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APPROACHES FOR SUBSTRATE SURFACE FUNCTIONALIZATION WITH AgNPs

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I. INTRODUCTION

Metals have a long history in the treatments of dentistry and orthopedics. Pure titanium is commonly used as artificial joints and implants in both dental and orthopedic clinics because of its biocompatibility and mechanical properties. A major factor that determines the success of dental implantation is osseointegration, which is the stable anchorage of an implant in living bone achieved by direct bone-to-implant contacts [1, 2]. It is commonly known that the implantation of a foreign object into the human body may be rejected. Moreover, a wide range of local tissue reactions, in particular inflammation, giant cell formation and fibrosis can be induced [3]. Consequently, the task of biomedical materials science is the formation of biocompatible and antibacterial implant surfaces for medical use. Besides necessary to formation the structural and functional connection between organised vital bone and the surface of a titanium implant, capable of bearing the functional load [4]. Furthermore, biomaterials should support cell attachment, migration, proliferation, interact actively with cells and tissues and stimulate regeneration [5], which allows to avoid rejection and speed up the treatment and recovery process [6, 7]. Films composed of noble metal nanoparticles (typically, Au or Ag) currently have attained wide popularity and aroused intense research interest in nanotechnology. The most recently available methods for the fabrication of antibacterial films include electron beam lithography and nanoimprint lithography, both can completely control the micromorphology of the nanostructures for the design with unique localized surface plasmon resonance spectrum [8, 9]. However, these methods require sophisticated fabrication equipment and are limited by either expensive cost or small sample size in practical applications. Instead, some simpler bottom-up approaches based on self-assembly, e.g., Langmuir-Blodgett, dip coating, and electrochemical deposition, have shown great conveniency in large-scale fabrication and much less defectivity [10, 11]. Such techniques can surely produce noble metal nanoparticle thin films with large areas.

The paper considered a series of rapid and simple methods of silver coatings fabrication such as dip coating, sessile drop and room temperature electrophoretic deposition (EPD).

II. EXPERIMENT DESCRIPTION

According the results of [12-14] the negatively charged AgNPs were synthesized by wet chemical reduction method of silver nitrate (Fluker, p.a.) using glucose (D-(+)-glucose, Baker) as a reductant and polyvinylpyrrolidone (PVP K30 Povidon 30; Fluka, molecular weight 40000 g mol^{-1}) as a stabilizer. Initially 2 g glucose and 1 g PVP were dissolved in 40 g water and heated to 90 °C. Then 0.5 g $AgNO_3$ dissolved in 1 mL water was quickly added. The dispersion was kept at 90 °C for 1 h, PVP-stabilized AgNPs and then

left to cool to room temperature. The particles were collected by ultracentrifugation (3 times, 30 000 rpm, 30 min), redispersed in pure water and collected again by ultracentrifugation. Thereby NO3-, excess glucose and its oxidation products, excess PVP, and excess Ag+ were all removed. The silver nanoparticles were further redispersed in water. The final silver concentration in all dispersions was determined by atomic adsorption spectroscopy (AAS).

The hydrodynamic diameter (HDD) of the AgNPs were measured by Dynamic Light Scattering (DLS) using a Malvern Zetasizer Nano ZS and Nanoparticle Tracking Analysis (NTA) using a NanoSight LN 10. Zeta (ζ) potential of the AgNPs were measured by DLS. By scanning electron microscopy (SEM) the morphology and size of the AgNPs were estimated using an ESEM Quanta 400 FEG instrument operating in a high vacuum with gold/palladium-sputtered samples. The grazing incidence X-ray diffraction (GIXRD) at the incident beam angle of 2.0° and 2θ in the range from 5 to 110° with a step size of 0.05° (Panalytical Empyrean instrument with Cu Kα radiation, 1.54 Å; 40 kV and 40 mA) was used to determine the internal structure of studied AgNPs. The patterns of silver (#4-0783) and titanium (#44-1294) from the ICDD database were used as references.

The results of DLS analysis revealed that PVP-stabilized AgNPs had the ζ – potential of -15 mV, average HDD of 110 nm and PDI of –0.192, indicating the absence of large agglomerates and presence of a monodisperse system. Fig.1 illustrated the data describing PVP-stabilized AgNPs with the dispersion time 1 hour. Thus, SEM images showed that the PVP-stabilized AgNPs had a spherical shape with a diameter of the metallic core of 70±20 nm.

