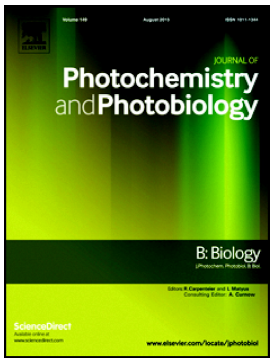

Photodynamic-active smart biocompatible material for an antibacterial surface coating

Mária Kováčová, Angela Kleinová, Ján Vajďák, Petr Humpolíček, Pavel Kubát, Michal Bodík, Zoran Marković, Zdenko Špitálský

PII: S1011-1344(20)30462-0

DOI: https://doi.org/10.1016/j.jphotobiol.2020.112012

Reference: JPB 112012

To appear in: *Journal of Photochemistry & Photobiology, B: Biology*

Received date: 24 February 2020

Revised date: 12 August 2020

Accepted date: 30 August 2020

Please cite this article as: M. Kováčová, A. Kleinová, J. Vajďák, et al., Photodynamic-active smart biocompatible material for an antibacterial surface coating, *Journal of Photochemistry & Photobiology, B: Biology* (2020), https://doi.org/10.1016/j.jphotobiol.2020.112012

Photodynamic-active smart biocompatible material for an antibacterial surface coating

Mária Kováčová[1], Angela Kleinová[1], Ján Vajďák[2], Petr Humpolíček[2], Pavel Kubát[3], Michal Bodík[4], Zoran Marković[5], Zdenko Špitálský[1,*]

[1]Polymer Institute, Slovak Academy of Sciences, Dúbravská cesta 9, 845 41 Bratislava 45, Slovakia

[2]Centre of Polymer Systems, Tomas Bata University in Zlín, Třída Tomáše Bati 5678, Zlín, Czech Republic

[3]J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Praha 8, Czech Republic

[4]Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta 9, 845 11 Bratislava, Slovakia

[5]Vinca Institute of Nuclear Sciences, Mike Alasa 12-14, Vinca, 11351 Belgrade, Serbia

e-mail: zdeno.spitalsky@savba.sk

Keywords: hydrophobic carbon quantum dots; photodynamic therapy; radicals; nanocomposite; antibacterial activity

Abstract:

Here we present a new effective antibacterial material suitable for a coating, e.g., surface treatment of textiles, which is also time and financially undemanding. The most important role is played by hydrophobic carbon quantum dots, as a new type of photosensitizer, produced by carbonization of different carbon precursors, which are incorporated by swelling from solution into various polymer matrices in the form of thin films, in particular polyurethanes, which are currently commercially used for industrial surface treatment of textiles. The role of hydrophobic carbon quantum dots is to work as photosensitizers upon irradiation and produce reactive oxygen species, namely singlet oxygen, which is already known as the most effective radical for elimination different kinds of bacteria on the surface or in close proximity to such modified material. Therefore, we have mainly studied the effect of hydrophobic carbon quantum dots on *Staphylococcus aureus* and the cytotoxicity tests, which are essential for the safe handling of such material. Also, the production of singlet oxygen by several methods (electron paramagnetic spectroscopy, time-resolved near-infrared spectroscopy), surface structures (atomic force microscopy and contact angle measurement), and the effect of radiation on polymer matrices were studied. The prepared material is easily modulated by end-user requirements.

1. Introduction

A lot of effort is currently being made to produce multifunctional materials that are also environmentally friendly, cost-effective, and time-saving, and this requires constant innovation in science and technology [1–4]. A specific case is, for example, textiles, which must often be waterproof, conductive, antistatic, antimicrobial, UV protected, and last but not least, have a long service life [5–10]. If we want to deal specifically with an antimicrobial, in

the narrower sense - antibacterial treatment of textiles, such treatments are possible using, e.g., different types of plasma - RF plasma or low-temperature plasma [11–13]. In general, the plasma treatment of textiles is often performed for the activation of the textile surface [12,14,15]. In order to minimize the damage of the fibers, the low-temperature plasmas are used [16].

The preparation of antibacterial textiles is often a combination of methods, for example, where different types of particles or nanoparticles counteract the adhesion and multiplication of bacteria. Commonly used antibacterial nanomaterials are TiO_2, ZnO, MgO, CuO, Al_2O_3, or silver ions [12,17–25].

For centuries silver has been used as a biocidal product [26]. On contact with moisture, a reaction occurs, releasing silver ions. They penetrate microbes, which are subsequently unable to be active, grow, or reproduce [27,28]. Currently, the largest consumers of silver-based biocidal products are food processing plants, pharmaceutical manufacturing plants, and medical facilities such as hospitals and nursing homes, offering the ideal environment for microbes [29]. However, the use of silver nanoparticles presents several disadvantages: silver nanoparticles exhibit uncontrolled antibacterial activity throughout their use, silver nanoparticles are susceptible to oxidation, so they lose their antibacterial effects after some time, the silver nanoparticles are water-soluble so that any exposure of the material containing the silver nanoparticles to water or biological fluids (urine, blood, sweat) results in its degradation, it is a relatively costly material, need a long contact time to be effective, and on top of that, silver-resistant organisms are already appearing [30].

At present, an auspicious new material is QDs. Louis Brus and Alexey Ekimov are considered as their discoverers [31,32]. Their name was due to their small size and quantum effects [33]. They are characterized by a number of excellent properties such as, for example, electrical and optical properties, photobleaching stability, photoluminescence, and

antimicrobial effect [34]. The new class of QDs is carbon quantum dots (CQDs), in our case, hydrophobic (hCQDs), miscible with polymer matrices with a confirmed antibacterial effect [35–37]. They can be prepared by burning conventional waste, biomass, or other carbon-containing precursors. It is, therefore, a very environmentally friendly preparation method [38–41]. The CQDs can be used in a number of applications as biomedical, pharmaceutical, biomonitoring, food analysis, but mainly for antibacterial treatments, of not just textiles [42–44].

The incorporation of quantum dots onto the surfaces of materials is a new strategy for removing unwanted microorganisms, thus significantly prevent antibiotic resistance. To reduce the expenses on the treatment of patients that are unnecessarily infected in day-to-day activities, or especially in hospital settings. Textiles modified with hCQDs, prepared in this way, are able to ensure the cleanliness of clothing even in super-clean rooms, and it is not necessary to disinfect them. This material can do this by producing reactive oxygen species that are harmful to bacteria, which has been published in several studies [35,36], and it is summarized in the review [45].

In this paper is described the preparation and characterization of hydrophobic carbon quantum dots (hCQDs) in two types of polyurethanes, which are commercially used for textile finishing. These two types of polyurethanes serve as polymer carriers for antibacterial hCQDs. Their chemical structure, physical and antibacterial properties, and cytotoxicity tests were investigated. The advantage of hCQDs is mainly in their production, which is in comparison to the known photosensitizers (PS), time, and cost-effective. Antibacterial activity of the material is controllable by conventional LEDs, requires only low light intensity, and shorter irradiation time in comparison to commonly used PS. Material is non-degradable, resistant to photobleaching, and stable over a long period (does not create chemical

compounds with atmospheric gases or molecules present in biological fluids). Finally, hCQDs are insoluble in water or biological fluids (urine, blood, sweat).

