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ANALYTICAL METHODS IN CHEMISTRY AND CHEMICAL TECHNOLOGY

АНАЛИТИЧЕСКИЕ МЕТОДЫ В ХИМИИ И ХИМИЧЕСКОЙ ТЕХНОЛОГИИ

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REVIEW ARTICLE

Chemical sensors based on photonic colloidal crystals

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Abstract

Objectives. *The paper analyzes the results of research into the formation of photonic crystal structures from polymer microspheres and the mechanisms of spectral shifts during selective reflection of non-monochromatic incident radiation from them in the visible and infrared light, as well as the use of polymer microspheres as sensors for detecting chemical substances having similar structures.*
Results. *Research carried out at the Ya.K. Syrkin Department of Physical Chemistry in the Institute of Fine Chemical Technologies of the RTU MIREA is presented. Issues related to the detection of substances with similar chemical structure using sensors based on photonic crystals made of polystyrene microspheres 160–300 nm in size, are considered. Spectral shifts of the reflected radiation from the crystal surface are registered in the visible spectrum when substances in the liquid or gas phase are detected by the crystal surface.*
Conclusions. *The method of electrophoretic deposition of colloidal particles in the form of polymeric microspheres on conducting surfaces can be used to create ordered structures over large areas. However, the detection of individual compounds by the optical method is impossible without controlling the kinetics of spectral shifts of reflected radiation from the surface of photonic colloidal crystals. The spectral characteristics of such radiation are directly related to the particle sizes that determine the period of the crystal lattice.*

The diffusion of chemical substances into a photonic crystal, which results in a swelling of the particles forming it and a shift in the spectrum of reflected radiation, is determined by a change in the period of the crystal lattice due to a change in the size of these particles. A kinetic model of swelling polymer microspheres, which describes the diffusion of substances into porous polymer particles, is proposed. An excess amount of substance deposited on the surface of a photonic crystal above the limit is shown to lead to its degradation, which is manifested in the "fading" of the crystal surface and the concomitant disappearance of narrow peaks of reflected radiation.

Keywords: *photonic crystals, colloidal crystals, optical sensors, polymeric microspheres, ordered structures, mathematical modeling*

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ОБЗОРНАЯ СТАТЬЯ

Химические сенсоры на основе фотонных коллоидных кристаллов

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Аннотация

Цели. *Проанализировать результаты исследований формирования фотонно-кристаллических структур из полимерных микросфер, механизмов спектральных сдвигов при селективном отражении от них немонохроматического падающего излучения в видимой и инфракрасной области, а также применения этих структур в качестве сенсоров для детектирования близких по строению химических веществ.*
Результаты. *Представлены разработки авторского коллектива, проводимые на кафедре физической химии им. Я.К. Сыркина Института тонких химических технологий РТУ МИРЭА. Рассмотрены вопросы, связанные с детектированием близких по химическому строению веществ с помощью сенсоров на основе фотонных кристаллов, изготовленных из коллоидных частиц, представляющих собой полимерные микросферы размерами 160–300 нм. Показано, что детектирование происходит в видимой области спектра за счет регистрации спектрального сдвига отраженного излучения от поверхности кристалла при нанесении веществ из жидкой или газовой фазы.*
Выводы. *Установлено, что метод электрофоретического осаждения коллоидных частиц в виде полимерных микросфер на проводящих поверхностях позволяет создать упорядоченные структуры на больших площадях. Детектирование индивидуальных соединений оптическим способом невозможно без контроля кинетики спектральных сдвигов отраженного излучения от поверхности фотонных коллоидных кристаллов. Спектральные характеристики такого излучения напрямую связаны с размерами*

частиц, определяющих период кристаллической решетки. Диффузия химических веществ в фотонный кристалл приводит к набуханию образующих его частиц и смещению спектра отраженного излучения, которое определяется изменением периода кристаллической решетки за счет изменения размеров этих частиц. Предложена модель для описания кинетики процессов набухания полимерных микросфер, описывающая диффузию веществ в пористые полимерные частицы. Показано, что увеличение количества вещества, наносимого на поверхность фотонного кристалла выше предельного, приводит к деградации кристалла, что выражается в «выцветании» его поверхности и проявляется в исчезновении узких пиков отраженного излучения.

Ключевые слова: *фотонные кристаллы, коллоидные кристаллы, оптические сенсоры, полимерные микросферы, упорядоченные структуры, математическое моделирование*

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INTRODUCTION

Research in the field of photochemistry, conducted at the Department of Physical Chemistry of the M.V. Lomonosov Institute of Fine Chemical Technologies (IFCT), have a long history. In his lectures on physical chemistry during the 1930s–1940s, Ya.K. Syrkin noted the fundamental nature of the interaction of matter and light. He emphasized that light can be regarded as a universal, inertialess chemical reagent, whose use and importance will continuously increase.

In recent decades, the work of the Department of Physical Chemistry in the field of photochemistry has been associated with three main areas of both fundamental and applied nature:

- development of photochemical and photocatalytic methods for waste-free and environmentally friendly storage and conversion of solar energy into thermal energy [1, 2];
- fundamental work on the creation of polymethine dyes, comprising molecular ensembles built from colored organic compounds [3–7];
- development and research of physical and chemical processes based on nanosized ordered structures called photonic colloidal crystals (PCCs). Based on these structures, sensors for the selective detection of various chemical objects can be created [8].