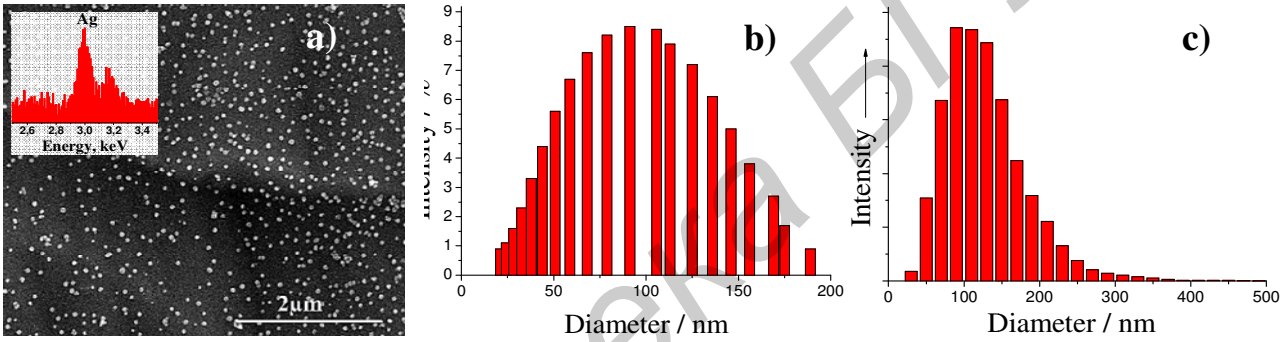

Figure 1 – Silver nanoparticles. a) SEM image and EDX spectra; b) DLS estimated distribution size of AgNPs, c) NTA estimated distribution size of AgNPs

The deposition of PVP stabilized AgNPs on sample substrate was carried out by three types of methods. The first and easiest method was a drop drying or sessile drop. The process of sessile drop method based on forming of a drop 120 µL of the working solution with the concentration 60 µg mL-1 and following drying at 55.5°C. The silver nanoparticles were ultrasonically dispersed in distilled water. The second method was a dip-coating where the sample was dipped in 5 mL of working solution with the same concentration and keep it at 24 hours with following drying at 55.5°C. The last method was an electrophoretic deposition of the PVP coated AgNPs on sample substrate. Prior to EPD, two types of working solutions were prepared. The first working solution was prepared with distilled water and the second based on ethanol with the concentration of AgNPs 60 µg mL^{-1}. Figure 2 shows the results of sample substrate functionalization with AgNPs.

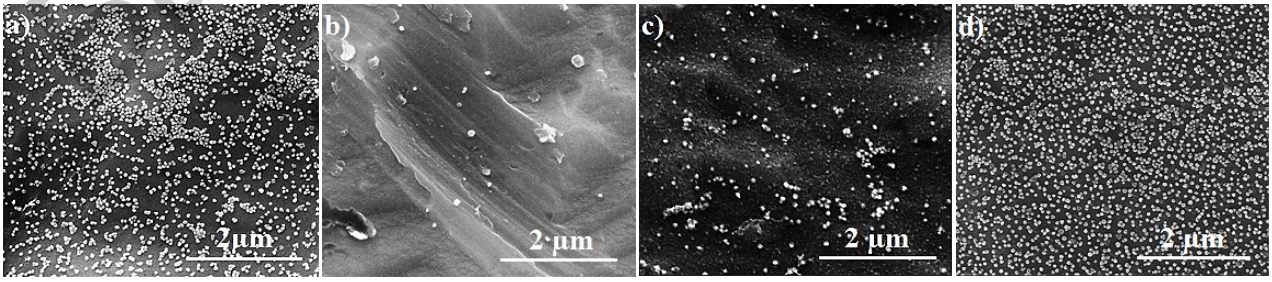

Figure 2. Titanium substrates functionalization with PVP-stabilized AgNPs a) sessile drop 120 µL, b) dip-coating, c) EPD in water (3 V, 60 min), d) EPD in ethanol (50 V, 30 min). The concentration of working solution was 60 µg mL^{-1} in each experiment

Figure 2 shows that the most effective methods of surface functionalization are sessile drop and EPD methods. The SEM analysis confirmed the ability to attain a uniform distribution of AgNPs in case of EPD method. Sessile drop method has the disadvantage associated with the surface tension and as a consequence the samples are not fully covered by the particles. Also in case of practical application the sessile drop method has the disadvantage associated with the deposition process on special design implants.

Structural investigation of system substrate-nanoparticles was carried out by X-ray analysis. Figure 3 shows the results of XRD analysis using the method Sessile drop and EPD to functionalize the surface of silver nanoparticles. Table 2 presented the results of Rietveld analysis.

