IRREVERSIBLE DESTRUCTION OF REFLECTED RADIATION FROM THE SURFACE OF A PHOTONIC CRYSTAL

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Abstract

Studies of the mechanism of irreversible changes in the reflected radiation from the surface of sensors of organic solvents, based on photonic crystals, are conducted when the dose of the registered substance exceeds the critical point with the use of microspheres with sizes equal to tens of micrometers.

Keywords: *photonic crystal, organic solvent, Bragg reflection, diffraction efficiency, swelling*

1. INTRODUCTION

Application of sensors, based on photonic crystals (PC) for the detection of chemical substances, are described in a significant number of overviews and original studies [1-7]. The detection itself is carried out by using the spectral response of the reflected radiation from the surface of the PC in most of these studies. A spectral shift of the reflected radiation, caused by the Bragg wavelength change [8,9], occurs when a chemical substance is applied to a PC. This kind of shift is caused by the changes in the period of the diffraction grating, more specifically the PC, and by the integrated refractive index which is also prone to change when a chemical enters the surface of the photonic crystal.

However, a lot of questions have occurred during the study process of the detector's response to a number of organic solvents (toluene, benzene, o-xylene, isopropanol) for which traditional methods of research have no answers, for example:

1) What is the detailed nature of spectral shift mechanisms in the photonic crystal sensor?

2) What is the mechanism for terminating the selective diffraction reflection when the dose of the detected substance exceeds the critical point?

3) What is the single and/or multiple critical dose of the detected substance during its application onto the photonic crystal?

4) Can an ordered structure be formed from polystyrene microspheres with a predetermined configuration?

This article contains information on studies concerning mechanisms for terminating selective diffraction reflection when the dose of the detected substance exceeds the critical point.

To answer this question, it is extremely important to observe the dynamics of interaction processes between the substance and the elements of which the photonic crystal consists. The photonic crystal elements used in our experiments were polystyrene microspheres with diameters equal to 170 ± 17 nm and 230 ± 25 nm. These polystyrene microspheres were obtained by using the *emulsion polymerization method in the presence of non-ionic oxyethylated emulsifiers.* [10] Initiating agent - potassium persulfate, surfactant – pluronic F-68.

The main insufficiency of the observation method, during interactions between the detectable substances and the surface of photonic crystals and other similar processes, is the absence of their dynamics. Generally, the observation of ordered structures and their changes when applying detectable substances on them is carried out by using a scanning electron microscopy (SEM) method or an

atomic force microscopy (AFM) method. However, these methods do not make it possible to visualize the dynamics of interaction processes between chemical substances and polystyrene microspheres to understand the changes of the microsphere structures and configuration of packages. A typical example of studies carried out for these processes is the comparison of electronic microphotographs of the active PC and the PC in the absence of the optical selective reflection from its surface when the analyte dose exceeds a maximum permissible value.

At the same time, the analysis of the morphological structure of the crystal's surface with the use of a scanning electron spectroscopy method did not detect any defects in the ordered structure. (Fig. 1 a) and b)).
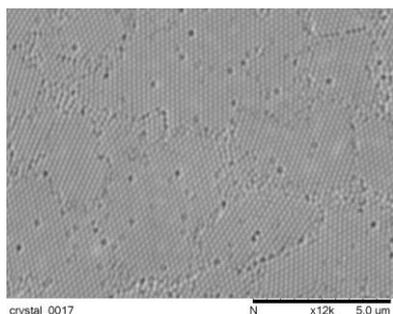
Fig. 1. a) Morphological structure of the photonic crystal's surface before the application of the analyte using the SEM method
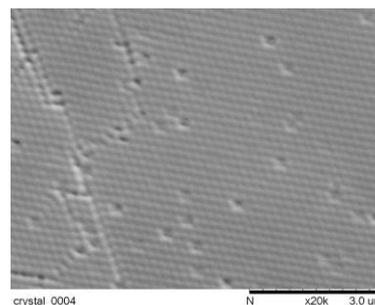
Fig. 1. b) Morphological structure of the photonic crystal's surface after exceeding a maximum permissible value of the analyte dose using the SEM method

Figure 1 b) shows the morphological structure of the photonic crystal's surface after treatment with the analyte.