Antibacterial properties were tested against *Staphylococcus aureus*. According, Kramer et al., *S. aureus*, including MRSA, can survive on dry inanimate surfaces 7 days to 7 months. Therefore, antibacterial treatment of textiles, especially in hospitals and clean rooms, as well as other aids and equipment, is crucial for human health and for preventing contamination and environmental contamination [46].

2. Experimental

The hydrophobic quantum dots (hCQDs) with a quantum yield of singlet oxygen production 0.31 were prepared according to the procedure, which was previously reported by Stanković et al. [43]. The hCQDs concentration in toluene (purchased from Lach:ner s.r.o., Slovakia) was approximately 0.4 mg/mL.

As polymer matrix, were used two types of commercially available transparent polyether-urethane with thickness 25 um (LAMETHAN 1 ET 25, next as PU25) and polyester urethane (LAMETHAN LB 15-1, next as PU15) with thickness 15 µm. Both polyurethanes were donated by CHT Montlingen, Switzerland AG. Selected PUs can be used to coat different types of textiles by laminating procedure up to 145°C, which ich not harmful for hCQDs. After previous experience with polyurethanes [35], both LAMETHANES were cut to the needed size and dipped into hCQDs/toluene solution for 48 hours. Encapsulation of hCQDs into the polymer matrix was running at room temperature. Samples were dried 12 hours at 80°C in a vacuum drying oven in order to remove any toluene residues.

The blue LED lamp (purchased from LEDart s.r.o., Slovakia) with wavelength 470 nm and the power 50 W was used as a light source in order to activate nanocomposites. The lamp was placed 50 cm above the tested samples in order to produce a homogeneous scattering of blue light (470 nm).

The swelling was measured every 2 hours. Pieces of PU15 and PU25 in size 1 × 1 cm were used and dipped into 5 ml of pure toluene and hCQDs/toluene. It was measured to a constant weight, which was obtained gravimetrically and compared. The experiment was performed in three parallel measurements.

The contact angle measurement of prepared nanocomposites was conducted using Surface Energy Evaluation System (SEE System; Advex Instruments, s.r.o., Czech Republic) and software to analyze results. The liquid used was deionized water, and the measurement was carried out ten times.

For surface analysis of samples, we used AFM Multimode 8 (Bruker, USA) equipped with ScanAsyst-Air. The morphology of samples was measured in PeakForce Tapping mode at room temperature (Bruker, USA). The root-mean-square roughness (RMS) of samples was determined by Gwyddion software. The mechanical properties of the composites were characterized by the Peak Force QNM scanning probe technique [47]. For the Peak Force QNM measurements, we used sapphire as a calibrant for ScanAsyst-Air tip.

The kinetics of singlet oxygen, $^1O_2$, after excitation of individual samples with Quantel Nd-YAG laser (excitation wavelength 355 nm, pulse length ~5 ns) was measured using time-resolved near-infrared luminescence spectroscopy. Luminescence of $^1O_2$ at 1270 nm was recorded in reflection mode using a Judson Ge diode and interference filters. The signal from the detector was collected in a 600 MHz oscilloscope (Agilent Infiniium, USA) and transferred to a computer for further analysis. The signal-to-noise ratio of the signals was

improved by the averaging of 1000 individual traces. The initial part (up to ~2 μs) was omitted due to a significant scattering of the laser pulse and luminescence of QDs and other compounds, and it was not used for evaluation. The resulting traces were calculated as the difference of the luminescence in the oxygen atmosphere, and vacuum. They were then fitted by a single exponential function to calculate the initial concentration of singlet oxygen and its lifetime (τ_Δ).

The antibacterial activity was performed according to ISO 22196 standard. As a model organism, the Gram-positive bacteria *Staphylococcus aureus* CCM 4516 obtained from the Czech Collection of Microorganisms (CCM) was used. Prior to experiments, the sample was sterilized by UV irradiation (258 nm). The concentration of started bacterial suspension was around $7.7x10^5$ cfu/ml. The antibacterial activity was initiated by irradiation of the samples for 1 h. The experiment was repeated three times for statistical relevance. Quantity of viable bacteria was calculated as reported in our previous studies according to ISO 22196 "Measurement of antibacterial activity on plastics and other non-porous surfaces" with modification [35,36].

Cytotoxicity was measured according to ISO standard 10993-5 on mouse embryonic fibroblast cell line (ATCC CRL-1658 NIH/3T3, USA). Media preparation follows the ISO standard 10993-12. Tested materials were incubated in culture medium for 24 hours at 37°C with stirring. Concretely, 6 cm^2 of tested samples per 1 mL of media were extracted to get a parent extract, which was subsequently diluted. The extracts were filtered using Syringe filter 0.22 μm. The parent extracts (100 %) were then diluted in culture medium to obtain a series of dilutions with concentrations of 75, 50, 25, 10, and 1 %. The extracts were used for up to 24 hours. Tetrazolium salt (MTT cell proliferation assay kit, Duchefa Biochemie, Netherlands) was used to determine cell viability. The absorbance was measured at 570 nm, and the reference wavelength was adjusted to 690 nm. The results are presented as the

reduction of cell viability in percentage when compared to cells cultivated in medium without the extracts of tested materials. Morphology of cells from the culture plates was observed using an inverted Olympus phase-contrast microscope (IX 81).

The mouse embryonic fibroblast cell line (ATCC CRL-1658 NIH/3T3, USA) was also used for the test of cell proliferation. Sterilization procedure and cultivation medium were the same as in the case of antibacterial activity. The staining with Hoechst 33258 (Invitrogen, USA) was used to visualize cell proliferation. Before staining, the cells were fixed and permeabilized using 4 % formaldehyde (Penta, Czech Republic) for 15 minutes, washed by PBS, and subsequently poured with 0.5 % Triton X-100 (Sigma-Aldrich, USA) for 5 minutes. After this time, cells were washed 3 times by PBS (Invitrogen, USA). Morphology of cells was observed using an inverted Olympus phase-contrast microscope (IX 81) after DNA staining using Hoechst.

3. Results and discussion

3.1 Swelling and contact angle measurement

The swelling ability of PUs was evaluated in toluene and hCQDs/toluene solution depending on time. The concentration of hCQDs in PUs increases with swelling time until saturation point. The incorporation of hCQDs inside polymers was linearly observed from the start of the experiment. The encapsulation proceeded most rapidly in the first 4 hours and then slightly decreased until stabilization, i.e., after 24 hours. Finally, the amount of incorporated quantum dots after dipping into the toluene solution (0.4 mg/mL) was calculated as the difference in weight between the pure sample and treated with hCQDs. Furthermore, based on the weight of the PUs, the resulting percentage of hCQDs in the matrix is approximately 2.0 wt% in both cases (for PU15 and PU25), which is maximal obtainable concentration.

The wettability of prepared materials was studied with contact angle measurement. Hydrophobicity and hydrophilicity of materials is a very important property, because of the adherence of bacteria. The more hydrophobic surface makes it difficult for bacteria adhesion and reproduction. According to our results, the contact angle of water of pure PU15 was 99.8° ± 4.6°. After the incorporation of hCQDs, it was increased to 109.11° ± 4.7°. Negligible differences in wettability were observed in the case of more hydrophobic PU25. Pure PU25 has the water contact angle 102.1° ± 1.9° and PU25/hCQDs only 104.4° ± 4.8°. However, since the concentration of quantum dots in such thin polymer matrices is low, both hCQDs modified samples of polymer sheets were hydrophobic with contact angle over 104°, and thus limit the ability of bacteria to colonize this polymer.

