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Formation of a Biopolymer Nano Layer by Electrolysis

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Abstract: Composite nanocoatings on the surface of a titanium electrode are obtained by electrochemical reduction of macroions and fibroin nanoparticles in the presence of tricalcium phosphate. Based on the measurements, the dependence of the reduced viscosity ($\eta_{уд}/C$) on C was constructed according to the Huggins formula $\eta_{уд}/C = [\eta] + k[\eta]^2C$ (where k is a constant). For FB_1 and $[\eta]$ = 75 ml/g the intrinsic viscosity value $[\eta]$ = 118 ml/g was found by means of $C \rightarrow 0$ extrazolation. The molecular masses M = 295000 for FB_1 and M = 175000 for FB_2 was calculated, respectively, as stated by Mark-Kuhn-Houwink equation $M \approx ([\eta]/1{,}23*10^{-3})^{1/0{,}91}$. The studies were carried out on a specially assembled electrolysis unit using as a solvent HCOOH: H_2O (50: 50) under the influence of a direct current of 2-8 mA in a temperature range of 25-50°C. within 0.5 - 10 hours. The thickness of the nanocoatings in the range of 50 - 350 nm was controlled by changing the electrolysis time in the range of 0.5 - 10 hours. Furthermore, we have shown that the obtained samples of composite nanocoating FB are characterized by stability in the process of sterilization in ethanol at 60°C, as well as in salt-containing.

Keywords: Electrolysis, Nanocoating, Surface Activity, Fibroin, Chitosan, Tricalcium Phosphate

1. Introduction

Biopolymers are considered as potential sources of raw materials for the development of nanomaterials, in particular, nanocoatings characterized by very valuable physicochemical and biomedical properties [1]. Nanocoatings are in fact divided into thickness "nanolayer", graininess "nanocomposite" and morphology "nanostructured" [2]. All types are widely used and in the case of biopolymers special attention is devoted to hydrophilicity, biocompatibility and bactericidal action, which are of great importance in the development of medical implants and instruments. It is well know that there are a number of methods for the formation of nanocoatings; however, in the case of biopolymers, the most suitable seems to be the electrochemical reduction of an ionogenic biopolymer (macroions) from solutions on a metal surface according to the Faraday principle of electrolysis [3]. In this case, selection of an ionogenic biopolymer and the conditions for conducting the electrochemical reduction of macroions from solutions remains most important**.** A specially assembled electrolysis device with systems that allow to control the temperature of the polyelectrolyte solution and thickness of the formed nanocoating is required to obtain nanocoatings.

In this aspect, the formation of nanocoatings of biocompatible polymers on the surface of implants, such as dental titanium prostheses, still remains to be very actual problem. To solve this problem, natural silk fibroin (FB) has been chosen as a biopolymer research object. The macromolecules of this biopolymer exhibit pronounced polyelectrolytes or, more precisely, polyampholytic properties in solutions due to the presence of ionic amine (NH_2 +) and carboxyl (COOH-) groups in the elementary joints of the chain [4]. Ionogenic groups determine the behavior of FB macromolecules in the form of macroions in solution and are electrochemically decreased during electrolysis [5]. Such solutions of macroions can be obtained by dissolving silk fibroin fibers in 2.5 M LiCl-DMF, 50% $CaCl_2$-water, formic acid (HCOOH), etc. In the case of strong acids, silk fibers are hydrolyzed, for example, fibroin nanoparticles can be obtained as a result of hydrolysis in hydrochloric acid (HCl) [6]. In principle, FB nanoparticles can be electrochemically reduced by electrolysis in the form of a nanocoating like macroions. The strength of the fixation of macroions and nanoparticles on the electrode surface can be increased by their reduction with tricalcium phosphate ions used in the preparation of coatings for dental and orthopedic implants [7]. This approach opens a qualitatively

new stage for the development of composite nanocoatings characterized by pronounced functional activity. In this context, the current work has been carried out by using the specially assembled electrolysis device.

