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Surface characterization and antibacterial response of silver nanowire arrays supported on laser-treated polyethylene naphthalate

M. Polívková [a,*], V. Štrublová [a], T. Hubáček [b], S. Rimpelová [c], V. Švorčík [a], J. Siegel [a]

[a] Department of Solid State Engineering, University of Chemistry and Technology Prague, 166 28 Prague, Czech Republic
[b] Institute of Hydrobiology, Biology Centre of the AS CR, 370 05 Ceske Budejovice, Czech Republic
[c] Department of Biochemistry and Microbiology, University of Chemistry and Technology Prague, 166 28 Prague, Czech Republic

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ABSTRACT

Polymeric biomaterials with antibacterial effects are requisite materials in the fight against hospital-acquired infections. An effective way for constructing a second generation of antibacterials is to exploit the synergic effect of (i) patterning of polymeric materials by a laser, and (ii) deposition of noble metals in their nanostructured forms. With this approach, we prepared highly-ordered periodic structures (ripples) on polyethylene naphthalate (PEN). Subsequent deposition of Ag under the glancing angle of 70° resulted in the formation of self-organized, fully separated Ag nanowire (Ag NW) arrays homogenously distributed on PEN surface. Surface properties of these samples were characterized by AFM and XPS. Vacuum evaporation of Ag at the glancing angle geometry of 70° caused that Ag NWs were formed predominantly from one side of the ripples, near to the top of the ridges. The release of Ag^+ ions into physiological solution was studied by ICP-MS. The results of antibacterial tests predetermine these novel structures as promising materials able to fight against a broad spectrum of microorganisms, however, their observed cytotoxicity warns about their applications in the contact with living tissues.

1. Introduction

Nowadays, polymeric materials are the most diverse kinds of biomaterials, which have a wide spectrum of use in the medicine, including e.g. an implementation of intravenous catheters and endotracheal tubes or implantation of bone cements [1–3]. However, using of polymeric materials during medical interventions can lead to emergence and spread of bacterial infections, which may seriously endanger the patients' lives. For this reason, the integral part of a routine postoperative treatment is comprised of antibiotics, which minimize the risk of infection. However, several bacterial strains have developed a resistance to commonly used antibiotics. Therefore, for a passive protection of patients, new improved materials with bactericidal properties are intensely searched for [4–6].

Currently, there are many techniques improving polymer processing to achieve more preferable properties of polymers in biological media, such as excellent antibacterial properties [1,7]. Hereby, nanotechnology is the most promising area for the development of such materials, applicable in medicine. Several types of nanomaterials have already been used in this way. Nevertheless, in the light of the last decade's research, the most suitable candidate in this field with excellent bactericidal properties is silver incorporated in biocompatible polymers in its various nanostructured forms. However, in recent days, cytotoxic studies warning about toxicity of silver nanostructures began to appear [3]. Some of these studies indicate that the most cytotoxic type of nanostructured silver materials are silver nanowires [8–10]. In case that it is so, it follows that these structures are potentially applicable only in vitro, e.g. integration into traumatic wound dressings and diabetic ulcers, treatment of dental and chirurgical instruments, etc. [11], and cannot be in a contact with living tissues in vivo (tissue engineering - cultivation of cells). Nowadays, Ag NWs are commonly used in vitro. One of these applications is thermotherapy. This is a kind of physiotherapy for effective treatment of joint injuries that occur most often due to obesity, aging and a frequent loading. In the study of Choi et al. [12], a soft, thin and downloadable heater composed of highly conductive Ag NWs/elastomer nanocomposite was effectively developed. Other in vitro applications of Ag NWs are wearable sensors for robotics. Yao et al. [13] developed highly sensitive and skin-mountable sensors based on highly conductive and stretchable silver nanowire arrays. Last but not least, all of these in vitro applicable materials, composed of a biocompatible polymer and silver nanostructures, should exhibit appropriate physicochemical properties [4–6].