The present review aims to summarize works on the creation of multilayer ordered structures from colloidal polymeric microspheres (PM) of submicron sizes, the description of the processes that occur when various substances are deposited on them, and the development of sensors based on them.

PCCs can become an effective means for developing sensors for express analysis, one of the most important tasks in analytical chemistry [9]. PCCs can be formed from various suspensions having a high-volume fraction of colloidal particles (CP) with the participation of external fields, for example, gravitational or electric [10]. Particles of small size can exhibit Brownian motion, moving randomly until the entire ensemble passes into an ordered state. As a result, CPs (often spherical in shape) form

PCCs in which the particles are arranged in a regular packing to form a two- or three-dimensional array.

The presence of periodicity in a PCC structure causes the occurrence of resonance phenomena in them when exposed to radiation; here, it is the characteristic size of the element base (100–500 nm) of the package that leads to the manifestation of such interactions (and, accordingly, structural coloration, i.e., the color of the sample) in the visible light in accordance with the Bragg–Snell law (Fig. 1):

$$m\lambda = 2d_{111}\sqrt{n_{\text{eff}}^2 - n_{\text{air}}^2 \sin^2\theta}\,, \qquad (1)$$

$$n_{\text{eff}} = \sqrt{f_\text{p} n_\text{p}^2 + f_\text{s} n_\text{s}^2}\,, \qquad (2)$$

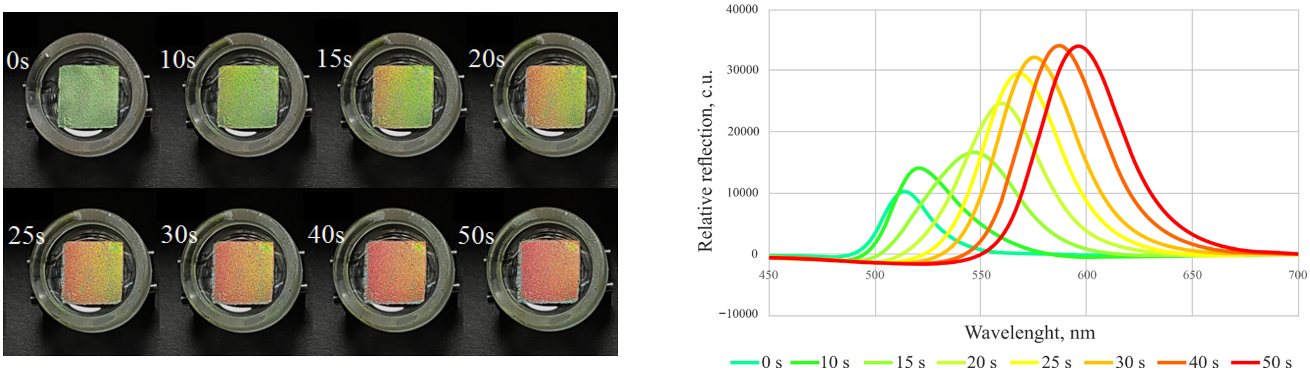
where m is the order of the diffraction maximum; λ is the wavelength of the maximum in the reflected spectrum; d_{111} is the interplanar distance between the (111) crystal planes; n_{eff} is the effective refractive index of the structure; n_{air} is the refractive index of the medium (air) from which light is incident; θ is the angle of incidence; f_p is the volume fraction of particles in the PCC; n_p is the refractive index of particles in the PCC; f_s is the volume fraction of matter (air) in the interparticle space in the PCC; n_s is the refractive index of the substance (air) in the interparticle space in the PCC.

The aim of the present work is to analyze the results of studies on the formation of photonic crystal (PC) structures from PMs, the mechanisms of spectral shifts upon selective reflection of non-monochromatic incident radiation from them in the visible and infrared light, and the use of these structures as sensors for detecting chemicals with similar structures.

CHEMICAL SENSORS BASED ON PCC

The analytical signal in PC sensors represents a shift in the maximum of the spectrally selective reflection band, which is recorded as a hypsochromic or bathochromic shift, as well as a change in the reflection intensity (hyper- or hypochromic effect). Spectrophotometers for specular and diffuse reflections are used to obtain a spectrum with high resolution. An illustrative example of such a bathochromic shift is the shift of the reflected radiation peak when *n*-octane is deposited on a PC made of polystyrene microspheres (Fig. 2). Similar dependencies are also observed in the study of other hydrocarbons, for example, toluene [11].

Fig. 1. Photographs of photonic colloidal crystals (PCCs) from polystyrene microspheres of different diameters: (1) 180 nm, (2) 200 nm, (3) 220 nm, (4) 230 nm, (5) 240 nm, (6) 260 nm.



(a) (b)

Fig. 2. Shift of the selectively reflected radiation from the surface of a photonic crystal during treatment with *n*-octane (a) and the corresponding normalized reflection spectra (b) in dynamics.

Using aromatic and aliphatic hydrocarbon vapors, the kinetic dependencies of the peak shifts from the PCC surface are also determined under the influence of volatile organic compounds on them during the course of the experiments [12]. PC-based sensors represent crystalline colloidal arrays of submicron polystyrene particles embedded in a polydimethylsiloxane matrix by the self-assembly method [13, 14]. In the case of applying a drop of a substance (for example, *p*-xylene) directly to the crystal surface, gradient color changes are observed. In the experiments, the reflection band of the PCC sensor was also found to broaden with an increase in the applied sample volume above a certain limit, resulting in a visual whitening of the crystal. This effect makes it impossible to register the spectral shift of light reflection. With prolonged exposure to substances, especially liquid samples of aromatic hydrocarbons, degradation of the treated area of the sensor occurs due to softening and adhesion of polystyrene particles [15], which leads to a visual clouding of the PC array and degeneration of the maxima in the spectra (Fig. 3).

