MODIFICATION OF CARBON MATERIALS SURFACES BY PLASMA: EFFECT OF THE INTRODUCED FUNCTIONAL GROUPS ON BIOCOMPATIBILITY AND ADHESION OF MICROORGANISMS

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Introduction

Carbon is one of the most common and fascinating elements on the Earth, present mainly in the form of biomolecules and organic compounds as well as elemental carbon materials. Carbon exhibit the unique ability to form strong covalent bonds between atoms, which is related with various hybridization states: sp, sp^2, sp^3. Additionally, carbon structures are relatively easy to functionalize with surface and bulk heteroatoms. As a consequence, a wide range of carbon-based nanomaterials can be formed offering a broad range of structures' including 0 - 3D dimensionalities.

Carbon materials are chemically inert, they are stable in strongly acidic and basic solutions. Nowadays, a majority of the academic and industrial research efforts is focused on the tuning of these unique properties for numerous applications. Indeed, in recent years carbon materials have attracted much attention in the field of biotechnology, medicine, and biomedical engineering. The research includes antibacterial and antiviral surfaces, tissue engineering, drug delivery, biosensing, cancer targeting, photothermal therapy, and electrical stimulation of cells to mention a few.

Although the investigations are carried out intensively and extensively, there is still a knowledge gap in the understanding of the interactions at the interface of these materials and surrounding biological moieties. Owing to the broad spectrum of possible structures and mechanical properties carbon lends great versatility in designing of implant materials. Nevertheless, each newly developed carbon material requires a specific assessment and optimization of the key functions required for medical devices: stability, biocompatibility, anti-infection and therapeutic.

The aim of the study was the controlled introduction of biologically-relevant surface species with a precisely adjusted concentration into the carbon materials surfaces: CNTs, graphenic sheets, carbon spheres. In the next step, we explored the correlation between the surface chemistry and biological response.

Materials and Methods

To modify the carbon-based materials, plasma treatment was carried out (Diener electronic Femto plasma system). The samples were characterized with the use of spectroscopic (RS, IR, XPS, SIMS-TOF, LDI-TOF-MS), microscopic (SEM, TEM) and microbiological (live/dead, adhesion rate) methods. The work function values (Φ) of the carbon materials, the contact potential difference (V_{CPD}) measurements were performed with KP6500 probe. The experimental results were supported by molecular modelling (DFT), according to our published computational models [1]. Four oxygen functional groups, corresponding to different ways of surface modification, were considered, namely, −OH, −CHO, −COOH, and =O.

Results and Discussion

The plasma parameters (power, pressure, time) have been optimized and the treatment was confined to the surface region changing its key parameters such as electronic properties (work function increase from 4.4 eV to 6.1 eV) and wettability (water contact angle decreased from 94° to 7°) while preserving the bulk structure. For quantification of the number of introduced functional groups, a combined experimental and theoretical approach was applied. The Helmholtz relation between measured work function values and calculated dipole moment of surface oxygen groups was successfully used. The examples of calculations results showing the formed surface dipoles with the imposed electrical isosurface are presented in FIG. 1.

Besides, a straightforward correlation between Gram-positive bacteria adhesion (*Staphylococcus aureus*) to the carbon-based surfaces, and their electrodonor properties (work function) was discovered. A similar effect was observed for Gram-negative bacteria strain (*Pseudomonas aerugionosa*). The bacteria coverage systematically increased (by a factor of three) with the plasma treatment from 3.2% (untreated) to 9.2% (oxygen plasma modified) [2]. Thus, it may be concluded that the colonization of graphenic surfaces strongly depends on the specific characteristics of the surface (oxygen concentration, wettability, electronic properties).

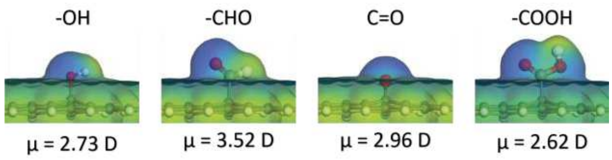

FIG. 1. The oxygen-containing groups on the graphenic sheets together with the electrostatic potential mapped on the electron density isosurface and calculated dipole moments (DFT, Dmol3, hybrid B3LYP).

Conclusions

The concentration of surface functional groups is a key factor in biocompatibility and bacterial adhesion to carbon-based materials surfaces. The plasma treatment can be successfully used as the modification method of these materials, however, the operating parameters have to be adjusted individually for each type of material. A straightforward correlation between bacteria adhesion to the carbon-based surfaces and their electrodonor properties was discovered. The obtained results provide the practical guidelines for the design and development of carbon-based nanomaterials.

References

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