MULTIFUNCTIONALIZATION OF INERT CERAMICS THROUGH GRAPHENE-DERIVATES IMMOBILIZATION

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Introduction

Bioinert ceramics, such as zirconia, provides the mechanical strength required in implants, but its limited bioactivity renders it incapable of osseointegration [1]. Thus, its biomedical application is limited [2]. Graphene and its derivatives exhibit excellent bioactivity and can enhance osseointegration, hemocompatibility and antibacterial properties [3]. Moreover, enzymes and proteins have been immobilized to graphene-derivates applying the reaction between the amine groups of proteins/enzymes and the carboxylic groups of GO/rGO to support biological properties or add another functions to graphene-derivates. Through immobilization of graphene-derivates to the ceramic inert surface, properties of rGO and ceramics could be merged to create a versatile biomaterial.
In the present study we introduce an innovative technique for functionalizing bioinert ceramic by immobilizing various graphene derivatives onto the surface by tailored self-assembled monolayer technique (SAM).

Materials and Methods

Several well-established and characterized graphene-derivatives exhibiting different morphologies, shapes and physico-chemical properties provided from Institute of Electronic Materials Technology, Warsaw (Prof. Lipińska), were selected to immobilize them on the ceramic surfaces (FIG. 1). Each graphene-derivative before coupling was biologically evaluated by using live/dead staining to ensure its cytocompatible character.

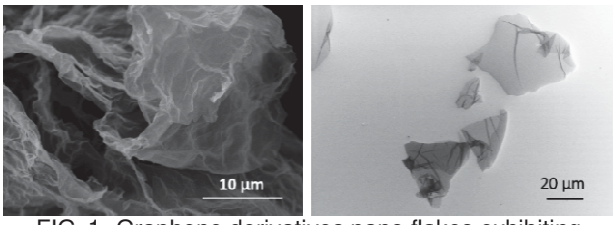

FIG. 1. Graphene derivatives nano flakes exhibiting different morphology, shape and properties as received.

For immobilization process zirconia surfaces were at first activated by using aminopropyl diisopropyl ethoxysilane (APDS). For the APDS-activated surfaces exhibiting –NH_2 active groups, additional catalysts, EDC and NHS were applied to reinforce the reaction between -NH_2-functionalities and activated –COOH-groups of graphene-derivatives. Two different techniques, drop casting and immobilization from graphene solution by immersing of the samples in the shaking system to avoid sedimentation, were performed. At the end, the samples were evaluated regarding to their morphology, graphene-derivatives coupling behaviour and the stability of the obtained graphene-layers by using SEM analysis. Additionally AFM measurements evaluated the morphological profile of the coated samples and determined the thickness of GO-coatings.

Results and Discussion

The cell culture tests approved the cytocompatible behaviour of all selected graphene nano-flakes before immobilization, since more than 95% of cells were viable after incubation time. It was shown, that owing to the catalysts a higher amount of graphene-derivatives could be found on the ceramic surface. The stability of the coatings was established via ultra-sonication treatments. All graphene-derivates could be immobilize to the activated ceramic surface. The most promising results were obtained by using graphene oxide obtained from exfoliation of Asbury 1 (GO A1). By using drop casting method a multilayer of GO A1 was attached to the surface, while during spontaneous immobilization from the graphene-solution a well distributed, surface-coverage self-assembled graphene oxide monolayer could be obtained (FIG. 2). AFM evaluation have confirmed that the ceramic surface was well covered with a thin layer of well distributed graphene nano-flakes. The thickness of obtained coating varied from 3-12 nm.

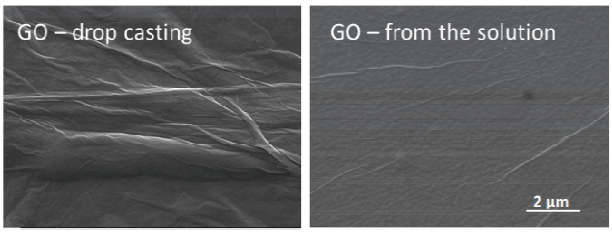

FIG. 2. Coating of graphene oxide on the silanized zirconia substrates by using drop casting method (left) and spontaneous immobilization from the graphene solution, which resulted in well distributed, surface-coverage graphene oxide monolayer (right).

Conclusions

In our study, the immobilization of graphene derivatives by using different methods was successfully performed. We could obtain well coved thin GO layer on ceramic surface.
Through this technique, the properties of graphene-derivatives and zirconia could be merged to create a versatile biomaterial. Moreover, through highly reactive graphene oxide additionally biological agents such as proteins, enzyms, antibacterial agent or drugs could be immobilized on the graphene-derivatives-modified substrates to reinforce its biological activity or enhance other functionalities according to application requirements.

Acknowledgments

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