2. Objects and Research Methods

Experiments have shown that the most suitable solvent FB for electrolysis is a mixture of HCOOH: H_2O (50: 50 ml / ml). This made it possible to obtain a solution of macroions, a molecular dispersed system of FB_1 for electrolysis. Nanoparticles with 50-150 nm in size have been obtained by hydrolysis of FB fibers in H_2SO_4 (50%) during 30 minutes at 50°C. Using HCOOH: H_2O (50: 50) a colloidal-dispersed solution of FB_2 has been obtained for electrolysis.

Electrochemical reduction of FB_1 and FB_2 from solutions and mixtures has been carried on the specially assembled electrolysis device (See Figure 1).

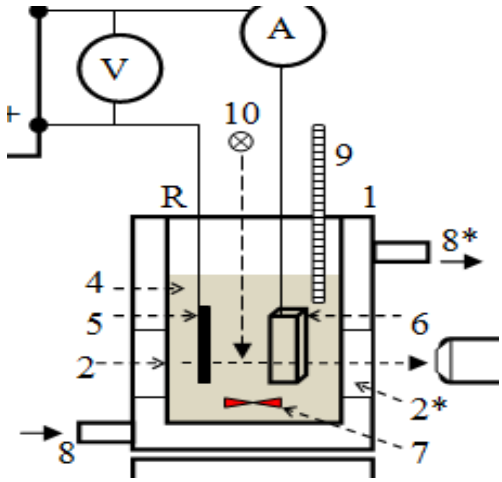


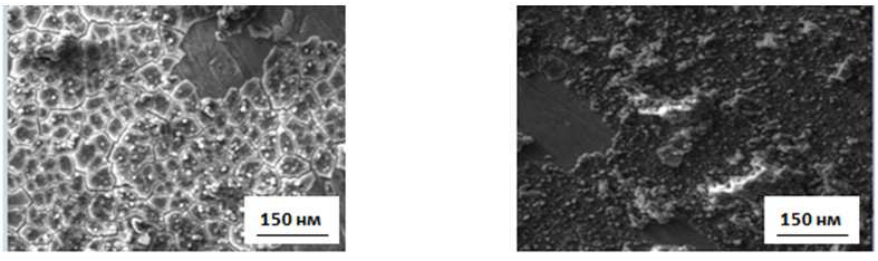
Figure 1. *Schematic diagram of the installation of electrolysis.*

There exists solution in the reservoir (4) in which the oxidation (5) and reduction (6) electrodes are filled at the level of the optical window. The rotation of the magnet (7) by means of an electric mixer provides intensive movement of the solution. The solution temperature is maintained by means of a water thermostat connected to the reservoir through the fittings (8) and (8*), and it is monitored with the help of a thermometer (9). The optical system consists of a light source (10) and a polarizing microscope (11). The supply of a light beam from top to bottom along the axis of the cylindrical reservoir and observation along the horizontal axis allows one to monitor according to the principle of polarization ultramicroscopy. This approach makes it possible to fix the appearance of nanoscale structures at the level 10^{-7} m [5]. The current can be supplied to the electrodes from a constant voltage source (E), and this is monitored with the help of a voltmeter (V) and a microammeter (A).

The experiments have been carried out by using a carbon rod (length 40 mm, 5 mm) as an oxidation electrode and a titanium plate ($40\times10\times2$ мм^3) as a reduction electrode. The thickness and composition of the coating were determined by using a ZEISS SIGMA SEM 500 scanning electron microscope [8, 9]. The strength of the fixation of the coating to the titanium plate was evaluated by washing in distilled water at 60°C in the period of 1 hour. The nanoscale was sterilized in ethanol under the same conditions and as well as the stability of the samples was also evaluated in a weakly acidic (pH = 3) solution of 50% HCOOH and solutions of neutral salts of 50% $CaCl_2$.

