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Vibrational spectroscopic analysis of a metal/carbon nanotube coating interface and the effect of its interaction with albumin☆

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) as a modifying phase on the titanium support can be potentially used for medical purposes as a material for the production of implants or implantable electrodes or for applications for cardiac surgery. Developing better blood compatible biomaterials must be connected with the condition of their anti-thrombogenic characteristic. A carbon nanotube layer was formed on a titanium plate coated in half with MWCNTs to have admission to: MWCNTs coating, to the Ti/MWCNTs interface region at the MWCNTs coating edge and finally to the Ti support. The Raman measurements were performed in two different locations: in the interface/edge region of the titanium and MWCNTs coating and in the center of the MWCNTs layer. For each of these positions, measurements in two different depths were performed: on the sample top surface of the MWCNT layer and near the bottom of the MWCNTs layer, i.e. at the titanium support interface. The studied sample regions differ in G-, D- and D′-mode structural characteristics as dispersion, crystallinity, the size of the arranged domains, and the distance between the point defects. The phase boundary region is more disordered and exposed to a greater surface tension. These features influence the interactions with albumin which represented the material behavior in contact with the tissue. The MWCNTs coating is hydrophilic (contact angle ~55°), in the border area this value increases to ~60°, then Ti support is hydrophobic (~98°). Two dimensional correlation analysis allows us to unravel albumin-MWCNTs' interaction. The cross-peaks show a contribution from G^+ and G^- carbon nanotubes bands and protein secondary structure demonstrating the formation of a film on the surface of the test sample and indicate the change of the albumin conformation during adhesion.

1. Introduction

Carbon nanomaterials are relatively new materials with many potential applications [1]. Carbon nanotubes are examples of carbon nanomaterials [2]. Their exceptional properties such as low density, high specific surface area, conductivity, thermal and mechanical stability makes them useful as composite materials, sensors, drug delivery, field emission devices or nanoscale electronic [3–5].

Nanoparticles in medical applications can provide various modifications in material chemical and physical properties which as a result influences biological features, so they can be successfully used as a modifier of polymeric materials or deposited on the surface of the metal to construct new, attractive materials [6–10]. Multi-walled carbon nanotubes (MWCNTs) as a modifying phase on the titanium support can be potentially used for medical purposes as material for the production of implants or implantable electrodes [4]. Interaction of such newly constructed materials with a living organism is a key issue in biocompatibility and cytotoxicity research [11]. The host response to biomaterials is largely determined by the surface or interfacial properties of the implanted material [12].

Various materials and their functionalization are taken into account in applications for cardiac surgery. Materials for cardiac

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surgery, e.g. valve, stents and other devices, intended to come into contact with blood (blood-contacting medical devices) require anti-thrombogenic characteristics. Developing better blood compatible biomaterials is of great significance in both the material and medical sciences. Thus protein adhesion is a factor in determining the functionality of these materials. It is believed that the adsorption of only certain types of proteins, especially those which are considered as inhibitors of the blood clotting process, e.g. albumin, are anti-thrombogenic materials [13]. Numerous studies in biomaterial development have indicated a role for surface nano-topography in affecting the cellular adhesion response.

This work focuses on carbon nanotube layer formed on a titanium (Ti) plate (support) coated in half with a MWCNTs layer to have access to investigate: MWCNTs coating, Ti support and also Ti/MWCNTs interface region (Fig. 1A). To model the implant surface modification by cell adherence the adsorption of albumin, protein not involved in coagulation or platelet adhesion, was studied. The albumin solution was set in a form of a line passing through a layer of MWCNTs, boundary layer and turned to titanium plate(Fig. 1B). The objective of this experiment was to recognize the fundamental concern and argument for their applications [14]. Raman microspectroscopy has been employed as the best and primary method to study carbon materials. Scanning electron microscope (SEM) and atomic force microscope (AFM) and also conventional contact angle tests completed the study.

2. Experimental

2.1. Preparation of the sample

A square Ti plate of 10 × 10 mm size was covered in one half with MWCNTs using the electrophoretic deposition (EPD) method (Fig. 1A). The MWCNTs (outside diameter 10–30 nm; inner diameter 5–10 nm, length of 1–2 μm and more than 95% purity) were obtained from Nanostructured & Amorphous Materials, Inc., USA. Before the EPD process, nanotubes were oxidized in a mixture of concentrated acids (H_2SO_4 and HNO_3). The presence of carboxylic groups on the surface of the MWCNTs after oxidation provides a negative charge on the surface and makes the electrophoretic deposition possible. A carbon nanotube deposition was performed for 30 s, using applied voltage of 30 V and titanium plate as a positively charged electrode.