The absence of the spectral selective reflection from the surface of the photonic crystal has been observed due to the chosen dosage of the applied analyte. When comparing sections of the electronic photographs (Fig. 1 a) and b)) it is noticeable that the edges of the microsphere in Fig.1 b) are less pronounced than the ones in Fig.1 a). Such image blurs may indicate friability of the microsphere's surface after treatment. For a more detailed analysis, an attempt has been made to simulate the microspheres of the photonic crystal by an analyte. For this purpose, polystyrene microspheres of sizes 6 – 213 μm with low divinylbenzene content have been chosen as a model for testing. After treatment with an analyte (toluene), the dynamic behavior of the microspheres has been recorded by an optical microscope. Observations have shown changes in the integrated transmittance coefficient of the visible radiation through such microspheres. These changes may relate to additional light scattering from the surface of the microspheres. Such scattering is caused by inelastic deformation of microspheres during their swelling caused by analyte diffusion and followed by its evaporation from them.

Clearly, the abovementioned methods are used to detect final states of these structures or any of their changes. The process itself cannot be observed by using those methods, which makes information on the changes of the state incomplete. Upon that, the possibility to observe dynamic processes, occurring in various objects, is provided by optical microscopy. In this case, an optical microscope, equipped with a digital camera and with the use of an interface connected to a personal computer, is used for the observation of kinetic processes. Microspheres with well observable diameters in an optical microscope can be used as a test subject for studies. Polystyrene microspheres with divinylbenzene (with different concentrations) and a diameter range of 6 – 250 μm have been used in our studies. A Biomed microscope with zooming functions, allowing to enlarge images up to 64*, 160*, 640* and 1600* times, was used as a video surveillance system for the control of dynamics. A digital camera DCM 310 connected to a computer with a Scopetek programme was used as an image detector. A line of polystyrene microspheres with diameters of 6, 20, 31, 55, 110 and 213 μm and different

divinylbenzene content (0 – 4%) was taken as model objects. Dry polystyrene microspheres with diameters of 6, 20, 31, 213 μm with different divinylbenzene content and without formation of ordered structures were placed on a flat surface of a microscope glass. A drop (~ 10 μL) of a non-polar organic solvent (toluene, octane or a combination of toluene and octane with different concentration ratio) is applied on top of the dry microspheres. A video of the visual examination of the behavior of polystyrene microspheres in the presence of these substances was recorded

2. PROCESS FLOW

Spheres are placed or a suspension is applied to a 3-5 mm high fragment of glassware in such a way that a monolayer of particles is obtained. This fragment was placed on the bottom of a glass vial (as flat-bottomed as possible) right in the center. The height of the glass vial was approximately 40 mm and the diameter was approximately 25 mm. The glass vial is then fixated on a microscope stage, the microscope eyepiece is lowered to obtain very clear boundaries of spheres (near the equator) and after that the filming/snapshots were taken. After ~10 sec of filming the microscope stage was lowered and 200 μL of toluene was added with a pipette along the wall of the glass vial, after that the microscope stage was raised until a clear picture was obtained. If the image is blurry because of the swelling of microspheres, the height of the microscope is adjusted to an optimal one. The filming continued for 8-10 minutes for the spheres to reach total swelling. In case it was necessary to take a picture of the package after the release of toluene, without stopping filming of the video, the microscope stage was lowered, very carefully the glass vial was taken out from under the ocular (it was very important to prevent sliding of the fragment of glassware towards the wall of the glass vial to avoid connection of the package with the liquid phase), after which the fragment was withdrawn from the glass vial and placed on a microscope glass. This is where the snapshots took place.