When using PCC-based sensors, it is the registration of a low vapor concentration of volatile organic compounds in dynamics (online) that is of the greatest interest, since in this case there is no significant degradation due to the dissolution of polymer particles.

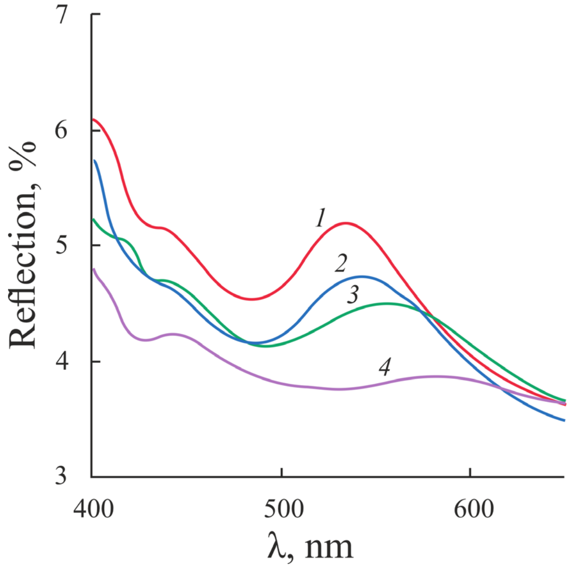


Fig. 3. Effect of liquid *p*-xylene on the photonic crystal sensor; three areas of change in the diffuse reflection spectrum along the radius of the treated spot: (1) untreated area; (2) and (3) affected areas; (4) degraded area in the center of the spot [11].

FORMATION OF THE PCC

Colloidal polystyrene particles that make up PCC with a narrow size distribution are obtained by emulsion polymerization in the presence of an anionic surfactant [16] (Fig. 4).

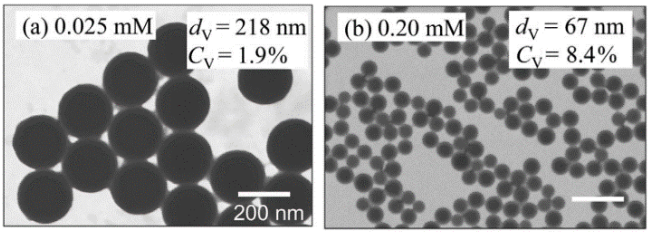


Fig. 4. Transmission electron microscopy images of polymer nanoparticles prepared by emulsion polymerization of styrene in the sodium octadecyl sulfate solutions with concentrations of (a) 0.025 mM and (b) 0.2 mM. The concentrations of styrene and ammonium persulfate were 0.3 M and 20 mM, respectively. Each scale bar shows 200 nm [16].

These particles arrange ordered arrays in the form of colloidal crystalline structures. Such arrays can be obtained in different ways. Although methods based on solvent evaporation [17–19], crystallization in a matrix [20], and sedimentation [21] are most widely used, films of the highest quality are mainly formed by vertical deposition [22, 23]. However, the low rate of film formation (in some techniques requiring from several weeks to months to form a sample) still remains one of the barriers hindering the entry of PC to markets.

One of the possible solutions to the problem is the deposition of colloidal crystalline coatings by electrophoretic deposition (EPD). The essence of the technologically-advanced EPD process, which is used in many areas of industry, lies in the migration of PCs in a liquid under the influence of an electric field; that is, using electrophoresis, followed by deposition on an electrode (Fig. 5).

By studying the EPD process using reflectance spectrophotometry in the visible wavelength range, a number of stages that accompany the formation of ordered colloidal arrays can be identified (Fig. 6) [24].

There are four such stages in colloidal crystallization (Fig. 7).

At the first stage, a concentrated disordered colloidal suspension acquires an ordered structure of a loosely packed colloidal crystal due to the Alder phase transition, after which a Bragg diffraction peak and structural color appear. At the second stage following the evaporation of the solvent, the