3. Results and Discussions

Having measured the specific viscosity (sp) at various concentrations (C) of solutions in 2.5 M LiCl-DMFA [10], the average molecular mass (M) of fibroin in the reprecipitated sample (FB_1) and nanoparticle (FB_2) was determined by the method of Ubbelohde viscometry. Based on the measurements, the dependence of the reduced viscosity ($\eta_{уд}/C$) on C was constructed according to the Huggins formula $\eta_{уд}/C = [\eta] + k[\eta]^2C$ (where k is a constant). For FB_1 and $[\eta]$ = 75 ml/g the intrinsic viscosity value $[\eta]$ = 118 ml/g was found by means of $C \rightarrow 0$ extrazolation. The molecular masses M = 295000 for FB_1 and M = 175000 for FB_2 was calculated, respectively, as stated by Mark-Kuhn-Houwink equation $M \approx ([\eta]/1{,}23*10^{-3})^{1/0{,}91}$.



a b

Figure 2. *Composite nanocoatings FB_1 (a) and FB_2 (b) on the surface of the titanium electrode. Experiments carried out on the specially assembled electrolysis device showed that the reduction of isolated FB macroions in HCOOH: H_2O (50: 50) in the form of micro- and nanocoatings is possible under the action of a direct current with 2 - 8 mA in the temperature range of 25 - 50°C. The thickness of the nanocoatings in the range of 50 - 350 nm was regulated by changing the time of electrolysis in the range of 0.5 - 10 hours. In the case of adding tricalcium phosphate, a joint reduction of macroions and ions occurs, being more efficiently realized when the ratio of FB: $Ca_3(PO_4)_2$ is about 1≥10 (Figure 2a). Whereas the electrochemical reduction of FB nanoparticles in HCOOH: H_2O (50: 50) in the presence of tricalcium phosphate allowed to obtain a composite nanocoating. In this case, the reduction of nanoparticles was more efficient when the FB: $Ca_3(PO_4)_2$ ratio is about 1≥15 (Figure 2b).*

The strength of the fixation of the nanocoatings was assessed by washing them with distilled water [11]. It was found that the course of noticeable microscopic changes are not observed while washing in the range of 15-60°C in the period of 1 hour, i.e., the viscosity and pH neutrality of water remain practically unchanged in the case when the thickness of the nanocoating on the electrode surface is expanded up to 0.5 times [12, 13]. Approximately, the same result was shown by a study of the stability of nanocoatings FB: $Ca_3(PO_4)_2$ on the effect of fibroin solvents, namely, aqueous solutions 50% $CaCl_2$ and 50% HCOOH and 2,5 M LiCl-ДМФА as well. This in turn allows us to assume that electrochemically reduced fibroin in the form of a nanocoating does not pass into a dissolved state in its solvents at 25°C [14]. Experiments on sterilizing samples in ethanol, which were carried out at 60°C, also showed the stability of nanocoatings.

In general, experiments carried out in determining the stability of samples of composite nanocoating of fibroin on the surface of a titanium implant have shown a noticeable swelling of nanocoatings in distilled water, as well as in salt-containing and weakly acidic solvents [15]. Apparently, a certain part of ionogenic groups is not reduced during electrolysis and its being in the composition of the nanocoating interacts with solvents. However, it does not pass into a dissolved state and exhibits a functional activity characteristic of fibroin.

4. Conclusion

Based on the results obtained, we have shown that it is possible to obtain composite nanocoatings with a thickness of 50 - 350 nm by electrochemical reduction of macroions and fibroin nanoparticles in the presence of tricalcium phosphate on the surface of a titanium electrode. We have found that the process of electrochemical reduction of these systems is effectively implemented in HCOOH: H_2O (50: 50) in the form of micro- and nanocoatings, possibly under the action of a direct current of 2 - 8 mA in the temperature range of 25 - 50°C in the period of 1-10 hours. Furthermore, we have shown that the obtained samples of composite nanocoating FB are characterized by stability in the process of sterilization in ethanol at 60°C, as well as in salt-containing and weakly acidic solutions in the range of 25 - 50°C.

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