The scheme of the experiment is presented in Fig. 2.
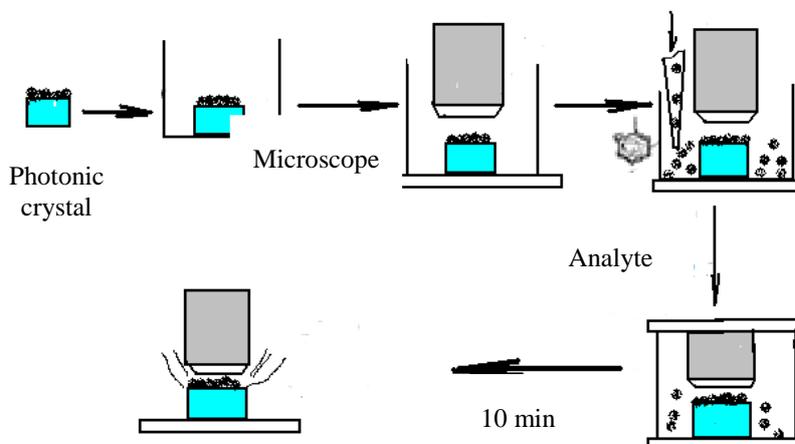
Fig. 2. Scheme of the experiment for modeling of selective diffraction reflection of degradation processes from the surface of photonic crystals.

The size changes of microspheres, after drops of organic solvents are applied, consist of several stages: 1) a solvent diffusion inside the microspheres leads to volume changes; 2) an increase in volume of the microsphere leads to "stretching" of its surface. This kind of "stretching" is followed by straightening of the polymeric chains from which the microsphere consists. The presence of cross-linking in the form of divinylbenzene limits the swelling of microspheres; 3) the surface of the microspheres becomes more friable; 4) the polystyrene is partially washed out of the microspheres due to their dissolution in an organic environment; 5) changes occur in the rheological characteristics of the microspheres. In particular, changes occur in their viscoelastic properties; 6) horizontal capillary forces appear between the microspheres which tend to bring them closer together and form a hexagonal close-packed structure. When the solvent evaporates from the microspheres, their

compression almost returns to the initial stage. The friability of the surface, upon contact with the microspheres and their following compression, forms polymeric bridges between them. It was observed, that restoration of the microspheres' sizes does not lead to regeneration of their surface properties. The surface becomes less elastic and less capable of deformation. This is observed when the solvent is reapplied to the surface of polystyrene microspheres. After application, the polymeric bridges between microspheres dissolve and the microspheres begin to swell again. However, due to the lack of the original elasticity of the microspheres' surface, their diameters do not reach the initial values as it was observed during the first application. The calculation shows a decrease of the maximum volume in comparison with the maximum volume at the initial application of the solvent by 1.5 times. For a photonic crystal (PC) it means that the regeneration properties, including optical properties during evaporation of the solvent from the surface of the PC, have been terminated.. The subsequent applications of the solvent may lead to irreversible consequences of the microspheres' properties and termination of the photonic crystal's performance.

3. RESULTS AND DISCUSSION

a) Swelling of microspheres

The dynamics of swelling of polystyrene microspheres are influenced by relaxation processes. The linear dimension enlargement of the microspheres during swelling is possible due to the straightening of macromolecules and the shifting of structural elements inside the microsphere. The speed of these processes depends on the physical state of the system. The quantitative parameter of the processes' speed is the time of relaxation. The relaxation time decreases when the content of the solvent (analyte) increases. This means that the major influence of relaxation processes takes place at the initial stage of swelling. When a solvent is applied, the surface concentration does not immediately reach the equilibrium value. It varies according to the [11]:

$$c = c_e(1 - e^{-t/\bar{\tau}})$$

where: $\bar{\tau}$ - mean time of relaxation, c_e - equilibrium concentration of a solvent.