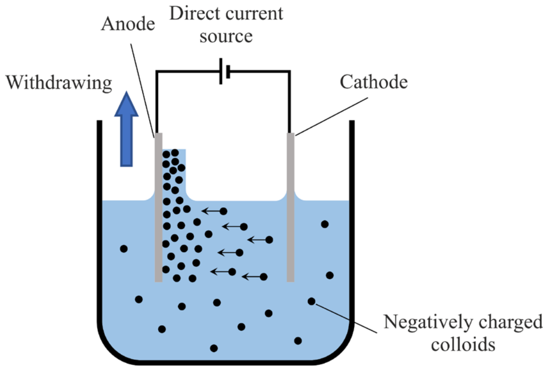
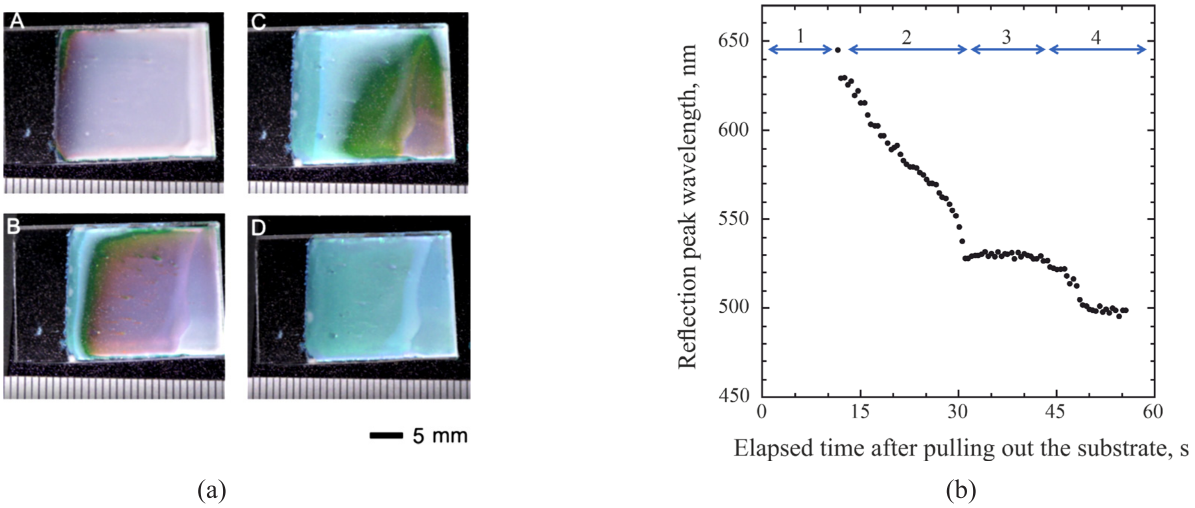


Fig. 5. Scheme of electrophoretic deposition (EPD) of negatively charged particles [17].

maximum of the selectively reflected radiation shifts to the short-wavelength region due to a decrease in the distance between the particles of a loosely packed colloidal crystal. This peak shift continues until a close-packed colloidal crystal lattice is formed. The evaporation of liquid film covering the PCC, which occurs at the third stage, does not change the position of the diffraction peak for some time. However, the complete drying of the colloidal crystalline film at the fourth stage leads to a hypsochromic shift in the structural color of the film (Fig. 7) as the solvent evaporates from the interparticle spaces of the PCC. Such a change in color is associated with a change in the effective refractive index of the medium (1).



(a)

(b)

Fig. 6. (a) Photographs of various colloidal crystallization stages (A) 11.5 s, (B) 25 s, (C) 35 s, (D) 55 s. (b) Position of the maximum of the spectrally selective reflection as the dispersion medium evaporates [24].

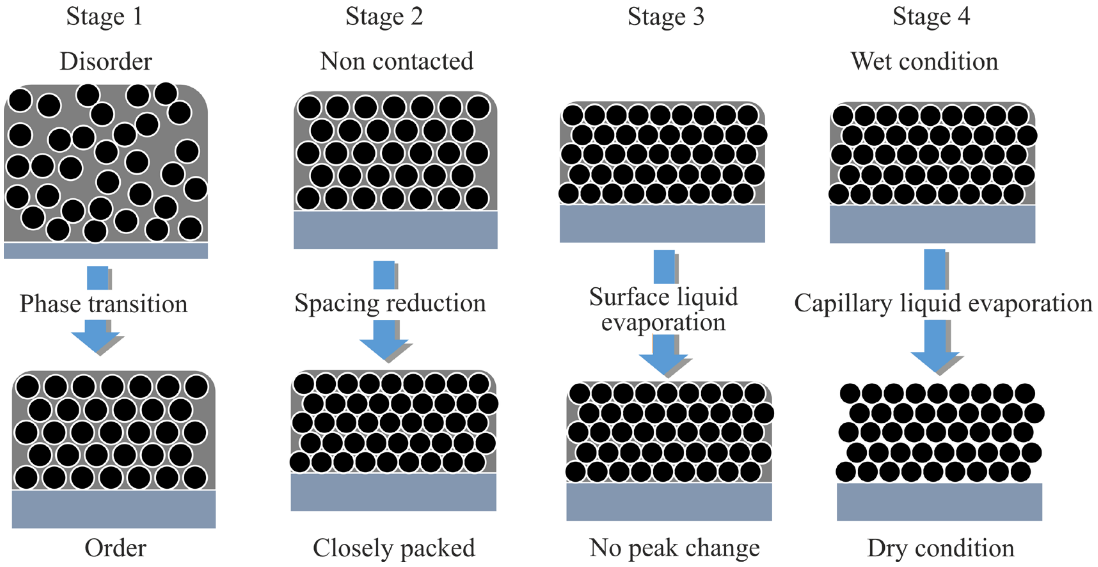


Fig. 7. Schemes of EPD stages [24].

KINETIC STUDY OF THE CP SWELLING PROCESSES IN PCC

The main disadvantage in the interaction of detectable substances with the PC surface is the lack of data on their kinetics due to the small sizes of CPs (<1 μm). As a rule, the observation of ordered structures and their changes when substances are applied to them is carried out using scanning electron microscopy or atomic force microscopy. However, such methods cannot be used in visualizing the kinetics of the interaction of chemicals with PCC to determine the relationship between the spectral responses of reflected radiation and changes in the morphology of CP, i.e., PM, affecting the optical properties of the entire package.

