fig. 4c) vary between 3.66 and 3.97 eV, which are the typical values for semiconductor materials. After thermal treatment of the samples (Fig. 4d) the

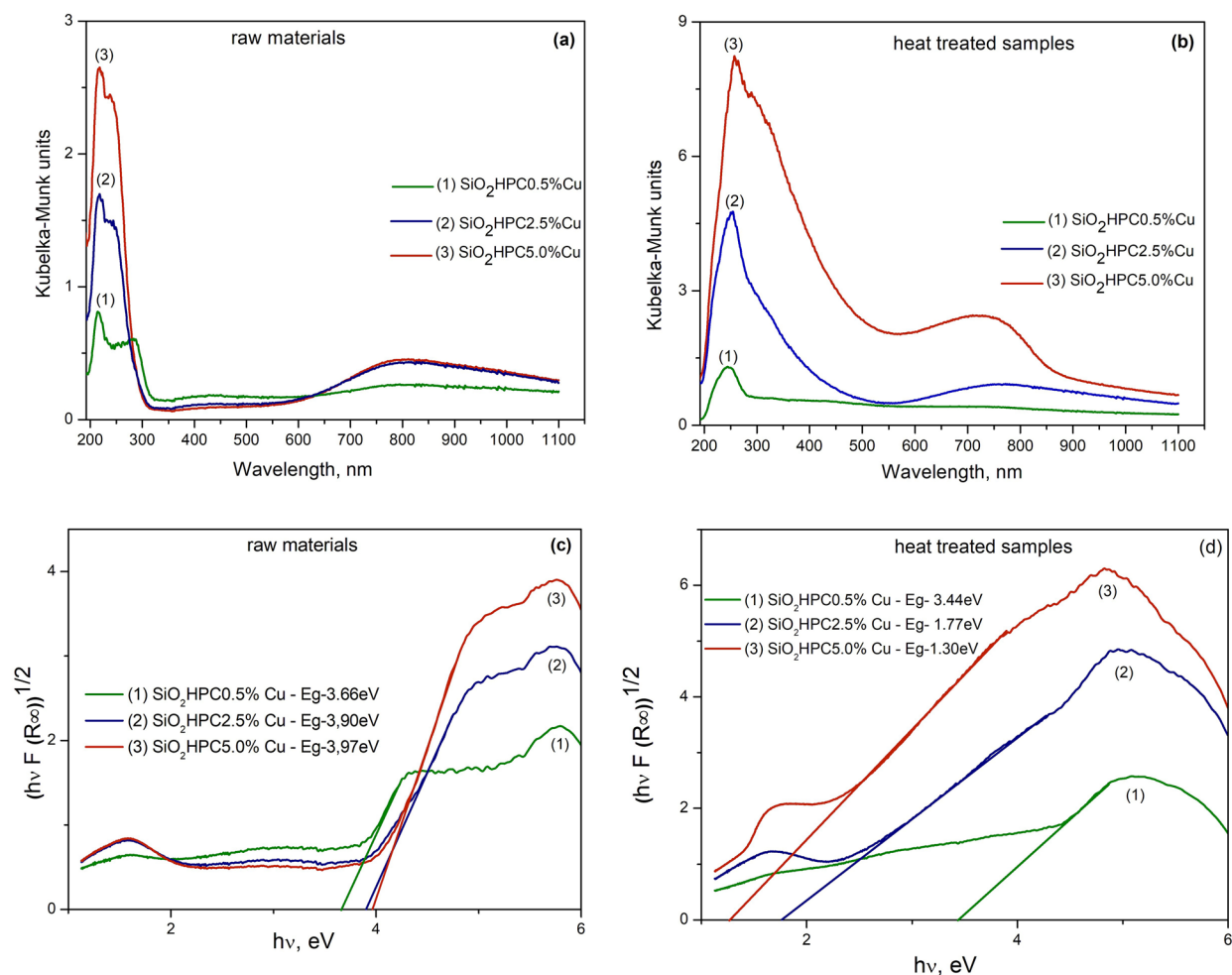


Fig. 4. UV-Vis spectra and Band gap energy of Cu doped SiO₂/HPC hybrid materials before and after thermal treatment.

band gap energy decreases in the range from 3.44 to 1.3 eV with increase of copper content. Compared with the reported data for Eg value of bulk CuO vary between 1.0 and 1.5 eV [30]. This data confirm the results from XRD analysis for the formation of CuO after thermal treatment of the samples.