To test the impact subjected to material in a living organism the interaction with albumin was modeled. The plate was covered with albumin from chicken egg white to simulate interactions in the matrix of the human body. The 1% solution of albumin was

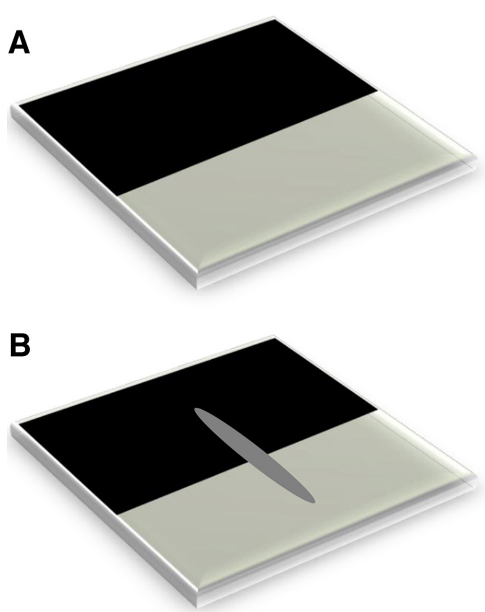

Fig. 1. Scheme of studied sample, titanium support: (A) covered in half with MWCNTs (black); (B) treated with an egg albumin solution (gray).

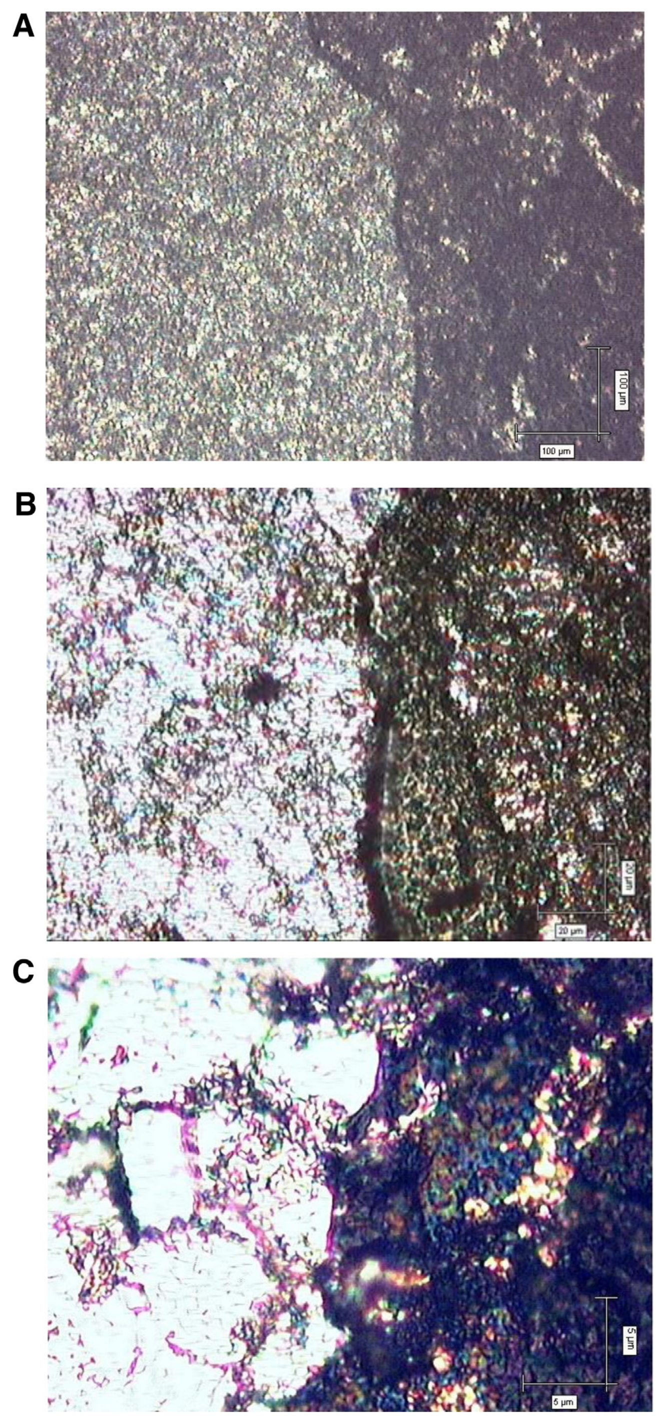

Fig. 2. Photomicrophotographs of studied sample showing the interface area, objective magnification: (A) 5×; (B) 20×; (C) 100×.