Optical Materials 36 (2014) 932–935

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Determination of refractive index and concentration of iodine solutions using opals

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ARTICLE INFO

Article history:
Received 13 August 2013
Received in revised form 16 December 2013
Accepted 24 December 2013
Available online 10 January 2014

Keywords:
Photonic crystals
Opal
Optical spectroscopy
Refractive index
Ethanol-iodine solutions

ABSTRACT

The determination of refractive index of iodine-ethanol solutions using SiO_2 opals has been presented. For the first time concentration of solution iodine in ethanol has been determined by applying a simple method of using opal and de Feijter's relation. Basing on wavelength of diffraction peaks the appropriate formula describing concentration of iodine ethanol solution has been evolved. The uncertainty of the determined concentration has been established, too. The coefficient $dn_c/dC = 0.0201(4)$ (% w/w^{-1}) of the linear dependence between refractive index and the concentration of iodine solution has been determined. The procedure of calibration of the used opal sensor is described. The opal sensor is not distracted by the measurement and can be used repeatedly.

1. Introduction

All over the world the investigations of photonic structures called photonic crystals (PCs) are performed [1]. These crystals have potential applications in optoelectronics, e.g. optical filters, antireflective surface coatings, lossless frequency selective mirrors. Despite this, opals can serve as sensors, e.g. they are sensitive to glucose at physiological concentrations [2].

Characteristic feature of opals is the presence of diffraction peak in the reflectance spectra. Its position depends on the size of nanospheres (D) building opal, refractive index (n_{sph}) of nanospheres, filling factor (f) and refractive index (n_{medium}) of material filling the spaces between them. This fact may be used for structural studies of opal, where it is filled with a liquid of known refractive index. It can also be used to determine the refractive index of the liquid, if the size and filling factor of nanospheres are known. So, one can exploit opal as a sensor of refractive index of different liquids. There are many methods of determining of refractive index of solutions. Most of them are based on the measurement of transmission. However, not for all solutions, especially at high concentration, transmittance is measureable. The main aim of this work is using opals for determining of refractive index of iodine solutions and applying this knowledge as a method of determining iodine concentration in unknown ethanol solutions. Control of iodine concentration in ethanol solution is useful for optimization of chemical processes, e.g. sonochemical fabrication of antimony sulfoiodide (SbSI) nanowires [3], antimony selenoiodide (SbSeI) nanowires [4], as well as $Sb_xSe_{1-x}SI$ nanowires [5] and filling of carbon nanotubes with SbSI [6] and SbSeSI [7].

2. Experiment

Monodisperse silica particles were prepared following the Stöber method [8,9]. This method generally proceeds with the hydrolysis and condensation of tetraethylorthosilicate (TEOS) [$Si(OR)_4$ with $R = C_2H_5$] in a mixture of alcohol and water, with ammonia used as a catalyst. TEOS (99%) (purchased from Aldrich Chemical Co.) as well as ethanol (96%) and ammonia (25%) (purchased from POCh, Gliwice) were used as starting materials without further purification. In order to obtain monosize silica spheres, the following working conditions were maintained: constant temperature of reaction (40 °C) and appropriate molar concentrations of the TEOS/NH_3/H_2O reagents. These conditions were chosen in order to reach final diameters of SiO_2 particle in the several hundreds nanometer range. TEOS was added into the thermoregulated round bottom flask containing solution of ethanol, water and ammonia under stirring. The mixture was stirred for 2.5 h with a magnetic stirrer. Subsequently, the silica suspensions were centrifuged at 4000 rpm for 30 min and washed with ethanol. The centrifuging/washing procedure was repeated six times and the final product was well ultrasonically dispersed and stored in the ethanol. For opal fabrication we used gravity sedimentation method [10]. The suspension of SiO_2 spheres in ethanol was poured into plastic

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http://dx.doi.org/10.1016/j.optmat.2013.12.036

vessel. After sedimentation the liquid was removed and the residue was dried at room temperature. The obtained plates of opals had thickness of 0.17 mm. Afterwards the plates of opal were sintered at temperature 1010 °C for 3 h to give the opals higher stability.

The morphology of opal was characterized by scanning electron microscopy (SEM) using Hitachi S-4200 scanning electron microscope. Typical SEM micrographs presented in Fig. 1 confirm the rather good quality of the obtained opal.