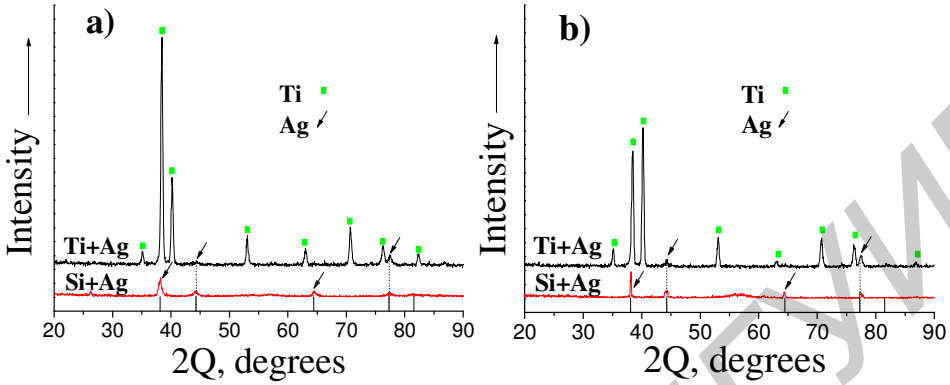

Figure 3 – XRD patterns of the AgNPs layer on titanium and silicon substrates created by:
a) sessile drop b) EPD, where deposition time is 30 min, working solution concentration 60 μg mL^{-1}.

XRD pattern of Sessile drop method and EPD on the titanium substrate showed the presence of reflexes at 2 Theta angles of 44.3° and 77.3°, which can be indexed to (200) and (311) planes of pure silver. Since the main reflection of titanium and silver were very close it was decided to use a silicon substrate as a control the presence of silver. The typical XRD pattern, which illustrates the formation of intense lines of reflection of the Ag, is shown on silicon substrate (Figure 3). The presence of peaks at 2 θ values 38.1°, 44.3°, 64.4° and 77.3° corresponded to (111), (200), (220), and (311) planes of silver, respectively. Thus, the XRD pattern confirmed the cubic crystalline structure of silver. Rietveld analysis gave the crystallite size of the nanoparticles from X-ray diffraction peak broadening to 13/14 nm and the silver unit cell parameter a with 4.085/4.093 Å for silicon/titanium substrate respectively. S. Banerjee et al. [15] and A. Ivanova et al. [16] are presented the similar results of X-ray diffraction analysis.

III. CONCLUSIONS

Functionalization of the sample substrate surface with AgNPs was carried out by Sessile drop method, dip-coating and EPD. According the SEM data the most effective methods of surface functionalization was EPD. The PVP-stabilized AgNPs were synthesized in aqueous solutions with a diameter of the metallic core of 70 ± 20 nm, negative charge of -15 mV and PDI of –0.192, indicating the absence of large agglomerates and presence of a monodisperse system. Dynamic Light Scattering, Nanoparticle Tracking Analysis, X-ray diffraction and scanning electron microscopy have been used to characterize the prepared silver nanoparticles. Scanning electron microscopy showed that the silver nanoparticles were evenly distributed over the surface moreover the particles had a spherical shape. The XRD data obtained for the PVP-stabilized AgNPs on Ti substrate showed the typical peaks of Ag at 2 Theta angles of 44.3° and 77.3° with the coherent scattering region of 14 nm.

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DEVELOPMENT OF THE MICROPLASMA SPRAYING TECHNOLOGY FOR APPLYING BIOCOMPATIBLE COATINGS

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I. INTRODUCTION

Currently, the methods of thermal spraying of coatings for various purposes are being developed all over the world [1, 2]. As noted in the work [2], properly applied thermal spray coatings have many uses and many advantages over the coatings obtained by competing methods. The process of thermal spraying is based on the heating or melting of coating material and spraying it onto the surface with the aim of obtaining coatings with desired properties and adhesion strength to the substrate. The processes of thermal spraying are distinguished by technological simplicity, compactness and transportability of the equipment. The use of the methods of thermal spraying of coatings allows to adjust in a wide range of mechanical and other properties of the resulting coatings (adhesion, hardness, porosity, wear resistance, etc.) depending on the kind of sprayed material, surface treatment products, spraying, etc. These features of processes of thermal spraying determine the universality of their application, the diversity of areas and types of possible use.

For optimum coatings by thermal spraying are required to conduct several consecutive technological processes [2-5]. For example, to ensure proper adhesion of the coating it is important that the substrate was previously prepared, for example, increased its roughness by means of sandblasting or in any other way. Some coatings require additional heat treatment or sealing after application. The treatment of surfaces of complex configuration presents a challenge for the implementation of the thermal spraying technology and requires automated manipulations of the plasma source along with robotic control for appropriate treatment of a surface [1, 2].

One of the main methods of thermal deposition of coatings is plasma spraying. The E. O. Paton Electric Welding Institute (EWI) has developed of a new method of thermal coating- microplasma spraying