3.2 Singlet oxygen production characterization

The time-resolved measurement of singlet oxygen luminescence in NIR (1270 nm) showed that both PU25/hCQDs and PU15/hCQDs generated singlet oxygen upon pulse irradiation by Nd-YAG laser (355 nm, Fig. 1). The simple analysis based on comparison of the amplitudes of the single exponential fits (proportional to the initial concentration of singlet oxygen) indicates that PU25/hCQDs (A_{PU25} ~ 0.95) was a more efficient producer of singlet oxygen in comparison with PU15/hCQDs (A_{PU15} ~ 0.85), which corresponds with results of Electron paramagnetic resonance spectroscopy (EPR) measurements (Fig. S1). The lifetime of singlet oxygen (τ_Δ) was 12±2 μs for both samples similar to those in polystyrene or polyurethane [48]; this value is a three times higher than that for singlet oxygen in water (3.5 μs) [49]. The difference between lifetimes shows that polymeric matrix gradually releases singlet oxygen for a few tens of microseconds after excitation to the environment, where deactivated quickly by interaction with water and/or biological targets (bacteria).

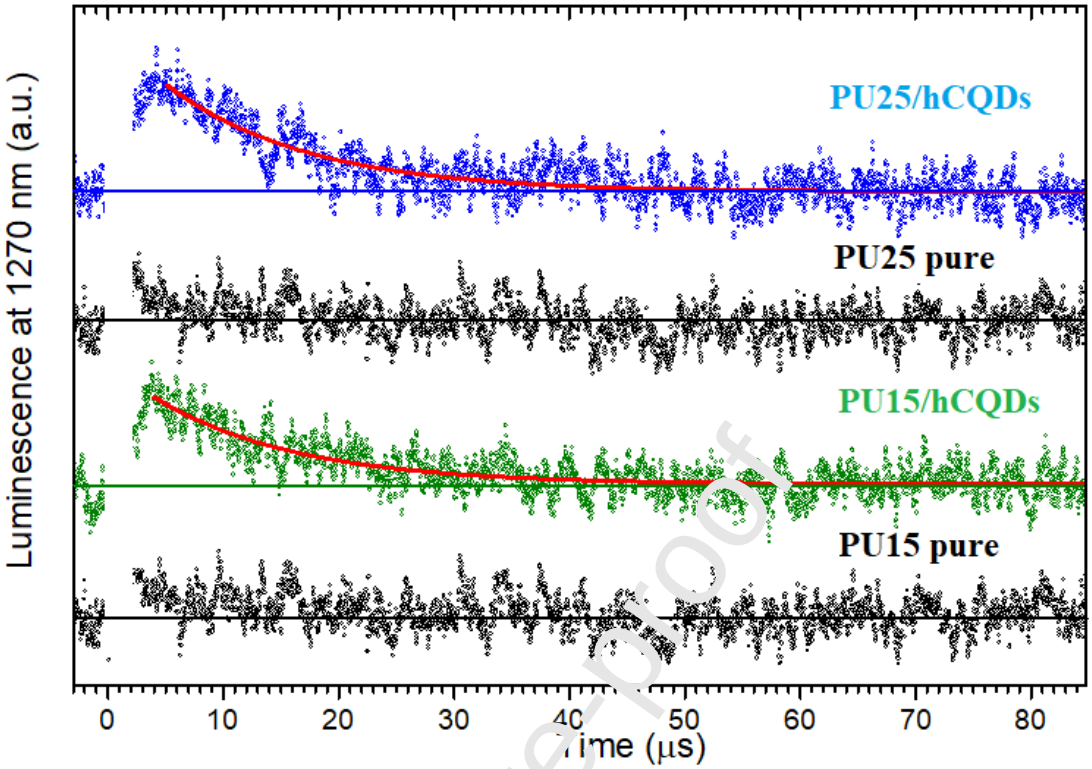

Figure 1. Time-resolved luminescence of singlet oxygen at 1270 nm. Samples were excited by Nd-YAG laser (355 nm, pulse length of ~5 ns). Red lines are single exponential fits into experimental data. Data are offset.

3.3 Surface morphology study

The samples of PU15 were analyzed with AFM. The morphology of pure and modified PU15 exhibits differences in the structure. The pure PU15 has a smoother surface with line-like structures (Fig. 2). These structures are directly caused by the manufacturing process since it is a commercially available product. The RMS roughness of pure PU15 is 8.6 nm. The hCQDs modified samples have, on the other hand, more variable structure (Fig. 3). The addition of hCQDs changes the mechanical properties of the polymer matrix, and the hardening of the polymer film results in a different structure. The RMS roughness of hCQDs modified PU15 is 14.8 nm.

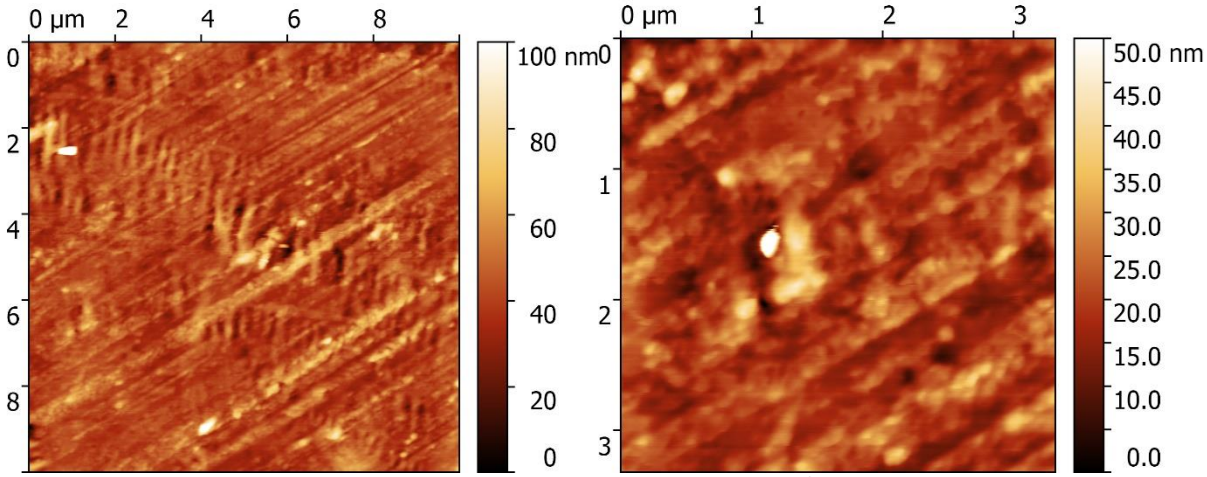

Figure 2. The AFM image of pure PU15, 10×10 µm^2 (left), 3.3×3.3 µm^2 (right).