Iodine solutions were prepared with ethanol as a solvent. Mixtures of appropriate quantities of iodine and 1 ml of ethanol have been put into hermetic containers and ultrasonically mixed for about 10 min. Maximum weight percentage concentration of iodine solution was $C = 30\%$ w/w (w/w means weight solute/weight total solution after mixing). Preparation of solutions with higher concentrations is much more difficult. Such solutions require much longer time of sonication which significantly increases temperature. This can cause unsealing of containers, uncontrolled evaporation of the solution and unreliable concentration of iodine in the investigated sample.

The spectral investigations of opal's optical reflectance (R) were performed in room temperature using PC2000 (Ocean Optics Inc.,) spectrophotometer with master card with 600 lines grating blazed at 500 nm. Investigations have been performed for wavelengths (λ) from 380 to 1050 nm. The spectrophotometer was equipped with appropriate reflection probe R7x400-2-LOH and the deuterium-halogen light source DH2000-FHS from Ocean Optics GmbH. The opal has been placed on 1 mm thick glass plate and it has been illuminated perpendicularly through the substrate. The multiple averaged spectral characteristics $R(\lambda)$ containing 2048 data points for various wavelengths were registered using the OOI-Base program from Ocean Optics Inc.

The measurement procedure consisted of two stages. The first one was the calibration of used opal. This process required the measurement of reflectance spectra alternately in the dry state and after filling opal with liquids of known refractive indices. We applied ethanol, water and isopropanol because they easily evaporate and allow subsequent measurements for the same opal. In the second stage reflectance spectrum of opal filled with investigated iodine solution was measured. After that opal was washed in ethanol and the whole procedure was repeated for next iodine solution. The washing procedure consists of immersing used opal in container with 5 ml pure ethanol three times for about one minute.

3. Results and discussion

Typical normalized spectra of $R(\lambda)$ registered for dry opal and for opal infiltrated with ethanol, water and isopropanol are presented in Fig. 2. One can identify the Bragg's diffraction peaks

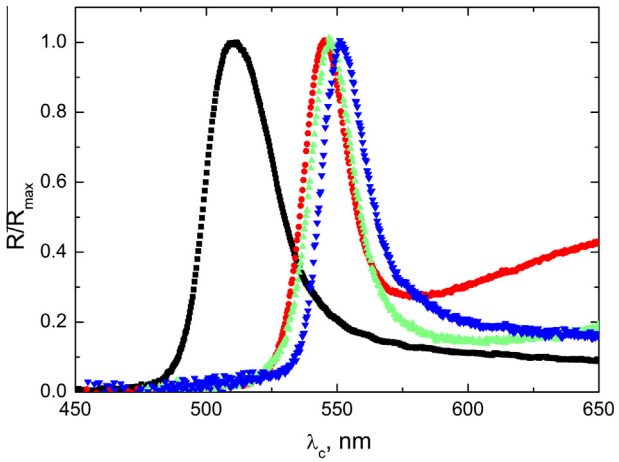

Fig. 2. Normalized spectra of optical reflectance measured for dry opal (■) and opal infiltrated with water (●), ethanol (▲) and isopropanol (▼).

(maxima in $R(\lambda)$). Their positions exhibit red-shift connected with increasing of refractive index of filling media. The same effect is commonly observed [11].

The wavelength of the reflection peak (λ_c) is described by the modified Bragg equation:

$$\lambda_c = 2 \cdot d \cdot \sqrt{n_{\text{eff}}^2 - \sin^2\theta} \tag{1}$$

where $d = \sqrt{2/3} \cdot D$ is the interplanar spacing between (111) planes in photonic crystal, D is diameter of silica spheres, $n_{\text{eff}}^2 = n_{\text{sph}}^2 \cdot f + n_{\text{medium}}^2 \cdot (1 - f)$ is the effective refractive index, f is the filling factor of the spheres, n_{sph} and n_{medium} are the refractive indices of silica nanospheres and the surrounding medium, respectively, θ is the angle of incidence of light. For normal incidence of light upon an opal $\theta = 0°$. According to [12], the refractive index of the SiO_2 spheres produced with the presented above method equals $n_{\text{sph}} = 1.425$.