Optical microscopy images on the surface of Cu doped SiO₂/HPC as prepared hybrid materials are shown on Fig. 5. As can be seen the samples containing 0.5 and 2.5 wt.% copper are homogenous but the sample with 5 wt.% Cu is characterized with indigested CuSO₄*nH₂O probably due to the presence of limited functional groups. As was mentioned above the linkage between HPC and silica network is due to the interaction of OH groups of precursors and formation of H-bonds. This leads to the presence of limit free OH functional groups capable to link with the doped metal ions. Because the silica network is too dense and there is no other possibility for surplus amount of the metal ions to

connect with initial matrix and the only possible opportunity is to be deposited on the sample surface.

The antibacterial properties of hybrids were investigated by measuring the inhibition zones formed around the materials containing different copper amounts in presence of reference strain for Gram-negative (*E. coli* K 12) bacteria. Figure 6 represents the antibacterial activity of as prepared hybrids (Fig. 6a), thermally treated samples (Fig. 6b) and for comparison commercial CuO (Fig. 6c) was used. As can be seen the antibacterial activity exhibit only the as prepared hybrids (Fig. 6a). The thermally treated samples (Fig. 6b) and commercial CuO (Fig. 6c) did not show any antibacterial activity. This results can be explain by the fact that Cu–O bonds (in CuO) are extremely stable than the existence of Cu²⁺ ions in the copper sulphate where the distance between Cu and oxygen is too longer and is easy to separate and this will influence on the antibacterial activity. Moreover, Li *et al* [31]

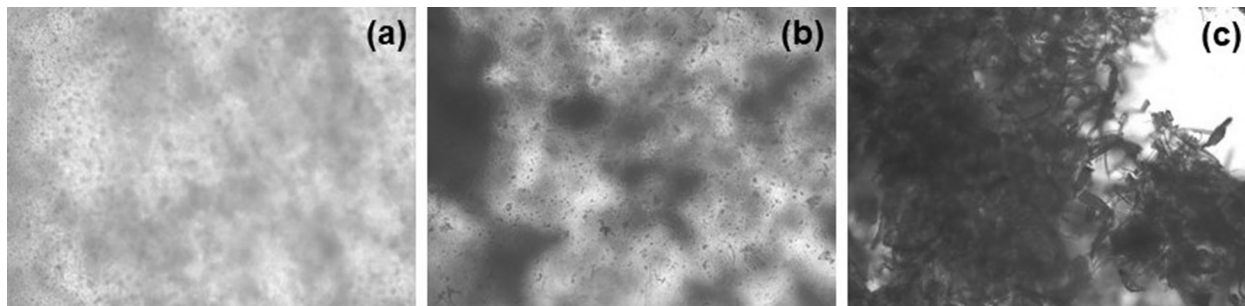


Fig. 5. Optical microscopy images on the surface of Cu doped SiO_2/HPC as prepared hybrid materials: (a) 0.5 wt.% Cu; (b) 2.5 wt.% Cu; and (c) 5 wt.% Cu.