The changes in physicochemical properties of polymeric materials in favor to the desired application can be achieved by a modification of their structure. A polymer can be connected to or copolymerized with another polymer or other material. The surface properties play also the key role in the deciding process of the future application of a

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* Corresponding author.
E-mail address: polivkoa@vscht.cz (M. Polívková).

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newly developed composite. Medicinal technology puts the emphasis especially on increased biocompatibility and improved antibacterial effects. To create the desired surface properties of biomaterials, various types of surface modifications can be used, i.e. mechanical, chemical, plasma, radiation and/or laser modification [14,15].

Patterning of materials by a laser enables the formation of defined structures on surfaces of polymers, metals, semiconductors, ceramics, inorganic materials, and glass. A necessary precondition is considerable absorption of these materials at the laser wavelength, but ablation at higher energies is also possible for less absorbing glass. To achieve highly defined structures, in case of very low absorption, admixtures might be used [16]. One of the many types of such prepared periodic structures - ripples are highly periodic structures formed on the surfaces of solids due to the laser modification. Their orientation depends on polarization, and their periodicity is closely related to the wavelength of the used radiation. The interference between the incident and reflected radiation plays an important role in the pattern formation of on a material surface. For this reason, the ripples of various properties, sizes and shapes can be prepared [17].

Under specific conditions the combination of polymer laser pretreatment and metal vacuum evaporation may result in the formation of metal nanowires, which was successfully used in this study. Self-organized, fully separated Ag nanowire (Ag NW) arrays were prepared on polyethylene naphthalate (PEN) and fully characterized. PEN is a frequently used material in health care industry for the preparation of very strong and thin catheters and other medical devices. This study aims to prepare PEN-based medical material of the next generation benefiting from synergetic effect of excellent PEN properties (biocompatibility, patterning capability) and Ag (antibacterial potency) by combining them into one compact material. Such material should exhibit strong antibacterial efficiency enabling prevention of hospital-acquired infections. However, it is also important to ensure their safer applications in healthcare industry. For this reason, not only antibacterial effects, but also cytotoxicity of prepared Ag NWs/PEN samples were tested. Samples were tested against *Escherichia coli* and *Staphylococcus epidermidis*, which commonly cause these types of infections. Mouse embryonic fibroblasts (L929) were chosen for cytotoxicity testing of metal-coated polymeric materials, as a routinely used cell line for this purpose.

2. Experimental

2.1. Materials, apparatus and procedures

Polyethylene naphthalate (PEN, supplied by Goodfellow Ltd., UK) in the form of 50 μm thick foil was used as a substrate. The samples with the area of 2 × 2 cm^2 were treated by KrF excimer laser (COMPexPro 50F, Coherent, Inc., wavelength 248 nm, pulse duration 20–40 ns, repetition rate 10 Hz). Periodic nanostructures (ripples) were produced under the following conditions: linearly polarized laser light with UV-grade fused silica prism (model PBSO – 248-100), an aperture with the area of 5 × 10 mm^2. The samples were irradiated by 6000 laser pulses (the laser fluence of 10 $mJ \cdot cm^{-2}$). Automated systems of step micrometer motors attached to sample holder were used to irradiate all sample area of 2 × 2 cm^2 stepwise.

Patterned PEN was used as a template for the deposition of silver (Ag pellets of 3.18 × 3.18 mm^2, purity 99.99%, Safina, a.s., Czech Republic). Silver nanowire arrays (20 nm thick) were prepared by vacuum evaporation on LEYBOLD-Heraeus, Univex 450 device at room temperature, the pressure of $3 \cdot 10^{-4}$ Pa, the deposition rate of 0.33 $nm \cdot s^{-1}$ by means of resistively heated tungsten crucible, at the glancing angle of $\varphi = 70°$, with respect to the substrate surface normal as shown in Fig. 1. Quartz crystal microbalance was used for in situ monitoring of Ag thickness (20 nm corresponded to $\Delta f = 640$ Hz) and verified by the measurement of Ag effective thickness by AFM scratch method (AFM VEECO CP II device) on a glass substrate, deposited simultaneously with PEN samples. The scratch was made in five different positions and scanned in a contact mode. Thickness variations did not exceed 5%.