Fig. 3 shows the dependency of changes in the microsphere's radius from the time of the diffusion process of the solvent (toluene) inside it.
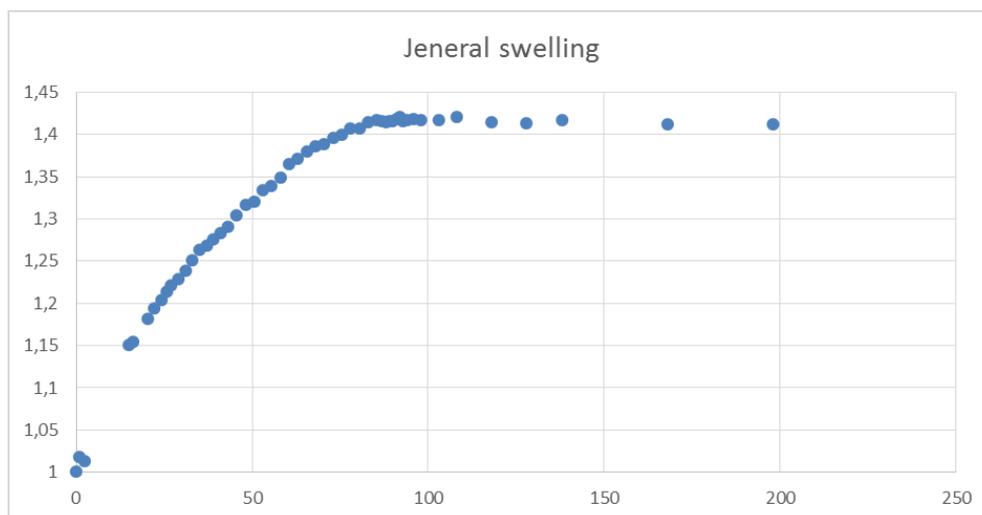
Fig. 3. Change of the microsphere's volume (axis of ordinates) from time (axis of abscissa) during swelling of the microsphere

Images of swelling and compression of polystyrene microspheres after injection of the analyte (toluene) are presented below in Fig.4.
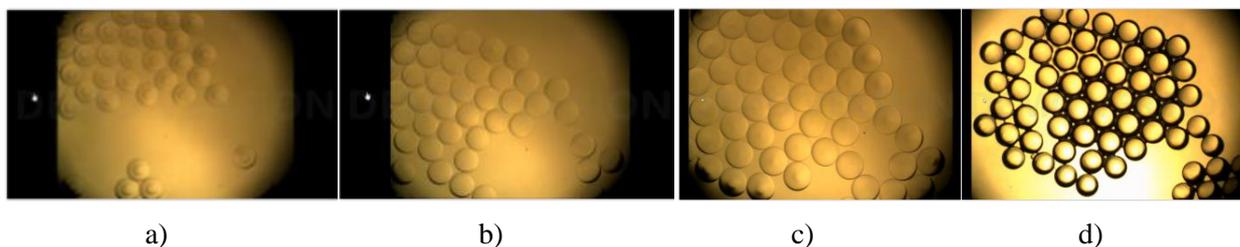

Fig. 4. a) , b) Images of swelling microspheres are presented, c), d) Images of polystyrene microspheres' compression after evaporation of the analyte (toluene) from them

b)   Compression of microspheres after the analyte evaporation

The studies [12] have shown, that the uniaxial deformation of polymeric films, with a thin layer of hard coating applied on them, is accompanied by the following general phenomenon: the appearance of a regular microrelief and regular destruction of the coating.

It has been found, that the microrelief is always orientated along the axis of the tensile of the polymer supports and it is positioned perpendicular towards the cracks of the damaged coating, respectively.

As it is well known, under tension of rubber-like polymers, their volume remains almost unchanged. Instead, a significant lateral contraction (compression) occurs, which leads to compression of the coating in a direction perpendicular to the tensile axis of the polymer. As a result, the compression of hard coating loses its stability and this causes the occurrence of the abovementioned microrelief. The conclusion made on the compression, that it is responsible for the occurrence of the microrelief, is very important for understanding of the studied phenomenon (Fig.5 a), b)).
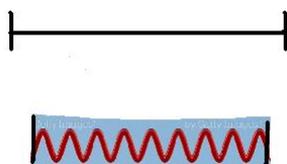
a)