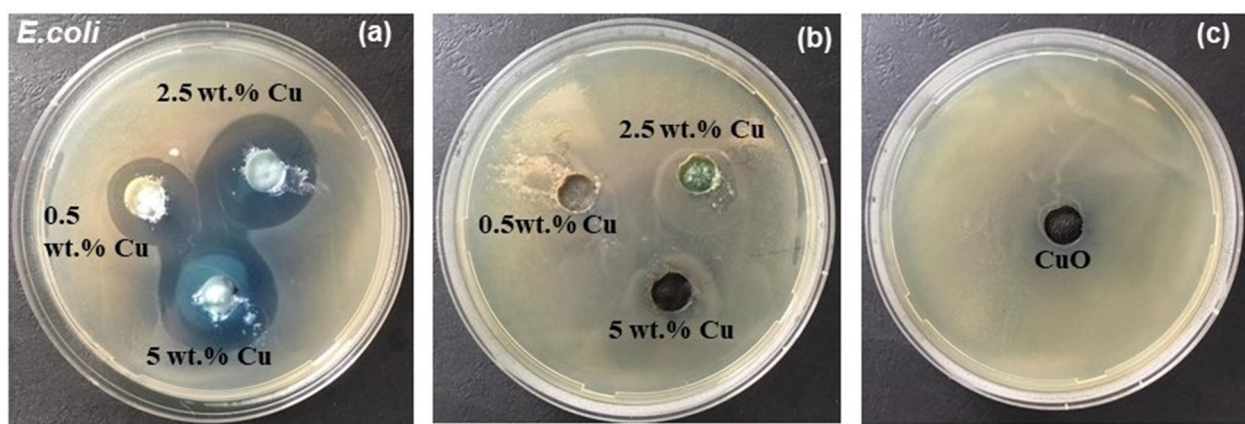


Fig. 6. Inhibition zones of *E. coli* K12 around Cu doped SiO_2/HPC hybrid materials: (a) as prepared materials; (b) after thermal treatment; and (c) commercial CuO.

discussed that the CuO did not produce measurable reactive oxygen species (ROS) which play most important role for antibacterial activity. After 24 h cultivation it was observed that as prepared hybrids proved clear zone of inhibition around the materials (Fig. 6a). The sample with the highest copper content (5 wt.%) showed the biggest zone of inhibition – 10.5 mm. The results reveal that 2.5 wt.% Cu formed an inhibitory zone of 9.5 mm. The lowest copper concentration (0.5 wt.%) also influence the strain growth and measured zone is 5.5 mm. It is clear that the size zone depends on the copper content. As above mentioned results for band gap in the present system the increasing of the copper content leads to increase of E_g values (Fig. 4c). Obviously, in our case the higher band gap prefer antibacterial activity. Due to the low E_g values of thermal treatment samples (Fig. 4d) we supposed probably good photocatalytical properties and this will be the next step of our investigations.

CONCLUSIONS

Copper doped SiO_2/HPC hybrid materials have been prepared by sol-gel method. The hybrids were thermally treated in order to obtain CuO. The phase analysis shown that the all samples are in amorphous state except heat treated sample containing 5 wt.% Cu characterized with well-defined diffraction peaks corresponding to CuO. According to structural investigation the formation of hydrogen bonds between organic and inorganic parts was proposed. The morphology investigation of as prepared hybrids showed that the samples containing 0.5 and 2.5 wt.% copper are homogenous but the sample with 5 wt.% Cu is characterized with indigested phase separation between the matrix and doped copper sulphate due to the presence of limit functional groups. Based on optical spectra the band gap energy was calculated and parameters values vary in the regions 3.66–3.97 eV for as prepared samples

and 3.44–1.30 eV for thermal treatment samples. The antibacterial properties of hybrids were investigated against reference strain for Gram-negative (*E. coli* K 12) bacteria. It was found that the potential of materials as antimicrobial agents increase with increasing of copper content in the hybrids. It was established that size zone also depend on the copper content.

