FUNCTIONALIZATION OF CARBON BIOMATERIALS SURFACES: FUNCTIONAL GROUPS AND NANOPARTICLES

WOJCIECH PAJERSKI[1], PAULINA CHYTROSZ[1], MONIKA GOLDA-CEPA[1], MIROSLAWA PAWLYTA[2], WITOLD RECZYNSKI[3], DOROTA OCHONSKA[4], MONIKA BRZYCHCZY-WLOCH[4], ANDRZEJ KOTARBA[1]*

[1] FACULTY OF CHEMISTRY, JAGIELLONIAN UNIVERSITY, POLAND
[2] MATERIALS RESEARCH LABORATORY, FACULTY OF MECHANICAL ENGINEERING, SILESIAN UNIVERSITY OF TECHNOLOGY, POLAND
[3] FACULTY OF MATERIAL SCIENCE AND CERAMICS, AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, POLAND
[4] DEPARTMENT OF MOLECULAR MEDICAL MICROBIOLOGY, CHAIR OF MICROBIOLOGY, FACULTY OF MEDICINE, JAGIELLONIAN UNIVERSITY MEDICAL COLLEGE, POLAND
*E-MAIL: KOTARBA@CHEMIA.UJ.EDU.PL

[ENGINEERING OF BIOMATERIALS 163 (2021) 40]

Introduction

The application of nanomaterials in biomedicine is one of the most demanding challenges in the newly emerging bionanotechnology field. The main advantage of nanoparticles (NPs) is the possibility to control their physicochemical properties by modifying their bulk and surface composition, size, and morphology, which can be further optimized through various functionalities (e.g., peptides, antibodies, genes, drugs). Because of their biocompatibility and unique properties, such as surface plasmon resonance or superparamagnetism in some cases, NPs attract broad interest for applications in cancer therapy, pharmacology, advanced diagnostics, antiseptics, and treatment of bacterial infections. The last two applications are of particular interest for studies aiming at targeting pathogenic bacteria with alternatives to antibiotics. One of the approaches used in this context involves the use of NPs as biocidal agents. Among nanoparticles exhibiting antibacterial activity, previous studies have mainly focused on various metals and metal oxides, owing to specific features including electronic, magnetic, and optical properties. Although many metals exhibit antimicrobial properties, the NPs investigated in this context are based mainly on silver, copper, zinc, gallium, and gold. Metal oxide nanoparticles such as ZnO, CuO, Fe_3O_4, TiO_2, VO_2, MgO and NiO are also considered as potential antimicrobial agents.

In this study, we investigated the microbiological response of graphenic surfaces functionalized with oxygen surface groups and nanoparticles of Ag and Au. The obtained results provide fundamental insights which may be used for designing and developing smart materials with functional surfaces exhibiting bacteria-attracting and/or bacteria-killing properties.

Materials and Methods

Citrate-capped metallic nanoparticles were synthesized following the protocols described elsewhere [1]. Oxygen plasma was applied to generate –OH and –COOH surface groups on graphenic materials. A sonochemical method was employed for the deposition of the synthesized nanoparticles on model graphenic sheets (10 min, 30 W cm^{-2}). The obtained materials were characterized with the use of SEM, TEM, XPS, SIMS, work function measurements. Microbiological tests with the use of Gram-positive (*S. aureus*, *S. epidermidis*) and Gram-negative (*P. aeruginosa*, *E. coli*) were performed.

Results and Discussion

The main idea of the work is presented schematically in FIG. 1. Upon oxygen plasma treatment the graphenic surfaces were effectively functionalized: increase of hydrophilicity (decrease in water contact angle) and electrodonor properties (increase in work function). These changes in surface properties were strongly reflected in bacteria adhesion. The synthesized nanoparticles were sonochemically deposited over graphenic surfaces and their effects on bacteria adhesion were also evaluated. The nanoparticle sizes evaluated by TEM were 26 and 24 nm for AgNPs and AuNPs, respectively. It was found that surface functionalizations with AuNPs and AgNPs have opposite effects on bacterial attachment for all the investigated bacterial strains.

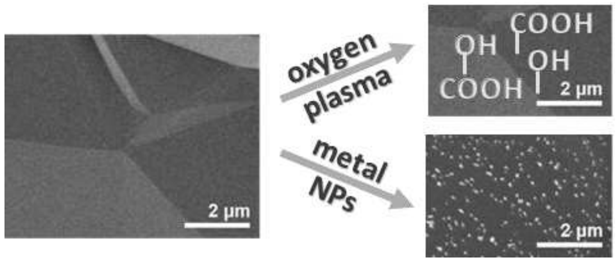

FIG. 1. SEM micrographs of graphenic sheet before (large image), after oxygen plasma treatment (upper insert) and decoration with gold nanoparticles (lower insert).

Gold NPs were found to be more effective in promoting bacterial adhesion (reaching a ~100% increase for Gram-positive bacteria after 1 h of incubation) than silver NPs (with a ~25% decrease). It was revealed that graphenic surfaces with co-deposited Ag and Au nanoparticles exhibited the combined effect of the double functionalization, i.e. increased bacterial adhesion (stimulated by AuNPs) and enhanced bactericidal effect (provided by AgNPs). SEM observations of bacteria morphology revealed the presence of many outer membrane vesicles. These structures are produced by microorganisms as a result of metabolic processes and participate in extracellular transport, bacterial biofilm formation, intercellular signaling; they are formed under the influence of stress factors such as AgNPs, Ag^+ ions, and reactive oxygen species. The latter was proposed as responsible for the observed antibacterial properties of the functionalized graphenic surfaces

Conclusions

The experimental correlations established in this study provide a background for the knowledge-based functionalization of graphenic materials via generation of oxygen functional groups and deposition of metal NPs. The observed effects were discussed in terms of surface–microorganisms interactions (attraction/repulsion and bacteriostatic/bactericidal effects) which can be dramatically change upon both kinds of modifications.

Acknowledgments

This study was funded by Polish National Science Centre project, award number 2020/37/B/ST5/03451

References

[1] W. Pajerski, et al. J. Nanoparticle Res 21 (2019) 186
[2] W. Pajerski, et al. Surfaces and Interfaces; *under review*