FABRICATION AND CHARACTERIZATION OF HYBRID NANOSTRUCTURE BIOCOMPOSITES BASED ON OXIDE NANOTUBES

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ПОЛУЧЕНИЕ И ИССЛЕДОВАНИЕ ГИБРИДНЫХ НАНОСТРУКТУРНЫХ БИОКОМПОЗИТОВ НА ОСНОВЕ ОКСИДНЫХ НАНОТРУБОК

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В данной работе приведен обзор научных трудов, по получению титановых оксидных нанотрубок. В таблице представлены наиболее часто используемые электролиты, значения напряжений и времени проведения процесса электрохимического анодирования, а также соответствующие им размеры оксидных нанотрубок. Описано влияние напряжения и времени на процесс получения нанотрубок. По результатом данной работы был сделан вывод, что наноструктурные оксидные нанотрубки могут использоваться в качестве системы доставки лекарств.

The process of implantation and rehabilitation may take many months or years in the case of rejection of the implant. Titanium is widely used for biomedical applications due to its good mechanical properties, high corrosion resistance, and high biocompatibility. Various methods for surface modifications are being utilized to support the osseointegration of an orthopaedic implant. Some of these follow a purely mechanical approach, e.g. by increasing the surface roughness by sand-blasting, which has in the case of femoral shafts been found to be advantageous for the integration of the implant into adjacent bone tissue. A more sophisticated approach to surface structuring on the nanometer scale is the electrochemical treatment in fluoride containing electrolytes, which results in the formation of arrayed vertical titanium dioxide (TiO2) nanotubes. If these structures occur in appropriate dimensions, they may enable the adherence of mesenchymal stem cells and support growth and regeneration of bone tissue. Furthermore, the increased surface area of these tube formations can be loaded with bioactive or medical agents and hence serve as in situ drug delivery systems, which have significant advantages as compared with systemic medical treatment [1].

The relevance of this work is to analyze the existing scientific publications on the synthesis of hybrid biomaterials based on oxide nanotubes and experiments with hydroxyapatite coating on the surface of the nanotubes. However, there is not enough information on the subject now and all information is in English.

The aim of this work is to review the progress of different researchers and use their experience in the fabrication of hybrid nanostructured biomaterials based on oxide nanotubes, with a view to synthesize and study the properties of oxide nanotubes in the future.

The most common method of obtaining oxide nanotubes is electrochemical anodization. Anodizing system includes a bath filled with an aqueous electrolyte solution, in which two electrodes are held: a cathode and an oxidized sample - the anode.

The application of anodic oxidation of Ti in a fluoride containing electrolyte enhances the natural passive layer of Ti, while fluoride ions etch channels into the oxide. Appropriate anodization conditions lead to the formation of nanotubes with widely controllable dimensions by self-organization [1].

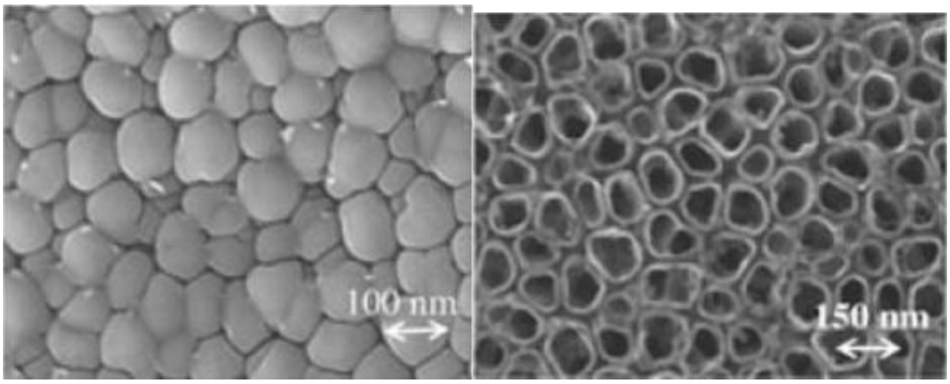
Table 1 shows the results of oxide nanotubes fabrication process adopted from various publications. In all experiments, the anode material was titanium and the cathode material was different [2-7]. Only some publications revealed the effect of distance between the electrodes on the prepared nanotubes properties.

Table 1

The experimental results obtained under different conditions and electrolytes [2-7]

№	*Electrolytes*	The experimental parameters		Dimensions nanotubes		
		Voltage, V	Time, h	Diameter, nm	Wall thickness, nm	Length, µm
1	$3\%C_2H_4(OH)_2$ + $0.3\%NH_4F+H_2O$	20	0.5	30.0±7.5	10.5±3.8	1.3±0.2
		80	0.5	128.3±12.4	23.4±0.9	8.0±0.1
2	$C_3H_5(OH)_3$ + 1% NH_4F+ H_2O	50	3	145.0 ± 5.0	15.0 ± 2.0	—
3	H_2O + 0.5%wt HF	20	0.5	100.0	15.0	0.250
4	1m $(NH_4)_2SO_4$ + 0.5%wt NH_4F + H_2O	20	—	100.0	—	2.5
5	$NaF+C_6H_8O_7$ + H_2SO_4	20	0.25	45.0±1.0	12.0±2.0	0.234±0.006
			0.5	43.0±8.0	12.0±2.0	0.245±0.014
			2	58.0±12.0	16.0±2.0	0.65±0.02
			4	50.0±9.0	15.0±2.0	0.625±0.023
6	1m $NH_4H_2PO_4$ + 0.5m HF	20	1	100.0	19.0	1.0

Figure 1 shows scanning electron microscope (SEM) images of self-organized porous titanium oxide formed to a thickness of approximately 2.5 µm in 1m $(NH_4)_2SO_4$ electrolyte containing 0.5 wt. % NH_4F. From the SEM images it is evident that the self-organized regular porous structure consist of pore arrays with a uniform pore diameter of approximately 100 nm and an average spacing of 150 nm. X-ray photoelectron spectroscopy (XPS) analysis revealed that the porous layer shown in Figure 1 consist of approximately 62 ± 5 atom % of oxygen and 38 ± 5 atom % titanium [2].



a) b)

Fig. 1. SEM images of titanium oxide nanotubes. The top and bottom views of a 2,5 nm thick self-organized porous layer. The titanium sample was anodized up to 20 V [2].

Table 1 shows that if the voltage and the electrolyte are constant, increasing the time leads to increase of the geometrical parameters of nanotubes to a maximum value. In addition, if the time and the electrolyte are constant, increase in the voltage leads to increase dimensions of nanotubes.

In conclusion, the dimensions of nanotubes will depend on the voltage, time, electrolyte composition, distance between the electrodes. Due to anodizing nanotubes usually reveal an amorphous structure. For a purpose of obtaining the crystal structure the nanotube are thermally annealed at a temperature of 450-550 °C for 1-3 hours [1-7].

The results of this work will help to obtain oxide nanotubes with desired dimensions, which will be coated with a film of hydroxyapatite by RF-magnetron sputtering. At the moment any research on the use of this method for hydroxyapatite film deposition has not been conducted.

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