REFERENCES

1. Y. H. Kim, D. K. Lee, H. G. Cha, C. W. Kim, Y.C. Kang, Y. S. Kang, *J. Phys. Chem. B*, **110**, 24923 (2006).
2. J. Ramyadevi, K. Jeyasubramanian, A. Marikani, G. Rajakumar, A. A. Rahuman, *Mater. Lett.*, **71**, 114 (2012).
3. P. Maniprasad, S. Santra, *J. Biomed. Nanotechnol.*, **8**, 558 (2012).
4. C. C. Trapalis, M. Kokkoris, G. Perdikakis, G. Kordas, *J. Sol.-Gel. Sci. Technol.*, **26**, 1213 (2003).
5. Y. Dimitriev, Y. Ivanova, R. Iordanova, *J. Univ. Chem. Technol. Metall.*, **43**, 118 (2008).
6. P. Gómez-Romero, C. Sanchez, *Functional Hybrid Materials*, WILEY-VCH Verlag GmbH & Co. KGaA, Germany, 2004.
7. N. Rangelova, S.Nenkova, L. Radev, B. Samuneva, B. Aleksiev, in: *Nanoscience & Nanotechnology*, E. Balabanova, I. Dragieva (eds), vol 7, Heron press, 2007, p. 230.
8. Ts. Angelova, N. Rangelova, R. Yuryev, N. Georgieva, R. Müller, *Mater. Sci. Eng. C*, **32**, 1241 (2012).
9. N. Rangelova, L. Aleksandrov, Ts. Angelova, N. Georgieva, R. Müller, *Carbohydr. Polym.*, **101**, 1166 (2014).
10. O. Akhavan, E. Ghaderi, *Surf. Coat. Technol.*, **205**, 219 (2010).
11. H. Pang, F. Gao, Q. Lu, *Chem. Commun.*, **7**, 1076 (2009).
12. N. Rangelova, N. Georgieva, K. Mileva, R. Yuryev, R. Müller, *C. R. Acad. Bulg. Sci.*, **65**(8), 1057 (2012).
13. Ts. Angelova, N. Georgieva, N. Rangelova, V. Uzunova, T. Andreeva, R. Tzoneva, R. Müller, *C. R. Acad. Bulg. Sci.*, **67**(10), 1355 (2014).
14. Ts. Angelova, N. Rangelova, H. Dineva, N. Georgieva, R. Müller, *Biotechnol. Biotechnol. Equip.*, **28**, 747 (2014).
15. Ts. Angelova, N. Rangelova, V. Uzunova, N. Georgieva, T. Andreeva, A. Momchilova, R. Tzoneva, R. Müller, *Turk. J. Biol.*, **40**(6), 1278 (2016).
16. Ts. Angelova, N. Georgieva, H. Dineva, N. Rangelova, R. Müller, *J. Chem. Technol. Metall.*, **49**(2), 121 (2014).
17. Ts. Angelova, R. Abdel Aty Eissa Mohamed, N. Rangelova, N. Georgieva, *J. Chem. Technol. Metall.*, **51**(2), 141 (2016).
18. T. Angelova, N. Rangelova, N. Georgieva, *Food Sci. Appl. Biotechnol.*, **1**(2), 104 (2018).
19. D. Pencheva, A. Sestrimska, A. Dimitrova, L. Borisova, R. Karamfilova, N. Rangelova, Ts. Angelova, N. Georgieva, *Problems of Infectious and Parasitic Diseases*, **46**(1), 41 (2018).
20. N. Rangelova, S. Nenkova, N. Lazarova, N. Georgieva, *Bulg. Chem. Commun.*, **47**(A), 39 (2015).
21. N. Rangelova, L. Aleksandrov, N. Georgieva, N. Lazarova-Zdravkova, S. Nenkova, *C. R. Acad. Bulg. Sci.*, **69**, 1563 (2016).
22. C. J. Brinker, S.W. Scherer, *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*. Academic Press, New York, 1990, p. 541.
23. R. M. Almeida, A. C. Marques, in: *Handbook of Sol-Gel Science and Technology*, L. Klein, M. Aparicio, A. Jitianu (eds.), Springer International Publishing, Switzerland, 2016, p. 1.
24. N. Rangelova, L. Aleksandrov, S. Nenkova, *J. Sol-Gel Sci. Technol.*, **85**, 330 (2018).
25. E. I. Kamitsos, A. P. Patsis, G. Kordas, *Phys. Rev. B: Condens. Matter.*, **48**, 12499 (1993).
26. E. I. Kamitsos, *Phys Rev B: Condens Matter.*, **53**, 14659 (1996).
27. A. A. Radhakrishnan, B. B. Beena, *Indian J. Adv. Chem. Sci.*, **2**(2), 158 (2014).
28. M. Nogami, Y. Abe, A. Nakamura, *J. Mater. Res.*, **10**, 2648 (1995).
29. G. De, M. Epifani, A. Licciulli, *J. Non-Cryst. Solids*, **201**, 250 (1996).
30. J. Koshy, M. S. Samuel, A. Chandran, K. C. George, *AIP Conf. Proc.*, **1391**, 576 (2011).
31. Y. Li, W. Zhang, J. Niu, Y. Chen, *ACS Nano*, **6**, 5164 (2012).