The behavior of PCCs when exposed to various chemicals strongly depends on the properties of the CPs that form them, such as the size distribution of particles, the presence of surfactants, and a number of other factors that affect their surface properties. This affects the rate of diffusion processes that result in a swelling of colloidal microspheres in PCCs and changes in their sizes (parameter d in Eq. (1)), which, in turn, affects the rate of change in the reflection spectrum from the PCC surface. Therefore, the study of the individual CP swelling dynamics is an extremely important task for analyzing the behavior of FAs under the action of chemicals.

The porous medium of CP has a very complex structure, which can be considered in fractal terms. Due to the geometry of the pores and their distribution over the volume, the diffusing substance performs complex movements when migrating through the pore channels. In this case, diffusion in a porous medium can be expected to be similar to anomalous diffusion occurring in the motion of elementary particles under the action of various force fields [25].

Thus, to study the kinetic processes of spectral shifts in PCCs, it is necessary to study the diffusion processes of substances in CPs, which are accompanied by their swelling. The methods of scanning electron microscopy and atomic force microscopy cannot be used to study the dynamics of processes in PCC; this is particularly true of the particle swelling processes under the action of deposited substances in real time. However, optical observation methods in the visible wavelength range can be used to eliminate this disadvantage. As model objects, CPs are selected for observation from the same material as particles for PCC in the visible light (submicron sizes), but with significantly larger diameters in order to visualize the dynamics of CP swelling.

In this case, the observation tool is an optical microscope [26]. In the experiments, CPs with an average diameter of 213 μm were used. When various substances are applied to such particles, the latter swell with visual changes in their size over time (Fig. 8). Such model experiments can be used to compare the kinetics of changes in the spectra [11] with the dynamics of swelling of microspheres and relate these kinetics with changes in wavelengths according to Eqs. (1) and (2). Differences in the sizes of the CPs for PCs determine the differences in the bands of the photonic band gap for PCCs of submicron and submillimeter particles. For submicron particles with sizes up to 300 nm, the photonic band gap is in the visible light, while, for particles larger than 100 μm, the gap occurs in the frequency band below 1 THz. Here, the optical properties of PCCs in terms of the spectral selectivity of radiation reflected from the surface are retained for both cases [27]. Therefore, submillimeter particles can be selected as objects for modeling the dynamics of changing the period of a PC as a diffraction grating.

To obtain images of CP during the swelling process, a setup is used, consisting of an optical microscope with various magnification factors, as well as a video camera connected to a computer for receiving and recording images from it.

All experimental time dependencies of the microsphere diameters with the introduction of various substances (aromatic hydrocarbons) into them have a similar shape (Figs. 9 and 10).

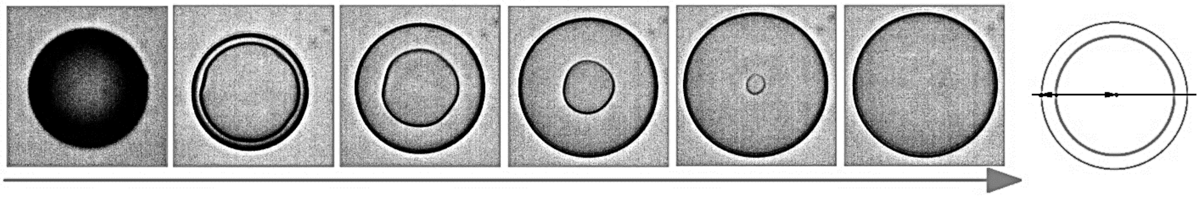


Fig. 8. Photos of the swelling process of colloidal particles from polystyrene d = 213 μm in a solvent.

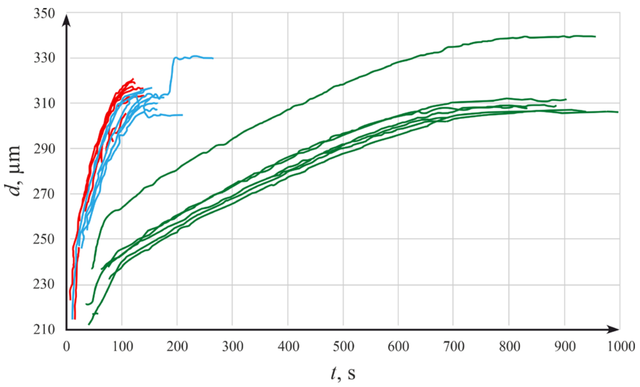


Fig. 9. Time changes in the diameters of polystyrene microspheres $d = 213 \pm 6$ µm upon swelling in benzene (red), toluene (blue), and o-xylene (green).

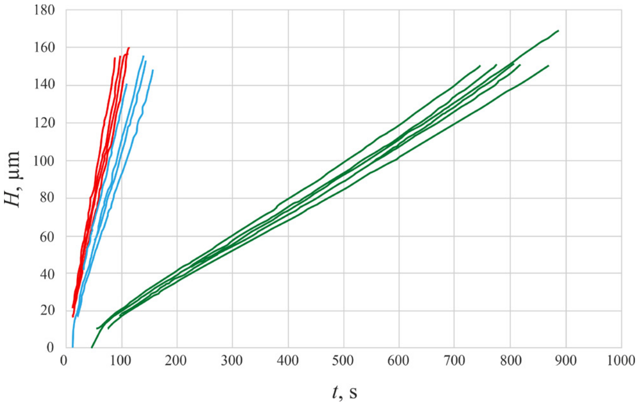


Fig. 10. Time changes in the thickness of the swollen layer (H) of polystyrene microspheres with $d = 213 \pm 6$ µm upon swelling in benzene (red), toluene (blue), and *o*-xylene (green).