Therefore,

$$\lambda_c = 2 \cdot \sqrt{2/3} \cdot D \cdot \sqrt{1.425^2 \cdot f + n_{\text{medium}}^2 \cdot (1 - f)} \tag{2}$$

Applying this dependence for known values of n_{medium}, one can calibrate the used opal, i.e. determine diameter D of silica spheres and filling factor f of the opal.

Fig. 3 presents the spectral positions of diffraction peaks in optical reflectance measured for dry opal ($n_{\text{air}} = 1$) and the same opal infiltrated with liquids of known refractive indices ($n_{\text{water}} = 1.33$, $n_{\text{ethanol}} = 1.36$, $n_{\text{isopropanol}} = 1.377$). The measurements have been

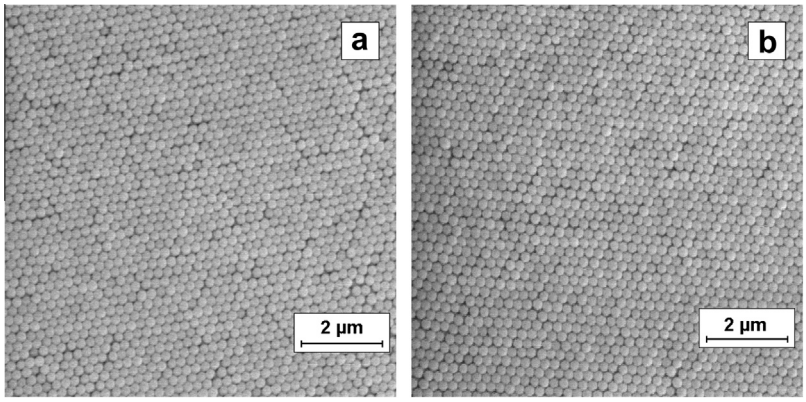

Fig. 1. Typical SEM micrographs of the top surface of an opal composed of silica nanospheres (a) before and (b) after filling it with 30% w/w iodine solution and then washing.

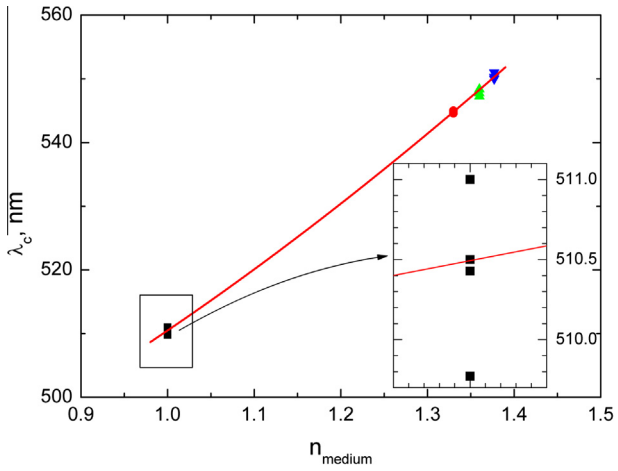

Fig. 3. Wavelengths of Bragg's peaks (shown e.g. in Fig. 2) for dry opal (■) and opal infiltrated with water (●), ethanol (▲) and isopropanol (▼) presented vs. refractive index of the filling medium; solid line represents the least square fitted dependence (2); parameters of the fitting are given in the text; the inset shows accurately results of λ_c measurements performed for dry opal.

performed a lot of times to determine the average values of λ_c and their uncertainties. The inset shows accurately results of these measurements performed for dry opal. One can see that discrepancies between λ_c registered in different experiments are less than 1.2 nm so we can consider the used piece of opal as optically homogenous.

Solid line represents dependence (2) calculated for the least square fitted values of diameter of silica spheres $D = 238.79(45)$ nm and filling factor $f = 0.6927(91)$ of used opal. Every opal should be treated in such a way because of differences between diameters of silica spheres and filling factors.

The obtained value of diameter of silica spheres is comparable with value 244.6(4) nm determined by the method based on angular investigations of optical reflectance described in [12,13].

Fig. 4(a) presents examples of normalized spectra of optical reflectance measured for dry opal and opal filled with various ethanol–iodine solutions. After every filling with iodine solution opal was washed in ethanol and dried. The reflectance spectra registered after such procedure, are presented in Fig. 4(b). Spectra obtained for bare (washed and dried) opal coincide with each other within measurement uncertainty. The morphology of used in investigation bare opal after filling it with 30% w/w iodine solution and then washing is presented in Fig. 1(b) in comparison with as-prepared opal (Fig. 1a). Thus it can be concluded that the opal was not destroyed during the measurements and could be used repeatedly.

