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Structural and biological properties of carbon nanotube composite films

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Abstract

Carbon nanotube composite films have been developed that exhibit unusual structural and biological properties. These novel materials have been created by pulsed laser ablation of graphite and bombardment of nitrogen ions at temperatures between 600 and 700 °C. High-resolution transmission electron microscopy and radial distribution function analysis demonstrate that this material consists of sp^2-bonded concentric ribbons that are wrapped approximately 15° normal to the silicon substrate. The interlayer order in this material extends to approximately 15–30 Å. X-ray photoelectron spectroscopy and Raman spectroscopy data suggest that this material is predominantly trigonally coordinated. The carbon nanotube composite structure results from the use of energetic ions, which allow for non-equilibrium growth of graphitic planes. In vitro testing has revealed significant antimicrobial activity of carbon nanotube composite films against *Staphylococcus aureus* and *Staphylococcus warneri* colonization. Carbon nanotube composite films may be useful for inhibiting microorganism attachment and biofilm formation in hemodialysis catheters and other medical devices.

Keywords: Pulsed laser deposition; Kaufman ion source; Antimicrobial materials

1. Introduction

A major concern in the treatment of hospitalized or chronically ill individuals is medical device infection. Infection of hemodialysis catheters is especially troublesome because these infections may quickly progress from the device site to involve other organs (e.g. endocarditis) or the entire body (e.g. septicemia). Colonization of polytetrafluoroethylene ultrafiltration materials may occur if dialysis membranes are exposed to persistent microbial contamination. There is considerable risk of bacteria and endotoxin discharge from bacteria, algae and/or fungi biofilms, which serve as reservoirs for continuous contamination. A recent study of tubing drawn from dialysis machine fluid pathways has demonstrated that these materials are often covered with biofilms that contain high concentrations of bacteria (1.10^3–1.10^6 cm^2), algae and endotoxins (1–12 endotoxin units cm^{-2}) [1]. In addition, dialysis catheter infection can cause other systemic diseases, including inflammation of the blood vessel endothelium and atherogenesis (blood vessel closure). For example, vascular access infections have been correlated with both an increase in the serum concentration of atherogenic proteins and an increase in mortality from cardiovascular disease [2].

Antimicrobial treatments for hemodialysis catheter biomaterials can greatly improve human health by reducing device infection and secondary disease [3]. Traditional strategies for disinfecting the fluid-containing vessels of hemodialysis machines involve the use of microbicidal solutions. Typical treatments include 500–750 ppm sodium hypochlorite solution for 30–40 min and 1.5–2.0% formaldehyde solution overnight. These treatments provide 10^5-fold reductions in microbial counts; however, they do not always result in complete microbial elimination [4]. Some work has been done on treating planktonic cells and aged biofilm cells of *Pseudomonas aeruginosa* and *Staphylococcus aureus*

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with ciprofloxacin-loaded poly (L-lactic acid) (PLA) microspheres. There are several limitations to biocidal pharmacologic coatings. Most importantly, current devices are only able to release pharmacologic agents and provide antimicrobial activity in short bursts (hours to days). In addition, ciprofloxacin is not universally effective against all microorganisms; for example, it does not eliminate anaerobic bacteria, ciprofloxacin-resistant bacteria, fungi, algae or viruses. Finally, antimicrobial agents may cause local or systemic side effects; for example, ciprofloxacin is prohibited for pediatric use because it has been shown to cause cartilage erosion [5].