SIMULATION OF THE KINETICS FOR CP SWELLING

The curves in Fig. 9 represent a family of sigmoidal curves, indicating anomalous processes occurring during the diffusion of organic nonpolar solvents into colloidal microspheres [15, 28]. At the same time, mathematical models for non-stationary modes of diffusion in media containing pores require a special solution of a set of differential equations [25, 29].

The experimental dependencies of the PM size changes due to diffusion of solvents on time (Fig. 9) are converted into the PM size rate υ_{V_i} (3):

$$\upsilon_{V_i} = \frac{V_{i+1} - V_i}{t_{i+1} - t_i}, \tag{3}$$

where V_i is the PM volume at time t_i.

This dependence υ_{V_i} can be used to determine changes in the PM size rate. The graph of the function υ_{V_i} for a microsphere with an initial size of 213 µm during the diffusion of paraxylene into it is shown in Fig. 11.

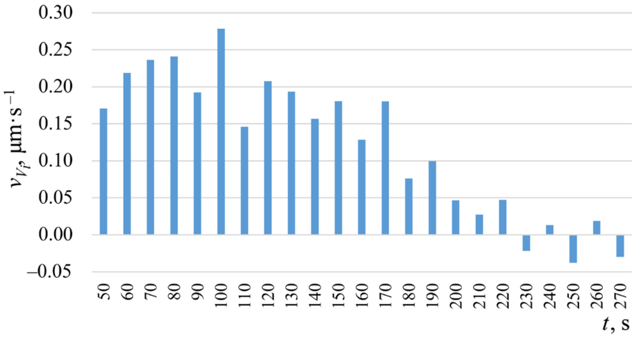


Fig. 11. Graph of the swelling rate υ_{V_i} of a polystyrene microsphere with the initial size of 213 µm during *p*-xylene diffusion.

In this case, diffusion into porous structures is characterized by strong interactions of the diffusing substance with PM, as well as unpredictable and anomalous transport processes in time, which generally deviate from the corresponding standard laws [30]. This approach in the analysis of the kinetics of diffusion processes can be represented in the form of fractional differential equations, whose solutions are apparently better adapted for such problems. At the same time, the replacement of the local time derivative with a fractional operator in the diffusion equation well describes the anomalous transport processes in porous media. For axisymmetric objects, spatial solutions in such models can have a dimension equal to one.

If the mass flux of the diffusing substance is proportional to the fractional derivative of the concentration c with respect to the spatial coordinate r [31], then the spatial derivative in the classical Fick diffusion equation should be accompanied by the additional inclusion of temporal nonlocality effects by introducing a fractional derivative with respect to time t. The non-local character of the change in the mass flow over time has been confirmed by numerous theoretical and experimental studies [30, 32, 33].

In this case, for the mass flux J_c [30] (4):

$$J_c = D_f \partial_t^{1-\gamma}\left(\frac{\partial^{\beta} c}{\partial x^{\beta}}\right), \ \gamma > 0, \ \beta < 1, \tag{4}$$

where D_f is the effective diffusion coefficient (subscript f means the distinguished spatial direction of diffusion); x is the diffuse flux; γ and β indicate the order of time and spatial fractional derivatives; respectively.

If in Eq. (4) the effective diffusion coefficient D_f is represented as a function of the spatial coordinate r, then the diffusion equation $\partial c/\partial t = -\partial/\partial r\,(J_c)$ in a porous medium can be rewritten as follows (5):

$$\frac{\partial c}{\partial t}=\frac{D_f}{r^{d_f-1}}\frac{\partial}{\partial r}\left(r^{d_f-1-\theta}\frac{\partial c}{\partial r}\right), \tag{5}$$

where d_f is the fractal size; θ is the anomalous diffusion index (the fractional derivative of the concentration with respect to the spatial coordinate).

The solution of Eq. (5) agrees well with the results of exact diffusion calculations performed by the fractal method using Sierpiński triangles [34].

The solution of differential Eqs. (4) and (5) is a combination of gamma functions [35], involving the choice of the corresponding parameters D_f, β, γ and initial conditions. If we represent the solution of Eq. (5) in the form of the lower incomplete gamma function (6):

$$\gamma(m,x)=\int_0^x \alpha^{m-1}e^{-\alpha}d\alpha, \tag{6}$$

where α and m are the integration parameters, and x is the upper limit of the γ-function, then the integrand is the product of the exponential and the other exponential functions that determine the rate of change in the concentration of the diffusing substance inside the PM.

Assuming a linear nature of the relationship between the rate of mass transfer of a substance and the change in volume V of the CP during their swelling $\partial c/\partial t = K\,\partial V/\partial t$, we can write the integrand function (6) $\left(\frac{t}{t_0}\right)^m e^{-k\left(\frac{t}{t_0}\right)}$ in the form (7) with the coefficients k and m as parameters that determine the rate of volume change υ_V CP:

$$\upsilon_V = KV_0\exp\left[-k\left(\frac{t}{t_0}\right)\right]\cdot\left(\frac{t}{t_0}\right)^m = KV_0\exp(-k\alpha)\alpha^m, \tag{7}$$

where V_0 is the initial volume of CP; K is the coefficient of proportionality; $\alpha = t/t_0$; t is the current time; t_0 is the saturation time of the CP with the diffusing substance. The parameters m and k were selected by superimposing function (5) on the experimental graphs shown in Fig. 9.

