The formation of a sensitive structure of a contact lens sensor

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Abstract. Smart photonic crystal structures have attracted great attention in various areas of life. For medicine application smart photonic crystal films is promising as highly sensitive elements of contact lenses for monitoring the lacrimal glucose and intraocular pressure. To obtain structures with desired properties, the process parameters must be controllable, and the properties of structures must be reproducible and satisfy specified requirements. This article describes the controllable electrodeposition method and equipment for producing polystyrene opal photonic crystal films onto the surface of hydrogel contact lenses. We obtained quality three-dimensional ordered films with reproducible properties.

1. Introduction

The development of nanotechnology is associated with the creation of new materials. The optical properties of smart photonic crystal (PhC) can be switched by using external triggers such as change of solvent, temperature, ionic strength, light, electric or magnetic fields or mechanical stress [1].

Opal PhC films are highly ordered structures consisting of silicon dioxide (SiO₂), polystyrene (PS) or polymethylmethacrylate (PMMA) spheres with diameter in the range from 200 to 1000 nm. Opal matrix has a face-centered close-packed crystal lattice [2,3]. The photonic band gap (PBG) of opal and opal based structures can be stably tuned by deformation of the photonic lattice (stretching, bending and compressing) [3]. Inverse opal PhC films is promising as highly sensitive elements of contact lenses for monitoring the lacrimal glucose and intraocular pressure [4-6]. Calculations show that when the pressure changes by 1 mmHg, the PBG will shift by a tenths of a nanometer. The technology for producing inverse opal structures has been worked out quite well. The main problem when creating a sensor structure is to obtain a high-quality template on the surface of the lens. It should have an opal matrix structure and pronounced photonic crystalline properties.

In this paper we describe the electrodeposition of the PhC PS colloidal film (template) on the surface of a hydrogel contact lens. Self-organization of colloidal particles (microspheres) plays the main role in the formation of colloidal opal PhC films [7]. To obtain structures with desired properties on the lenses surface, the process of self-organization must be controlled. However in addition to controlled process parameters, the properties of the resulting structures are affected by a large number of random factors. So it is critical to develop the technological support for the production of these self-assembled structures.

2. Method, equipment and materials

Opal PhC films is supposed to be used as a template for the formation of a sensor waveguide on the surface of a contact lens. Therefore, the choice of the material and the diameter of the colloidal microspheres was carried out after modeling the structure (Figure 1) and analyzing the technological route for manufacturing the waveguide, which will include the deposition of a PhC film, filling its
voids with the penetration material and etching of the initial film. A PS monodisperse carboxylated latex with a particle diameter of 220 nm was selected as the material of template. Particles had the smallest variation in shape and size (~5%). The concentrated of PS suspension was 1 %. The contact lenses material Senofilcon A was selected according to the following parameters: high resistance to the heat treatment; hydrophilicity from 38 % to 50 %; high strength; elasticity; thickness in the center from 40 microns to 80 microns.

Figure 1. The smart PhC structure: (a) the contact lens and (b) the waveguide modeling.

Ordering and matrix geometry is especially important for highly sensitive structures (Figure 2). There are several self-assembly methods: sedimentation, vertical deposition, spin coating, electrodeposition and melt-shear [8]. The fundamental difference between the methods is the matrix formation rate. It is determined by the sum of forces acting on the particle and the structuredness and uniformity of the colloidal films. The electrodeposition method is suitable to obtain a film with desired parameters because of its ability to vary the process conditions. The experiments were carried out at the universal laboratory equipment (Figure 3) [9]. The control unit of the equipment consists of five main modules: power supply unit, modes and process time setting module, display and indication module, electrophoresis module and vertical deposition module.

Figure 2. The principle of operation of the photonic crystal element: external pressure $p_3$ is greater than pressure $p_2$, which is greater than pressure $p_1$.