Fig. 5. a) a scheme of the stability loss of the rod with its one end attached to the polymer support
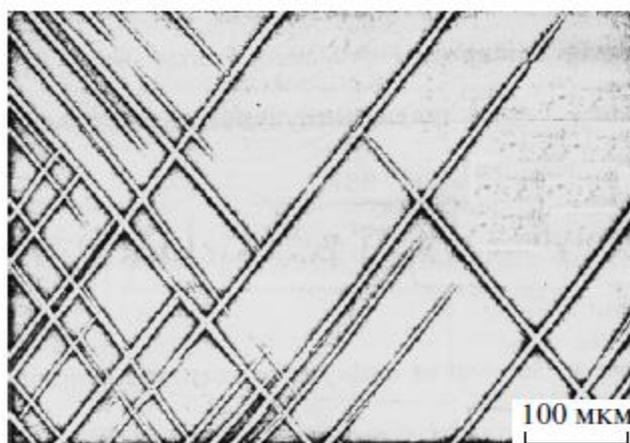
b)

Fig. 5. b) a microphotograph of a thin polystyrene sample cut under uniaxial vertical compression [12].

As a result of inelastic deformation after the evaporation of toluene, surfaces of polystyrene microspheres compress and additional friability occurs (Fig. 6). This effect causes additional scattering

of incident radiation on the surface of the photonic crystal, which reduces spectral selective reflection from its surface.
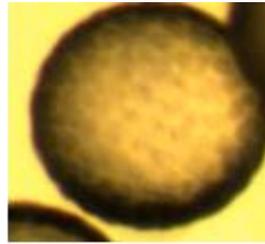

Fig. 6. Deformation of the microsphere's surface with a diameter of 213 µm after evaporation of toluene from its volume.

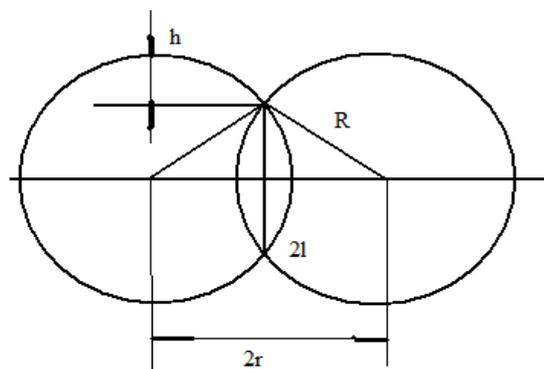Groove depth reduction of the diffraction grating.

An ordered structure of microspheres can be presented in the form of Bragg grating, which selectively reflects light with a certain wavelength (Fig. 7).
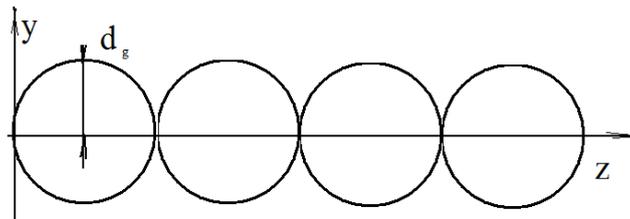
Fig. 7. Diffraction grating without the analyte
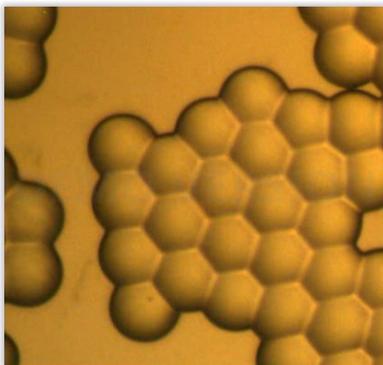
Fig. 8. a) a «depressed» structure of the microspheres at the time of swelling in a solvent

Fig. 8. b) depth change in the diffraction grating if the structure of the microspheres is "depressed'

Diffraction grating after application of the analyte

$$h = R - \sqrt{R^2 - r^2}$$

R- radius of the microsphere after swelling, r – radius of the microsphere before swelling, 2l – intersecting line of microspheres after swelling, h – depth of the diffraction grating.

