Preparation of inverse photonic crystals by ETPTA photopolymerization method and their optical properties

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Abstract. Inverse photonic crystal films were prepared by photopolymerization of ethoxylate trimethylolpropane triacrylate (ETPTA) using opal-type templates. Their high quality was proved by investigations of structural and optical properties. The unexpectedly high refractive index, \( n_{\text{ETPTA}} \approx 1.67 \), of polymerized ETPTA was obtained from a numerical approximation of the spectral positions of the reflectance peak of the films at different incidence angles. Fabricated samples were tested as sensors for water-ethanol mixtures, and a monotonous increase in the stop band shift with an increase in ethanol concentration was established.

1. Introduction
Since the beginning of the study of opal-type photonic crystals (PhCs) in the pioneer publication [1], it was found that inverse PhCs, consisting of close packed empty microspheres in a dielectric medium, have better properties. Despite the variety of materials and methods of inversion [2], a great problem is the preservation of the quality of the template structure after the inversion procedure. Especially strong degradation of the structure can be caused by annealing and sintering. That is why soft techniques, such as photo-curable resin polymerization, are very desirable. Good results in PhCs preparation gives a self-assembly of microspheres inside the ETPTA resin, followed by its photopolymerization [3-7]. In the present publication, we consider an alternative method of preparation of inverse ETPTA films using opal-type templates and demonstrate the possibilities of their application as liquid mixture sensors.

2. Experimental

2.1. Materials and apparatus
All chemicals, including TEOS (99%, Sigma-Aldrich), 95% ethanol, 25% aqueous ammonia, ETPTA (Sigma-Aldrich) containing approximately 2 wt. % of 2-hydroxy-2-methyl-1-phenyl-1-propanone (Sigma-Aldrich) as a photoinitiator, were used as received. The microstructure of the surface and the transverse cleavage of inverse films were studied by scanning electron microscopy (SUPRA 50 VP, Carl Zeiss, Germany) with the accelerating voltage of 5–21 kV (SE2 detector). Fourier transformed infrared (FTIR) spectra were recorded using a Perkin Elmer Frontier spectrometer at room temperature in the 1500 - 3500 cm\(^{-1}\) wavenumber range by...
directly applying sample onto a KBr plate. Optical properties of the samples were analyzed in the range from 200 to 800 nm using Perkin Elmer Lambda 950 and Lambda 35 spectrophotometers.

2.2. Synthesis of monodisperse SiO$_2$ microspheres and deposition of opal films
Monodisperse silica particles of various sizes were synthesized through sol-gel chemistry using the recipe of the method of seeded growth described in [8]. Initial nuclei ~ 35 nm in diameter were synthesized by the Stöber method [9]. As a result of the growth, the diameter of particles exceeds 200 nm and the dispersion of their size decreases. Opal films were grown on the glass coverslips (Menzel-Gläser) during 14 days by vertical deposition method [10]. The coverslips were prewashed thoroughly in ethanol and acetone. Properties of deposited films were described elsewhere [11].

2.3. Procedure of structure inversion
Inversion of PhC films was performed in three main steps: 1) infiltration of the opaline film with liquid ETPTA monomer by its capillary raising inside a planar gap, which is formed by two glass slides separated by 40 μm m spacers (sandwich method); 2) photopolymerization of ETPTA by UV irradiation and 3) removal of SiO$_2$ microspheres by etching in 8 vol. % HF for 1 min. The obtained ETPTA films of 40 μm thickness consist of two layers: a thin layer with inverse opal structure and a thick layer without it. The latter plays the role of the substrate for the former. The control of the polymerization was carried out by the registration of characteristic FTIR peaks assigned to acrylic C=C bonds (1620–1640 cm$^{-1}$) (Fig. 1). Before UV irradiation, the peaks located at 1620 and 1638 cm$^{-1}$ are clearly observed in accordance with Ref. [12], while after the irradiation they disappear, indicating the successful completion of ETPTA polymerization. Other peaks near 2970 and 2880 cm$^{-1}$ correspond to the stretching vibrations of methyl and methylene groups and the peak at 1750 cm$^{-1}$ - to the stretching vibration of ester carbonyl.