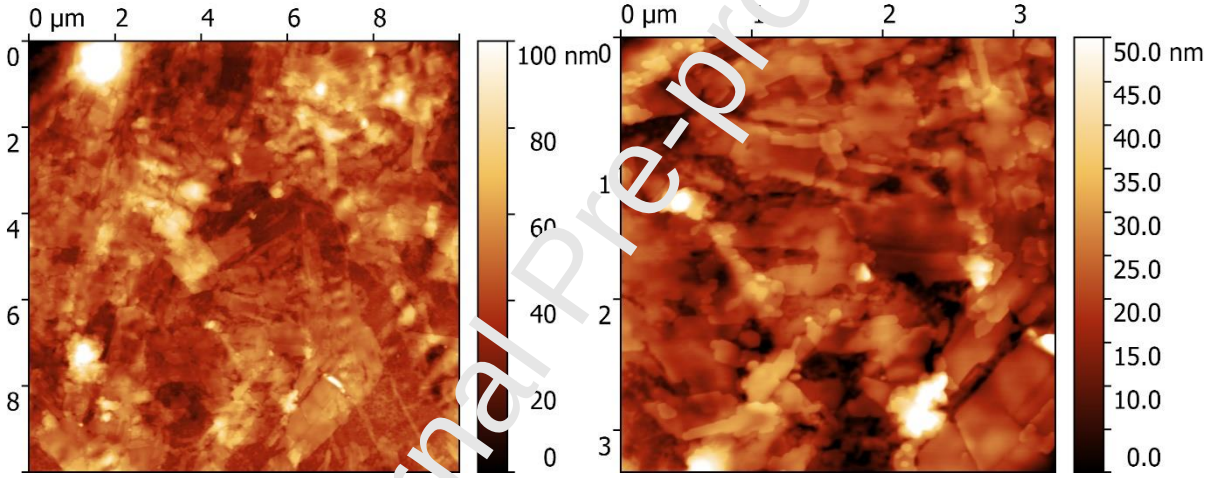

Figure 3. The AFM image of hCQDs modified PU15, 10×10 µm^2 (left), 3.3×3.3 µm^2 (right).

Both modified and pure PU25 are rougher than the PU15 samples. The pure PU25 still shows the line-like structure (Fig. 4), similar to PU15. The overall structure shows a grain-like structure with grains size approximately 100 nm. The RMS roughness of pure PU25 is 28.4 nm. The hCQDs modified PU25 have smaller grains (approximately 50 nm) in comparison with the pure PU25 (Fig. 5). The RMS roughness is smaller than pure PU25, with 22.3 nm, which is caused mainly due to the smaller grain size.

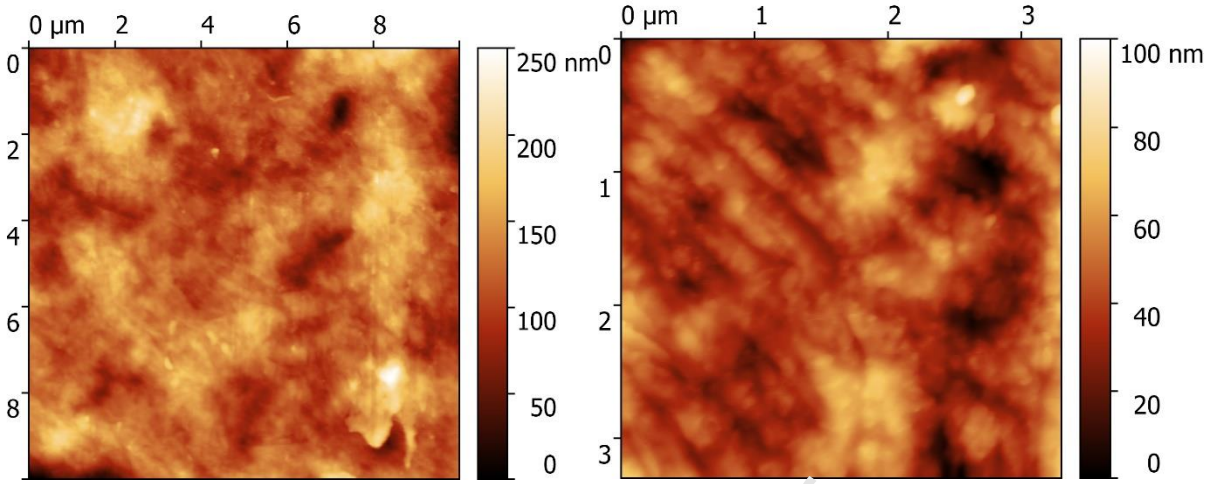

Figure 4. The AFM image of pure PU25, 10×10 µm^2 (left), 3.3×3.3 µm^2 (right).

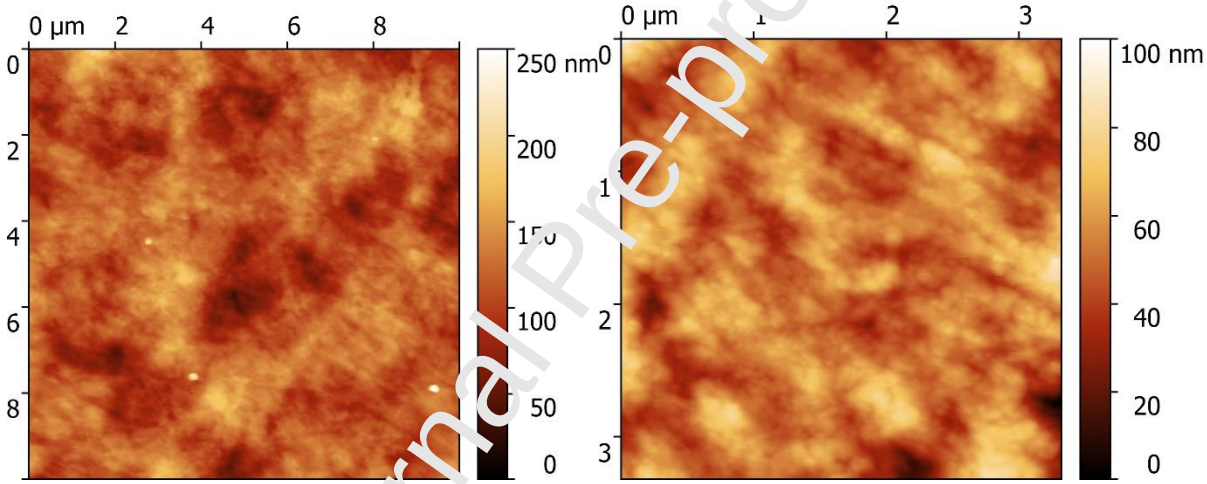

Figure 5. The AFM image of hCQDs modified PU25, 10×10 µm^2 (left), 3.3×3.3 µm^2 (right).

Also, we measured the deformation of the sample, using the Peak Force QNM scanning probe technique, which means the penetration of the tip into the measured sample at a constant force. The penetration depth of the AFM tip is larger for pure PU15 and PU25 compared to the hCQDs modified PU15 and PU25. The average penetration depth of the pure PU15 is 2.5 nm, and hCQDs modified PU15 has an average penetration depth of 0.3 nm. In the case of PU25, the pure polymer has an average penetration depth of 1.4 nm, and the hCQDs modified 0.04 nm. The values are measured at 10×10 µm^2 area.

Lower penetration depth suggests a tougher sample. It means that when incorporating the hCQDs into the polymer matrix, the resulting composite is tougher than the pure polymer. This fact can also explain the different morphology of the sample. The difference in the mechanical properties of the polymer can lead to different morphology because of the different interfacial interactions, similar to what was found to carbon nanotubes composites [50].