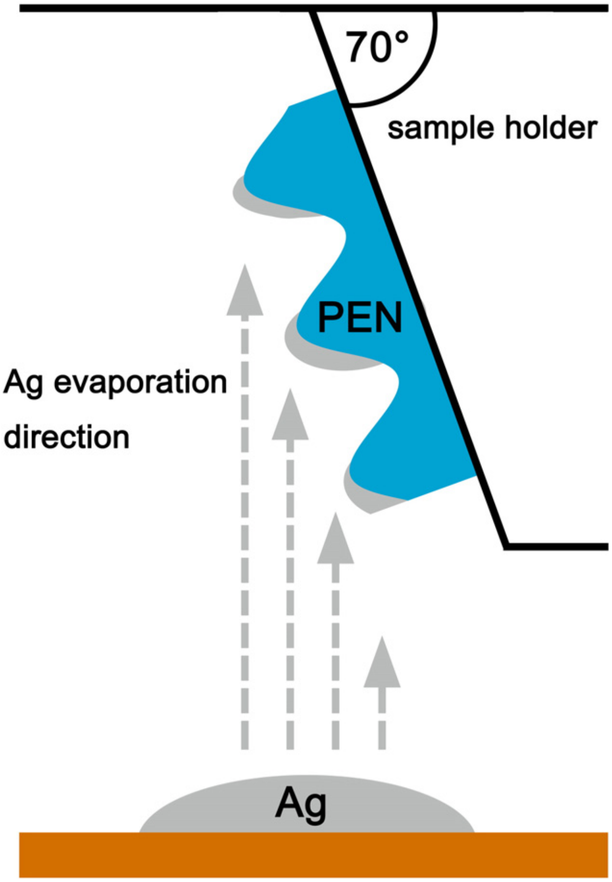

Fig. 1. Scheme of the experimental set-up during vacuum evaporation of Ag under the glancing angle (φ) of 70°.

2.2. Analytical methods

The atomic concentrations of silver Ag(3d), carbon C(1s) and oxygen O(1s) in pristine PEN, patterned PEN (ripples) and Ag NW s/PEN samples were measured by X-ray photoelectron spectroscopy (XPS) by Omicron Nanotechnology ESCAProbeP spectrometer. The X-ray source, which was monochromated at 1486.7 eV with the step size of 0.05 eV, was used. The samples were studied under the electron take-off angles of 0 and 81°. In the case of electron take-off angle of 81°, the samples were observed from the right and left side (see Fig. 2). The spectra evaluation was carried out by CasaXPS software.

Focused Ion Beam Scanning Electron Microscope (FIB-SEM, LYRA3 GMU, Tescan, Czech Republic) was used to visual representation of Ag nanowire arrays. FIB cuts were made by a Gallium ion beam. The polishing procedure was performed to clean and flatten the analyzed surface. The image was taken under an angle of 54.81° and the voltage of 5 kV.

Surface morphology of pristine PEN, patterned PEN (ripples) and Ag NWs/PEN samples was examined using AFM. The 3D-AFM images were taken by AFM VEECO CP II. For these measurements, tapping mode was chosen to minimize potential damage of the samples. A Veeco oxide-sharpened P-doped silicon probe RTESPA-CP attached to a flexible micro-cantilever was used near its resonant frequency of 300 kHz. The scans were acquired at the line scanning rate of 0.5 Hz. Four areas of each sample were scanned in order to obtain representative data. Surface roughness (R_a) of all samples, periodicity (Λ) and height (h) of ripples/wires were evaluated. Surface roughness, characterized by the