Function (7) has an extremum at point (8):

$$\frac{d\upsilon_V}{d\alpha}\Big|_{\alpha=\alpha_c}=0\,. \tag{8}$$

Then, using Eq. (9), we can derive the time of maximum swelling rate of PM t_c (10):

$$-k\alpha+m=0;\ \frac{t_c}{t_0}=\frac{m}{k}, \tag{9}$$

$$t_c=t_0\frac{m}{k}\,. \tag{10}$$

Figure 12 shows a theoretical approximation of the rate of change in the size of the PM.

Thus, the extraction of data on an individual substance can be carried out by differences in the swelling time of the CP, corresponding to the rate of diffusion of these substances in the PM and manifesting itself in different rates of spectral shifts of the reflected radiation from the surface of the PCC.

DEGRADATION OF REFLECTED RADIATION FROM PCC

In the section on chemical sensors based on PCC, it was shown that the reflection band of the PCC sensor broadens when the sample volume

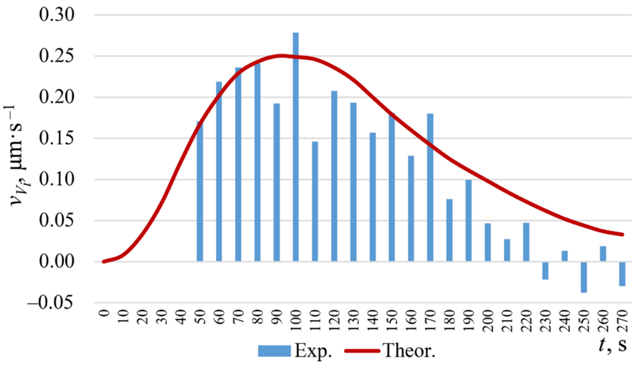


Fig. 12. Experimental graph and theoretical curve of the swelling rate of PM with a diameter of 213 ± 6 µm within p-xylene: $k = 6$; $m = 2.6$; $t_0 = 220$ s; $t_c = 95.3$ s.

applied to the crystal exceeds a certain limit, resulting in a loss of ability on the part of the crystal to selectively reflect non-monochromatic light from its surface. This occurs due to the processes of degradation of the structure of the PC during repeated application of samples of chemical substances to it. In [15], processes are described that lead to a change in the properties of CPs that form PCCs; this, in turn, changes the intensity of radiation reflected from the surface of the crystal as a whole. For example, Fig. 13 shows two electron micrographs of PCCs from polystyrene microspheres of submicron sizes (~240 nm) both before applying the substance and after the PCCs lose their optical properties.

A comparison of sections of electronic images (Fig. 13) reveals more blurred edges of individual CPs in the right image than in the left one. Such blurring indicates the smoothness of the microsphere surface following diffusion of the substance penetrating into them. To visualize the kinetics of these processes, polystyrene microspheres 213 ± 6 μm in size were chosen as model CPs. Following treatment of microspheres with a substance (toluene), an increase in the size of microspheres occurs due to the straightening of macromolecules when a substance is introduced into them and the concomitant change in the structure of internal pores.

The study [36] showed that uniaxial deformation of polymer films with a thin layer of hard coating deposited on them is accompanied by the appearance of a regular microrelief on it, followed by its destruction. In this case, the microrelief is always oriented along the tension axis of the polymer chains and located perpendicular to the cracks in the damaged coating. As is known, when rubber-like polymers are stretched, their volume hardly changes. Instead, significant lateral compression occurs, causing the coating to deform in a direction perpendicular to the tensile axis of the polymer. As a result of compression, the hard coating loses its stability, leading to the appearance of a microrelief.

The images of swelling and contraction of polystyrene microspheres following the introduction of the analyte (toluene) are shown below in Figs. 14.

Due to inelastic deformation following evaporation of the substance, the surfaces of the polystyrene microspheres are compressed to produce additional roughness (Fig. 15). This causes greater scattering of the incident radiation on the PCC surface, which introduces additional noise into the reflected radiation.

Thus, the degradation of PCC under the action of substances can be divided into the following stages:

- swelling of CP with formation of dense packing;
- an increase in the friability of the CP surface under the action of a substance, increasing the scattering of the incident radiation and reducing the spectralefficiency of the Bragg reflection from the PCC surface;

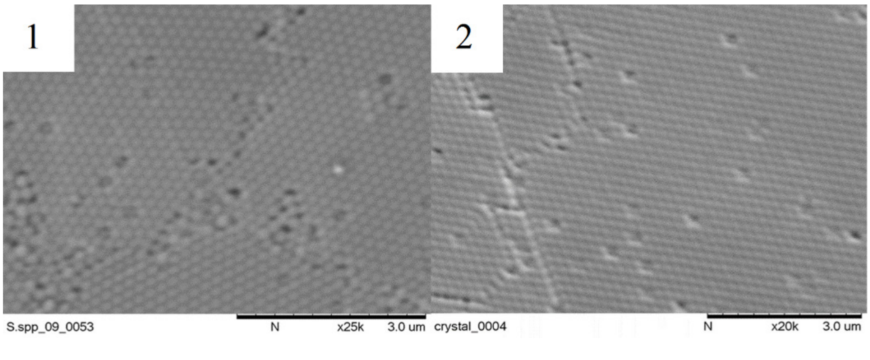


Fig. 13. Scanning electron microscope images of PCCs: (1) before the application of the analyte, (2) after the degradation of PCCs [15].