If the diameter of the microsphere is d = 200 nm, then the radius is r = 100 nm. If the swelling coefficient of microspheres (after swelling) is equal to 25%, then the radius is R = 125 nm. In this case, the depth will be equal to h = 50.0 nm. If the wavelength of the shifted reflection spectrum is λ = 530 nm, then the grating depth / wavelength ratio will be equal to ~ 0,09λ. The depth of non-swollen microspheres for a non-shifted wavelength is 100 nm, it is defined as 0.22λ for a wavelength equal to λ = 470 nm.

An example of the binary grating functioning with a single stroke (d/2) at period d has been considered during studies [13]. Figure 9 shows intensity dependence of 0 and -1 from the depth of stroke h.

The intensity shown on Fig. 9a) was calculated for the angle of incidence $\theta = 30°$ and TM polarization. The intensity shown on Fig. 9b) was calculated for TE polarization.

a)   b)
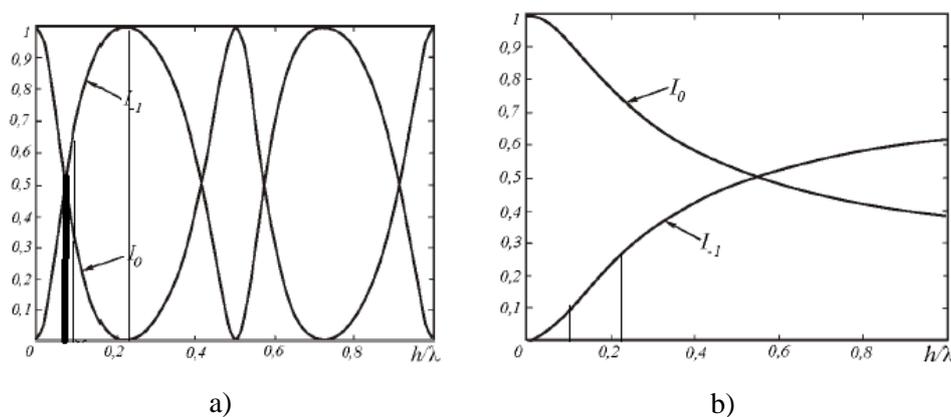
Fig. 9. Binary grating intensity calculation of 0 and -1 for the angle of incidence $\theta = 30°$ a) for TM polarization, b) for TE polarization [13].

It is possible to evaluate the reduction of the diffraction efficiency for this model, if the depth of the grating stroke will be changed.

From the diagram of the TM polarization, it appears that the reflection coefficient of the first diffraction order is about 1.0, if the depth of the stroke is h = d/2, and about 0.5 if h=0.22λ. For TE polarization the intensity ratio is equal to 0.25 and 0.1, respectively.

4. CONCLUSIONS

Observation of processes in model systems of polystyrene microspheres with sizes of 6 – 200 μm can lead to a number of conclusions on their behavior after the application of analyte vapours (in our case it is toluene).

1. Swelling of polystyrene microspheres occurs when an analyte is applied to the surface of the photonic crystal;

2. When analyte vapours are injected with low content of divinylbenzene in the polystyrene microspheres (< 1%), acting as a cross-linking agent, the microsphere surface creates additional friability during the swelling and during evaporation of the analyte;

3. The surface of the microspheres becomes friable. This effect reduces the spectral efficiency of the diffraction reflection from the surface of the microspheres;

4. The structure of the microspheres loses firmness when the analyte is evaporated. If the microspheres are self-organized, then they may become "depressed", i.e. one microsphere presses into the other. This may lead to depth reduction of strokes in a composed reflected diffraction grating during the interaction with coherent waves, that reduce the efficiency of its reflection;

5. The line crossings between microspheres for observations of diffraction patterns are becoming less distinct, in other words smoother. This situation also reduces the efficiency of the spectral reflection from the surface of the photonic crystal

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