3.4 Antibacterial activity

As mentioned above, the antibacterial activity of composites of hCQDs depends on many factors, such as the irradiation time, concentration of the quantum dot in the polymer matrix, the type of used polymer, its diffusion coefficient and surface roughness, as well as on the microorganism species. Since quantum dots are a special type of photosensitizer and their activator is blue light, they are capable of producing singlet oxygen, which is one of the most powerful radicals. Radicals disrupt the bacterial cell wall, which leads to their destruction. To induce the antibacterial activity, the samples must be irradiated by blue light to produce singlet oxygen.

The antibacterial testing was performed using *S. aureus* as a common model organism. From table 1., it is clear that pure PU15 and PU25 have no antibacterial effect, even after 1-hour irradiation with blue light. On the other hand, the modified PU15/hCQDs and PU25/hCQDs nanocomposites exhibit a significant antibacterial activity after irradiation and, thus, the quantum dots activation. The combination of the effects of hCQDs, a relatively smooth surface, and an increase in contact angle (increased hydrophobicity) are parameters that affected the antibacterial effect in both types of here investigated PUs.

Table 1. Antibacterial activity of pure and modified PU15 and PU25 after 1 hour of irradiation

Samples	*Staphylococcus aureus CCM 4516*	
	N (cfu/cm^2)	**R = U_t - A_t**
PU25 pure	2.0×10^5	**U_t=5.7**
PU25/hCQDs	5.0×10^2	**3.0**
PU15 pure	6.1×10^4	**U_t=4.7**
PU15/hCQDs	5.6×10^2	**2.0**

Note: N means the number of viable bacteria recovered per cm^2 per test specimen; R = the antibacterial activity where U_t is the average of the common logarithm of the number of viable bacteria (cells/cm^2) recovered from the untreated test specimens, and A_t means the average of the common logarithm of the number of viable bacteria (cells/cm^2) recovered from the treated test specimens.

3.5 Cytotoxicity

In vitro determination of cytotoxicity is the essential requirement applied to any medical device. The low cytotoxicity is a prerequisite for further development of materials with appropriate surface and mechanical properties.

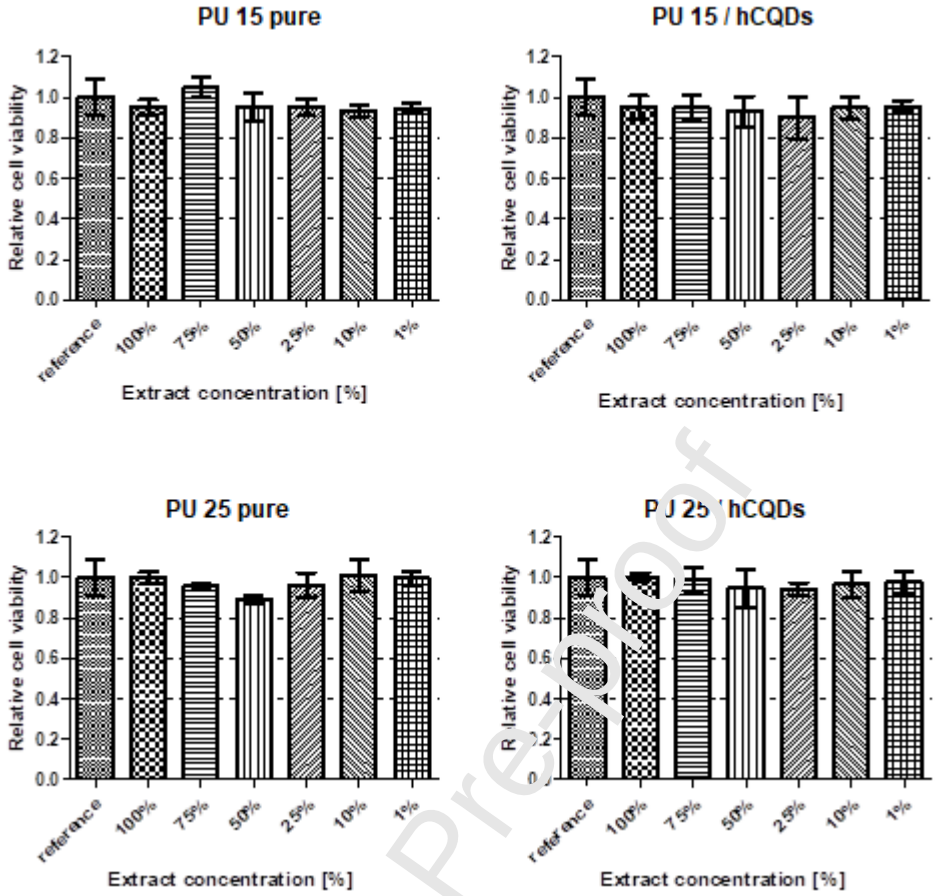

Figure 6. Cell viability of individual samples' extracts in various concentrations.

In general, two main types of cytotoxicity determination can be used. Specifically, this is direct contact of cells with the material or mostly used testing of cytotoxicity of extracts. Since the direct contact method often results in the so-called intrinsic toxicity of materials, and the results are significantly affected [51]. Prepared samples were therefore tested by cytotoxicity testing of extracts, as defined by ISO 10993-5 and ISO 10 993-12. From the results presented in Fig. 6., it is clear that none of the tested PU based materials possess cytotoxicity.

3.6 Cell proliferation

Proliferation is one of the crucial properties determining the application of materials in contact with living tissues. The cell proliferation is dependent on the ability of cells to adhere to the surface, and on their subsequent growth and division. Cell proliferation can be quantified and examined by a number of methods. Here, the visualization of the cell nucleus was used as the samples were in the form of solid films. As shown in Fig. 7., cell proliferation was highest on the reference (tissue culture on plastic polystyrene). The proliferation on all other samples was lower compared to the reference, and the presence of debris is clearly seen. The inability of cells to proliferate is particularly visible in the case of hCQDs composites. In the case of pure PU15 and PU25, there is a lower number of cells (which moreover do not cover the surface homogeneously, but mainly form clusters), but in the case of hCQDs composites, the cells are almost not present. This fact can be correlated to either the cytotoxicity of material (which is low – see Fig. 6) or by the surface properties of PU based materials. This parameter is, however, not critical for the application of the material, as a variety of methods can modify the surface properties. Thus the cell proliferation can be modulated.