![Figure 1. FTIR spectra of ETPTA acrylic C=C bonds before and after UV irradiation (red solid and green dotted curves, correspondingly).](image)

3. Results and discussion
SEM images of SiO$_2$ colloidal crystal template and inverse ETPTA film are shown in Fig. 2. The cross-section shown in the inset to Fig. 2b demonstrates the excellent structural quality of the inverse film throughout its thickness. The regularity of the structures, despite the small film thickness and the presence of some defects, leads to high specular reflection peaks corresponding to the photonic stop bands (Fig. 3).
Figure 2. (a) SEM image of the surface of the opal film composed of 230 nm SiO$_2$ microspheres; (b) Surface of the inverse ETPTA film. In the inset a cross-section of the same film is shown.

The stop band position of the opal structure can be described using the Bragg-Snell law [13]:

$$\lambda = 2d_{111} \sqrt{n_{\text{eff}}^2 \sin^2 \theta}$$

where $\lambda$ is the wavelength of the reflection peak, $\theta$ is the incidence angle, $d_{111}$ is the distance between neighboring planes with hexagonal packing and $n_{\text{eff}}$ is the effective refractive index of the structure. Two parameters $d_{111}$ and $n_{\text{eff}}$ can be determined from a linear approximation of $\lambda^2$ vs. $\sin^2 \theta$ dependence. For the data shown in Fig. 3b, we got $d_{111} = 211 \pm 3$ nm and $n_{\text{eff}} = 1.21 \pm 0.02$. In the effective medium model:

$$n_{\text{eff}} = \sqrt{n_{\text{etpta}}^2 V_{\text{etpta}} + n_{\text{air}}^2 (1-V_{\text{etpta}})}$$

where $n_{\text{etpta}}$ is the refractive index of ETPTA, $V_{\text{etpta}} = 0.26$ is the volume fraction of ETPTA and $n_{\text{air}} = 1$. Correspondingly, a value $n_{\text{etpta}} \approx 1.67$ can be derived from $n_{\text{eff}}$. This value is much higher than the refractive index of the ETPTA monomer close to 1.47 and allows us to consider ETPTA as a very promising photoresist for PhCs construction.

Figure 3(a, b). (a) Reflectance spectra recorded at 8$^\circ$ incidence angle for the silica opal film (dashed line) and the inverse ETPTA film (solid line); (b) Plot of $\lambda^2$ vs. $\sin^2 \theta$ (see the text). The straight line approximates the experimental data.

According to Bragg’s law, the stop band position of PhCs shifts with the effective refractive index, making them promising materials for refractive index sensing. Fig. 4 demonstrates the use of our inverse film as a sensor. The transmittance spectra are recorded for one and the same film impregnated
by various water-ethanol mixtures. The stop band position is monotonically shifted with increasing ethanol concentration. This is not a trivial result, because the refractive index of an 80% ethanol solution is greater than that of absolute alcohol, and this is one of the main problems for alcohol refractometry. Our sensor solves this problem. The cause is probably related to a stronger ethanol absorption by ETPTA [7].

Figure 4(a, b). (a) Transmittance spectra of inverse ETPTA PhC films soaked in water-ethanol mixtures with various ethanol volume fraction (0 % corresponds to pure water); (b) Dependence of the spectral position of the transmittance dip on the ethanol concentration.

4. Conclusions
ETPTA photopolymerization is a suitable process for soft inversion of opal-type films, preserving the structural quality of the template. A high refractive index $n_{\text{ETPTA}} \approx 1.67$ was determined for the polymerized state of ETPTA. Inverse films with excellent photonic crystal properties were obtained. Their use as PhC sensors was tested for water-ethanol mixtures, and the monotonous increase in the stop band shift with increasing ethanol concentration was established.

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