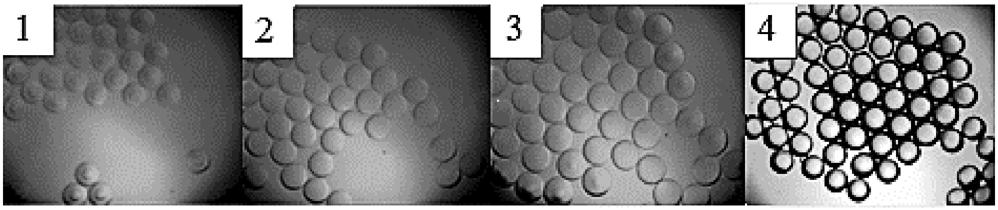


Fig. 14. Images (1) and (2) represent swelling of PCC from polystyrene CPs; (3) and (4) show compression following evaporation of the substance (toluene) from the PCC [15].

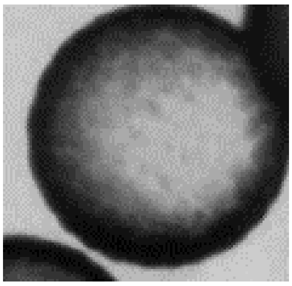


Fig. 15. Loose surface of the microsphere following the evaporation of toluene from its volume [15].

- the friability of CP is accompanied by a decrease in their hardness, which leads to the "pressing" of microspheres into each other (Fig. 16). This reduces the depth of slits in the formed reflective diffraction grating during the interaction of coherent reflected waves from the PCC surface.

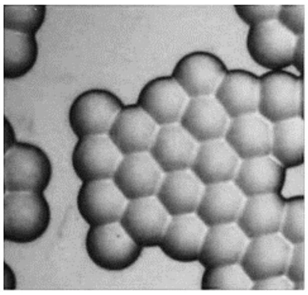


Fig. 16. The "pressed in" structure of the PCC, after the dose of the analyte is exceeded maximum [15].

CONCLUSIONS

Developments undertaking by the authorial team of researchers in recent years, carried out at the Ya.K. Syrkin Department of Physical Chemistry of the IFCT of the RTU MIREA, have been presented. Issues related to the detection of substances with similar chemical structure using CP-based sensors made from CP are considered. The particles are PMs 160–300 nm in size. Detection occurs in the visible wavelengths due to the registration of the spectral shift of the reflected radiation from the surface of the crystal when substances are deposited from the liquid or gas phase. Such crystals can be obtained by the EPD method: by migration of CPs in a liquid under the action of an electric field, followed by their deposition on an electrode. Special additional coatings are used to protect the PCCs obtained from the negative influence of the external environment.

In order to separate substances that are close in chemical structure, it is necessary to use the differences in the kinetics of spectral shifts of reflected radiation from the of photonic colloidal structure surfaces, which is directly related to the diffusion of substances in the CPs that form them. The kinetics of spectral shifts in PCCs are related to processes of diffusion of substances in CPs, which are accompanied by their swelling. For studying the properties of PCs formed from submicron particles, scanning electron microscopy and atomic force microscopy methods are mainly used. However, these approaches cannot be used to study the dynamics of processes in a PCC, in particular, the processes of swelling of particles under the action of a substance in real time. However, by using optical observation methods in the visible wavelength range, this disadvantage can be eliminated.

To visualize the dynamics of CP swelling processes, CPs made of the same material as the particles for PCC in the visible range, but having much larger diameters (213 μm), were chosen as model objects. In this case, the instrument of observation is an optical microscope. When substances are applied to such particles, the latter swell with visual observation of changes in their size with time.

Experimental curves of the polymer particle swelling during the diffusion of chemical substances in them reveal information about the kinetics of these processes. At the same time, the complex structure of the particles themselves significantly complicates the description of these processes. empirically selected coefficients, permits a description with sufficient agreement of the kinetics of diffusion processes of nonpolar organic substances into such polymer particles. The peak position of the swelling rate curve in time forms a basis for identifying substances of the same class, as well as distinguishing between substances that are similar in chemical structure and deposited on a PC. In this case, the repeated application of such substances to PCs leads to a degradation of their optical characteristics caused by changes in the morphological properties of such ordered structures. Such changes are due to the looseness of the surface of CPs during their swelling under the action of substances diffusing in them, which is accompanied by a change in the morphology of the entire crystal as a whole, reducing the spectral efficiency of Bragg reflection from its surface. A decrease in the hardness of the CP leads to a visual clouding of the PC and a degeneracy of the maxima in the reflection spectra. In this case,the use of such structures as sensors of chemical substances is no longer possible.

Further development of similar sensors involves increasing their sensitivity and selectivity, as well as reducing the response time to the injected substance. An important additional task in the development of engineering systems using such devices involves an increase the number of cycles of PC-based sensors.

Authors' contribution

All authors equally contributed to the research work.

The authors declare no conflicts of interest.

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