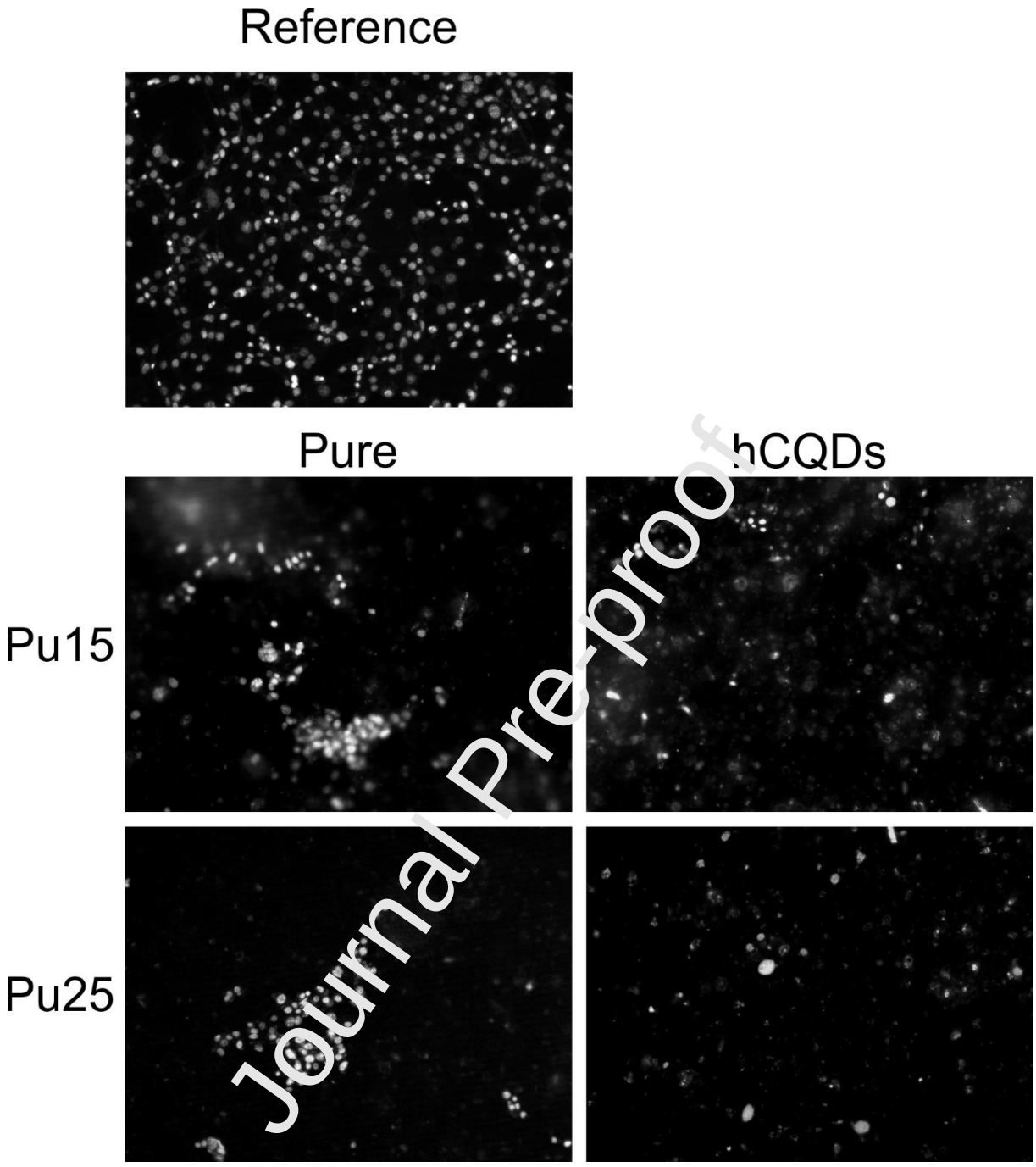

Figure 7. Cell proliferation of mouse embryonic fibroblast cell line NIH/3T3. The cell nuclei were visualized Hoechst. Magnification 100x.

4 Conclusion

In this paper, we prepared a new antibacterial polymer and described its structural, physical, and antibacterial properties. Hydrophobic carbon quantum dots incorporated in polymer matrices have been able to produce singlet oxygen, after irradiation with blue light. The production of $^1O_2$ has been evaluated with EPR and time-resolved NIR spectroscopy. Both PU15 and PU25 produced singlet oxygen, while the PU25 exhibited higher production of singlet oxygen than PU15. The polymer's chemical structure before and after irradiation has been tested using Fourier-transform infrared spectroscopy with minimal chemical changes observed due to the incorporation of hCQDs. Also, AFM measurements have provided the necessary information about the surface structure and roughness of the sample. The incorporation of hCQDs changes the roughness of PU15 and PU25 while toughening both samples. Antibacterial testing has been done on model bacteria *S. aureus*. After using hCQDs, the number of vital bacteria has significantly decreased. Zero cytotoxicity predestines this material as a suitable surface treatment for textiles, which must necessarily be antibacterial. PU15 is suitable for all conventional lamination processes, but preferably for foam lamination and PU25 can be laminated by means of dry as well as wet laminating. Compared to the currently used antibacterial nanoparticles (for example, silver nanoparticles) and methods, hCQDs-nanocomposites are cheaper, more environmentally friendly, more efficient, do not degrade, and not only can kill bacteria but also do not allow bacteria to develop bacterial resistance.

Supplementary information

Spectroscopic analyzes, such as EPR, Fourier-transform infrared, and Raman spectroscopy, are presented in the supplementary information.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors are grateful for the financial support of Ministry of Education of the Slovak Republic and Slovak Academy of Sciences, Grant VEGA 2/0051/20. Authors Petr Humpolíček and Jan Vajďák acknowledge the project funded by the Czech Science Foundation (19-16861S). The authors thank Petra Bajmóczová for her important help with testing cytotoxicity and cell proliferation. Pavel Kubát thanks ERDF/ESF "Centre of Advanced Applied Sciences" (No. CZ.02.1.01/0.0/0.0/16_019/0000778) for support.

References

[1] C. Ye, J. Ren, Y. Wang, W. Zhang, C. Qian, J. Han, C. Zhang, K. Jin, M.J. Buehler, D.L. Kaplan, S. Ling, Design and Fabrication of Silk Templated Electronic Yarns and Applications in Multifunctional Textiles, Matter. 1 (2019) 1411–1425. https://doi.org/10.1016/j.matt.2019.07.016.

[2] S. Yao, J. Yang, F.R. Poblete, X. Hu, Y. Zhu, Multifunctional Electronic Textiles Using Silver Nanowire Composites, ACS Appl. Mater. Interfaces. 11 (2019) 31028–31037. https://doi.org/10.1021/acsami.9b07520.

[3] L. Liu, W. Chen, H. Zhang, Q. Wang, F. Guan, Z. Yu, Flexible and Multifunctional Silk Textiles with Biomimetic Leaf-Like MXene/Silver Nanowire Nanostructures for Electromagnetic Interference Shielding, Humidity Monitoring, and Self-Derived Hydrophobicity, Adv. Funct. Mater. 1905197 (2019) 1905197.

https://doi.org/10.1002/adfm.201905197.

[4] Q.W. Wang, H. Bin Zhang, J. Liu, S. Zhao, X. Xie, L. Liu, R. Yang, N. Koratkar, Z.Z. Yu, Multifunctional and Water-Resistant MXene-Decorated Polyester Textiles with Outstanding Electromagnetic Interference Shielding and Joule Heating Performances, Adv. Funct. Mater. 29 (2019) 1–10. https://doi.org/10.1002/adfm.201806819.

[5] M. Sala de Medeiros, D. Chanci, C. Moreno, D. Goswami, R. V. Martinez, Waterproof, Breathable, and Antibacterial Self-Powered e-Textiles Based on Omniphobic Triboelectric Nanogenerators, Adv. Funct. Mater. 1904350 (2019) 1904350. https://doi.org/10.1002/adfm.201904350.

[6] S. Shi, Y. Han, J. Hu, Robust waterproof and self-adaptive breathable membrane with heat retention property for intelligent protective cloth, Prog. Org. Coatings. 137 (2019) 105303. https://doi.org/10.1016/j.porgcoat.2019.105303.

[7] H. Hardianto, B. Malengier, G. De Mey, L. Van Langenhove, C. Hertleer, Textile yarn thermocouples for use in fabrics, J. Eng. Fiber. Fabr. 14 (2019). https://doi.org/10.1177/1558925019836092.