Nanotubes may provide a more effective biocidal surface for use in hemodialysis catheters and other medical devices. The antimicrobial activity of nanotubes has been attributed to physical interaction between nanotubes and bacterial cell walls [6]. It is believed that nanotubes may act as "nanosyringes", and cause highly localized disruption of bacterial cell walls [7]. Nanotubes can penetrate the lipid bilayer of microbial cells, and allow release of intracellular contents through the artificial pore. However, individual nanotubes cannot be used in the body because needle-like particles may induce foreign body neoplasia. In vivo experiments have shown that particles with high length-to-diameter ratios (>100) can cause reactions analogous to that of asbestos-related mesothelioma. [8]. Carbon nanotubes must be firmly anchored to surfaces in order to overcome these concerns. Methods for preparing aligned single-walled and multi-walled carbon nanotubes include plasma enhanced chemical vapor deposition [9,10], thermal chemical vapor deposition on porous substrates [11], pyrolysis of hydrocarbon–ferrocene mixtures [12,13] and pyrolysis of organometallic precursors [14,15]. Perhaps, the most well known mechanism for aligning single-walled carbon nanotubes on surfaces involves the use of silica-containing iron, anodized alumina and other nanoporous templates [16–20]. This technique provides highly aligned arrays of amorphous single-walled carbon nanotubes with uniform lengths and uniform diameters. Unfortunately, conventional nanotube array fabrication processes are not suitable for fabricating medical devices for several reasons, including poor adhesion between the aligned nanotubes and the substrate, bundling of the exposed nanotubes after template etching and non-uniform template etching [21–26].

We have developed novel carbon nanotube composite films that possess unusual antimicrobial properties. These novel materials are formed by pulsed laser ablation of carbon and bombardment of nitrogen ions from a Kaufman ion source. We have synthesized these novel structures at substrate temperatures greater than 600 °C in order to avoid growth of CN_x and other impurity phases. The carbon nanotube composite films were examined using high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and antimicrobial testing. These novel surfaces may be useful for inhibiting microorganism attachment and biofilm formation in next generation medical devices.

2. Experimental details

1 cm × 1 cm pieces of silicon (1 0 0) were cleaned in acetone and methanol using an ultrasonic cleaner. The silicon substrates were subsequently dipped in 20% hydrofluoric acid to remove silicon oxide and produce a hydrogen-terminated surface. Depositions were performed in a stainless steel high vacuum chamber at background pressures of $\sim 5 \times 10^{-7}$ Torr. A Lambda-Physik LPX 210 excimer laser ($\lambda = 248$ nm, $t_s = 25$ ns) was used to ablate a high purity graphite target (Fig. 1). The laser was operated at an energy density of ∼2–3 J cm^{-2}, which provided an average power density of $\sim 10^8$ W cm^{-2}. Ultra high purity nitrogen was used as an input to the Kaufman ion source, which was placed at an angle of 45° to the substrate. The N_2^+ species generated in these experiments possessed beam energies of 500 eV. Two beam currents (10 and 20 mÅ) were used in a defocused

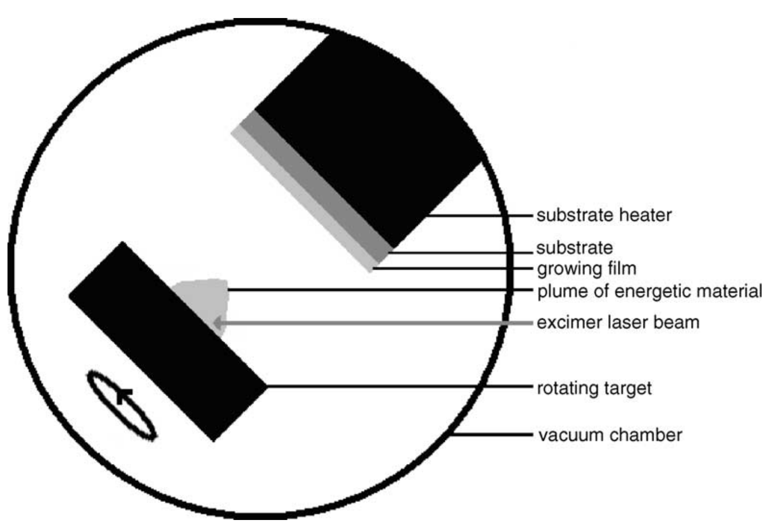

Fig. 1. Pulsed laser deposition (PLD) system.