Figure 3. The general scheme of the electrophoresis deposition process on the contact lens surface (a) and the laboratory equipment.
The process of electrodeposition is based on the phenomenon of electrophoresis. Two conductive electrodes are immersed in an electrochemical bath with a colloidal suspension of the deposited material. Because of an external double electric layer PS particles have a negative surface charge, therefore when an electric field is applied, the particles move to the positively charged electrode (anode). The velocity of the electrophoresis deposition process is determined by the applied potential. The ordering of the structure is determined by the ability of the particles to coagulate, which is determined by zeta potential or surface external charge of the microspheres. The experiments were carried out under the following conditions: applied voltage was varying from 0.8 V to 6 V; deposition time was varying from 5 min to 10 min; pH was equal to 7. The distance between the electrodes was 10 mm. The deposition time was measured by the electronic stopwatch with accuracy of ± 0.1 s. Voltage control during the experiment was carried out by the multimeter with accuracy of ± 0.5 % per one unit account. The concentration of the colloidal phase was set by adding distilled water to the initial 10 % suspension by a medical syringe with the accuracy of ± 0.1 ml. Spectrophotometric monitoring was carried out by Izovac Epsilon SphE spectrophotometer. Three observations at various points were carried out for every sample. Verification control was carried out by special setup for the study of reflection spectrum of photonic crystal at near-zero incidence angle [10].

3. Results and discussion
PS colloidal films deposition on lenses’ surface was carried out in four modes in accordance with the plan of the full factorial experiment in the above ranges of factor values. Figure 4 shows the photo of the PS film obtained on the surface of the contact lens and the reflection spectrums of the best sample.

Figure 4. The result of film deposition: (a) the photo of PS film and (b) the reflection spectrum of PS film deposited at the voltage of 1.6 V and deposition time of 10 min obtained by Izovac Epsilon SphE spectrophotometer for three dots on the sample and (c) the reflection spectrum of the same film obtained by special setup for the study of reflection spectrum of photonic crystal.
A pronounced irisation was observed on each sample. More intensive film’s growth was observed on the periphery of the surface of the contact lens. We assume that the film thickness gradient is due to the radius of lenses curvature. It was revealed that the value of the reflection coefficient remains practically unchanged with increasing application time and low voltage (U = 0.8 V). With a higher voltage (U = 1.6 V) and an increase in the application time to 10 min, we get a sharp increase in the reflection coefficient by 1.75 times. Thus we can conclude that with an increase in voltage, the time factor begins to have a stronger effect on the reflection coefficient of the colloidal polystyrene film and its structures ordering. At the same application time an increase in voltage leads to an increase in reflection coefficient.

Spectrophotometric analysis showed that all the samples have a photonic band gap (PBG) at wavelength $\lambda=490$ nm (Figure 4b). Verification testing of samples by special setup for the study of reflection spectrum of photonic crystal [10] showed similar results. According to Bragg diffraction law when PS particle diameter $d$ is 220 nm; effective refractive index of the material $n_{ef}$ is 1.35...1.50; Bragg diffraction angle under normal incidence $\theta$ of 90°; diffraction order $N$ of 1, the PBG wavelength $\lambda$ is in the range 488 ... 535 nm. Thus the results of theoretical calculation of PBG are consistent with the experimental results.

The aim of this work was not only to determine the most rational modes, but also to ensure the reproducibility of the electrodeposition process. Therefore, the number of random factors was analyzed and then significantly reduced. The suspension storage phase was excluded, the temperature of the medium was constant, and the contribution of vibrations was reduced. But structural defects arising due to the sticking of colloidal particles do not reduce the uncertainty of PBG reflection intensity measurement. It is about 20 %. However we have achieved a reduction in the uncertainty of PBG wavelength measurement to 5 nm. This indicates the receipt of structures with the same packing density of the opal matrix.

4. Conclusion
This work shows that electrophoresis provides convenient and fast deposition of highly ordered colloidal PS opal films on the contact lenses surface. The voltage of 1.6 V and deposition time of 10 min allows to obtain the highest values of the reflection coefficient of PBG. Since most of the process parameters are well controlled and the influence of random factors is minimized, it will be used to research the technology of smart contact lenses.

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