[8] H. Hong, J. Hu, X. Yan, UV Curable Conductive Ink for the Fabrication of Textile-Based Conductive Circuits and Wearable UHF RFID Tags, ACS Appl. Mater. Interfaces. 11 (2019) 27318–27326. https://doi.org/10.1021/acsami.9b06432.

[9] G. Chen, H. Haase, B. Mahltig, Chitosan-modified silica sol applications for the treatment of textile fabrics: a view on hydrophilic, antistatic and antimicrobial properties, J. Sol-Gel Sci. Technol. (2019) 461–470. https://doi.org/10.1007/s10971-019-05046-8.

[10] M. Rehan, A. Barhoum, T.A. Khattab, L. Gätjen, R. Wilken, Colored, photocatalytic,

antimicrobial and UV-protected viscose fibers decorated with Ag/Ag2CO3 and Ag/Ag3PO4 nanoparticles, Cellulose. 26 (2019) 5437–5453. https://doi.org/10.1007/s10570-019-02497-8.

[11] M. Shateri Khalil-Abad, M.E. Yazdanshenas, Superhydrophobic antibacterial cotton textiles, J. Colloid Interface Sci. 351 (2010) 293–298. https://doi.org/10.1016/j.jcis.2010.07.049.

[12] T. Yuranova, A.G. Rincon, A. Bozzi, S. Parra, C. Pulgarin, P. Albers, J. Kiwi, Antibacterial textiles prepared by RF-plasma and vacuum-UV mediated deposition of silver, J. Photochem. Photobiol. A Chem. 161 (2003) 27–34. https://doi.org/10.1016/S1010-6030(03)00204-1.

[13] Z. Špitalský, D. Rástočná Illová, O. Žigo, M. Mičušík, Z. Nógellová, M. Procházka, A. Kleinová, M. Kováčová, I. Novák, Assessment of the Antibacterial Behavior of Polyester Fabric Pre-treated with Atmospheric Discharge Plasma, Fibers Polym. 20 (2019) 1649–1657. https://doi.org/10.1007/s12221-019-1127-7.

[14] L. Černáková, D. Kováčik, A. Zahoranová, M. Černák, M. Mazúr, Surface modification of polypropylene non-woven fabrics by atmospheric-pressure plasma activation followed by acrylic acid grafting, Plasma Chem. Plasma Process. 25 (2005) 427–437. https://doi.org/10.1007/s11090-004-3137-4.

[15] J. Kiwi, C. Pulgarin, Innovative self-cleaning and bactericide textiles, Catal. Today. 151 (2010) 2–7. https://doi.org/10.1016/j.cattod.2010.01.032.

[16] R. Chvalinová, J. Wiener, Sorption properties of wool fibres after plasma treatment, Chem. List. 102 (2008) 1473–1477.

[17] C.H. Xue, J. Chen, W. Yin, S.T. Jia, J.Z. Ma, Superhydrophobic conductive textiles

with antibacterial property by coating fibers with silver nanoparticles, Appl. Surf. Sci. 258 (2012) 2468–2472. https://doi.org/10.1016/j.apsusc.2011.10.074.

[18] M. Montazer, S. Seifollahzadeh, Enhanced self-cleaning, antibacterial and UV protection properties of nano TiO 2 treated textile through enzymatic pretreatment, Photochem. Photobiol. 87 (2011) 877–883. https://doi.org/10.1111/j.1751-1097.2011.00917.x.

[19] I. Perelshtein, G. Applerot, N. Perkas, J. Grinblat, A. Gedanken, A one-step process for the antimicrobial finishing of textiles with crystalline TiO 2 nanoparticles, Chem. - A Eur. J. 18 (2012) 4575–4582. https://doi.org/10.1002/chem.201101683.

[20] H. Zhang, G. Chen, potent antibacterial activities of Ag/TiO2 nanocomposite powders synthesized by a one-pot sol-gel method, Environ. Sci. Technol. 43 (2009) 2905–2910. https://doi.org/10.1021/es803450f

[21] H.J. Lee, S.Y. Yeo, S.H. Jeong, Antibacterial effect of nanosized silver colloidal solution on textile fabrics, J. Mater. Sci. 38 (2003) 2199–2204. https://doi.org/10.1023/A:1023736416361.

[22] A. Moqeet Hai, M. Ahmed, A. Afzal, A. Jabbar, S. Faheem, Characterization and antibacterial property of Kapok fibers treated with chitosan/AgCl–TiO 2 colloid, J. Text. Inst. 110 (2019) 100–104. https://doi.org/10.1080/00405000.2018.1466629.

[23] L.Y. Tan, L.T. Sin, S.T. Bee, T.T. Tee, C.T. Ratnam, K.K. Woo, A.R. Rahmat, Funtionalization and mechanical propeties of cotton fabric with zno nanoparticles for antibacterial textile application, Solid State Phenom. 290 SSP (2019) 292–297. https://doi.org/10.4028/www.scientific.net/SSP.290.292.

[24] G. Zhang, D. Wang, J. Yan, Y. Xiao, W. Gu, C. Zang, Study on the photocatalytic and

antibacterial properties of TiO2 nanoparticles-coated cotton fabrics, Materials (Basel). 12 (2019). https://doi.org/10.3390/ma12122010.

[25] M.C. Popescu, C. Ungureanu, E. Buse, F. Nastase, V. Tucureanu, M. Suchea, S. Draga, M.A. Popescu, Antibacterial efficiency of cellulose-based fibers covered with ZnO and Al 2 O 3 by Atomic Layer Deposition, Appl. Surf. Sci. 481 (2019) 1287–1298. https://doi.org/10.1016/j.apsusc.2019.03.268.

[26] S. Silver, L.T. Phung, G. Silver, Silver as biocides in burn and wound dressings and bacterial resistance to silver compounds, J. Ind. Microbiol. Biotechnol. 33 (2006) 627–634. https://doi.org/10.1007/s10295-006-0139-7.

[27] K. Mijnendonckx, N. Leys, J. Mahillon, S. Silver, R. Van Houdt, Antimicrobial silver: Uses, toxicity and potential for resistance, Biometals. 26 (2013) 609–621. https://doi.org/10.1007/s10534-013-9645-z.

[28] A.B. Lansdown, Silver. I: Its antibacterial properties and mechanism of action., J. Wound Care. 11 (2002) 125–130. https://doi.org/10.12968/jowc.2002.11.4.26389.

[29] A.I. Piskaeva, Y.Y. Siderin, A.Y. Prosekov, Comparative Analysis of the Activity of Silver Nanoparticles against Native Microflora from Poultry Processing Plants Wastes, Nano Hybrids Compos. 13 (2017) 176–182. https://doi.org/10.4028/www.scientific.net/nhc.13.176.

[30] M.A. Butkus, L. Edling, M.P. Labare, The efficacy of silver as a bactericidal agent: Advantages, limitations and considerations for future use, J. Water Supply Res. Technol. - AQUA. 52 (2003) 407–416. https://doi.org/10.2166/aqua.2003.0037.

[31] M. Pohanka, Quantum Dots in the Therapy: Current Trends and Perspectives, Mini-Reviews Med. Chem. 17 (2017) 650–656.

https://doi.org/10.2174/1389557517666170120153342.

[32] G.P.C. Drummen, Quantum dots - From synthesis to applications in biomedicine and life sciences, Int. J. Mol. Sci. 11 (2010) 154–163. https://doi.org/10.3390/ijms11010154.

[33] V.I. Klimov, A.A. Mikhailovsky, S. Xu, A. V. Malko, J.A. Hollingsworth, C. a Leatherdale, H.J. Eisler, M.G. Bawendi, Optical Gain and Stimulated Emission in Nanocrystal Quantum Dots, Science (80-.). 290 (2000) 314–317. https://doi.org/10.1126/science.290.5490.314.

[34] M. Tuerhong, Y. XU, X.-B. YIN, Review on Carbon Dots and Their Applications, Chinese J. Anal. Chem. 45 (2017) 139–150. https://doi.org/10.1016/S1872-2040(16)60990-8.

[35] M. Kováčová, Z.M. Marković, P. Humpolíček, M. Mičušík, H. Švajdlenková, A. Kleinová, M. Danko, P. Kubát, J. Vajďák, Z. Capáková, M. Lehocký, L. Münster, B.M. Todorović Marković, Z. Špitalský, Carbon Quantum Dots Modified Polyurethane Nanocomposite as Effective Photocatalytic and Antibacterial Agents, ACS Biomater. Sci. Eng. 4 (2018) 3983–3993. https://doi.org/10.1021/acsbiomaterials.8b00582.

[36] Z.M. Marković, M. Kováčová, P. Humpolíček, M.D. Budimir, J. Vajďák, P. Kubát, M. Mičušík, H. Švajdlenková, M. Danko, Z. Capáková, M. Lehocký, B.M. Todorović Marković, Z. Špitalský, Antibacterial photodynamic activity of carbon quantum dots/polydimethylsiloxane nanocomposites against Staphylococcus aureus, Escherichia coli and Klebsiella pneumoniae, Photodiagnosis Photodyn. Ther. 26 (2019) 342–349. https://doi.org/10.1016/j.pdpdt.2019.04.019.

[37] M. Bodik, P. Siffalovic, P. Nadazdy, M. Benkovicova, Z. Markovic, J. Chlpik, J. Cirak, M. Kotlar, M. Micusik, M. Jergel, E. Majkova, On the formation of hydrophobic

carbon quantum dots Langmuir films and their transfer onto solid substrates, Diam. Relat. Mater. 83 (2018) 170–176. https://doi.org/10.1016/j.diamond.2018.02.011.

[38] H. Tao, K. Yang, Z. Ma, J. Wan, Y. Zhang, Z. Kang, Z. Liu, In vivo NIR fluorescence imaging, biodistribution, and toxicology of photoluminescent carbon dots produced from carbon nanotubes and graphite, Small. 8 (2012) 281–290. https://doi.org/10.1002/smll.201101706.

[39] Z.A. Qiao, Y. Wang, Y. Gao, H. Li, T. Dai, Y. Liu, Q. Huo, Commercially activated carbon as the source for producing multicolor photoluminescent carbon dots by chemical oxidation, Chem. Commun. 46 (2010) 8812–8814. https://doi.org/10.1039/c0cc02724c.

[40] H. Peng, J. Travas-Sejdic, Simple aqueous solution route to luminescent carbogenic dots from carbohydrates, Chem. Mater. 21 (2009) 5563–5565. https://doi.org/10.1021/cm901533y.

[41] J. Briscoe, A. Marinovic, M. Sevilla, S. Dunn, M. Titirici, Biomass-Derived Carbon Quantum Dot Sensitizers for Solid-State Nanostructured Solar Cells, Angew. Chemie - Int. Ed. 54 (2015) 4463–4468. https://doi.org/10.1002/anie.201409290.

[42] Y. Wang, A. Hu, Carbon quantum dots: synthesis, properties and applications, J. Mater. Chem. C. 2 (2014) 6921. https://doi.org/10.1039/c4tc00988f.

[43] N.K. Stanković, M. Bodik, P. Šiffalovič, M. Kotlar, M. Mičušik, Z. Špitalsky, M. Danko, D.D. Milivojević, A. Kleinova, P. Kubat, Z. Capakova, P. Humpoliček, M. Lehocky, B.M. Todorović Marković, Z.M. Marković, Antibacterial and Antibiofouling Properties of Light Triggered Fluorescent Hydrophobic Carbon Quantum Dots Langmuir-Blodgett Thin Films, ACS Sustain. Chem. Eng. 6 (2018) 4154–4163. https://doi.org/10.1021/acssuschemeng.7b04566.

[44] R. Wang, K.-Q. Lu, Z.-R. Tang, Y.-J. Xu, Recent progress in carbon quantum dots: synthesis, properties and applications in photocatalysis, J. Mater. Chem. A. 5 (2017) 3717–3734. https://doi.org/10.1039/C6TA08660H.

[45] M. Kováčová, E. Špitalská, Z. Markovic, Z. Špitálský, Carbon Quantum Dots As Antibacterial Photosensitizers and Their Polymer Nanocomposite Applications, Part. Part. Syst. Charact. 37 (2020) 1–11. https://doi.org/10.1002/ppsc.201900348.

[46] A. Kramer, I. Schwebke, G. Kampf, How long do nosocomial pathogens persist on inanimate surfaces? A systematic review, BMC Infect. Dis. 6 (2006) 1–8. https://doi.org/10.1186/1471-2334-6-130.

[47] S.M. Applications, P.E. Ruhr-universit, Nanomechanical Analysis of High Performance Materials, 2014. https://doi.org/10.1007/978-94-007-6919-9.

[48] S. Jesenská, L. Plíštil, P. Kubát, K. Lang, L. Brožová, Š. Popelka, L. Szatmáry, J. Mosinger, Antibacterial nanofiber materials activated by light, J. Biomed. Mater. Res. - Part A. 99 A (2011) 676–683. https://doi.org/10.1002/jbm.a.33218.

[49] M. Bregnhøj, M. Westberg, F. Jensen, P.R. Ogilby, Solvent-dependent singlet oxygen lifetimes: Temperature effects implicate tunneling and charge-transfer interactions, Phys. Chem. Chem. Phys. 18 (2016) 22946–22961. https://doi.org/10.1039/c6cp01635a.

[50] M. Cadek, J.N. Coleman, V. Barron, K. Hedicke, W.J. Blau, Morphological and mechanical properties of carbon-nanotube-reinforced semicrystalline and amorphous polymer composites, Appl. Phys. Lett. 81 (2002) 5123–5125. https://doi.org/10.1063/1.1533118.

[51] T. Groth, P. Falck, R.R. Miethke, Cytotoxicity of biomaterials - Basic mechanisms and

in vitro test methods: A review, ATLA Altern. to Lab. Anim. 23 (1995) 790–799.

Author Statement

M. Kováčová - Roles/Writing - original draft, Investigation

A. Kleinová - Investigation

P. Humpolíček – Methodology, Project administration, Supervision

J. Vajďák- Investigation

M. Bodík – Investigation,

P. Kubát – Investigation

Z.Markovic - Supervision

Z. Špitalský – Methodology, Project administration, Supervision

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Highlights:

- Light-triggered antibacterial nanoparticles and photodynamic therapy
- Singlet oxygen produced by carbon quantum dots in a polymer matrix
- Prevention in bacterial resistance using smart polymer materials