The shift of the Bragg's peak to longer wavelengths with increasing weight percentage concentration of iodine solutions (see Fig. 4 and 5(a)) is due to the change of refractive index of the investigated liquid.

Fig. 5(a) also presents the wavelengths of Bragg's peak registered from the same opal infiltrated with pure ethanol before each investigation of iodine solution. These results and SEM image (Fig. 1) prove the possibility of using the same photonic crystal in subsequent measurements as a sensor of iodine solutions in ethanol.

Eq. (2) can be simply transformed into formula:

$$n_{\text{medium}} = \sqrt{\frac{3 \cdot \lambda_c^2 - 8 \cdot D^2 \cdot 1.425^2 \cdot f}{8 \cdot D^2 \cdot (1-f)}} \tag{3}$$

Using the last formula, the observed λ_c and the values of D and f determined during calibration stage one can determine refractive index of the media that infiltrates opal. Also uncertainty Δn_{medium} of the determined value of n_{medium} can be very easily calculated using total differential method:

$$\Delta n_{\text{medium}} = \frac{\lambda_c^2}{\sqrt{n_{\text{medium}}} \cdot D^2 \cdot (1-f)} \cdot \left(\frac{\Delta \lambda_c}{\lambda_c} + \frac{\Delta D}{D} + \frac{3 \cdot \lambda_c^2 - 8 \cdot D^2 \cdot 1.425^2}{8 \cdot \lambda_c^2 \cdot (1-f)} \cdot \Delta f \right) \tag{4}$$

where $\Delta\lambda_c$, ΔD and Δf represent uncertainty of the wavelength of the reflection Bragg's peak, uncertainty of the diameter of silica spheres, and uncertainty of the filling factor, respectively.

Fig. 5(b) presents such calculated refractive indices of the iodine solutions for spectral characteristics and positions of Bragg's peaks shown in Figs. 4 and 5(a). In Fig. 5(b) experimental data have been compared with values of the refractive indices of crystalline iodine ($n_{\text{iodine}} = 3.34$) [14] and pure ethanol ($n_{solvent} = 1.36$) [14]. One can see that the data can be approximated by a linear de Feijter's relation [15]:

$$n_c = a \cdot C + n_{\text{solvent}} \tag{5}$$

where n_c is refractive index for the iodine solution, the concentration of which is C, a is the refractive index increment. Dashed line in Fig. 5(b) represents linear dependence (5) for the least square fitted value of $a = dn_c/dC = 0.0201(4)$ (% w/w^{-1}). Knowledge of this parameter can be very helpful in determining the weight percentage concentration of iodine solution if its refractive index is

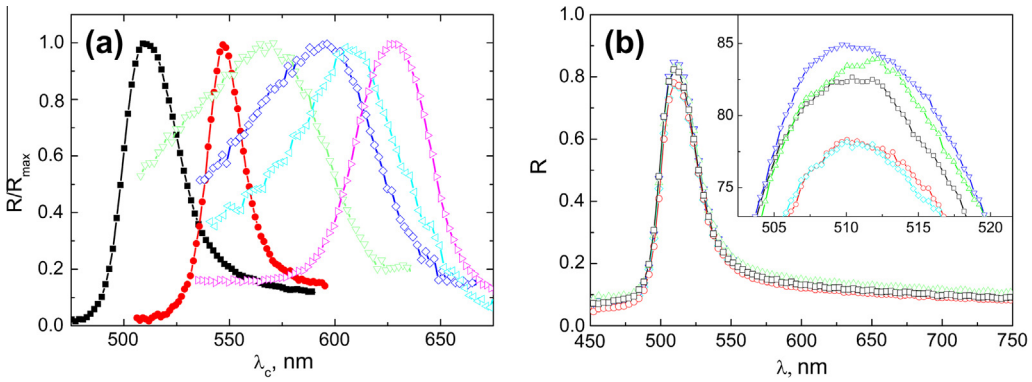

Fig. 4. (a) Spectra of normalized optical reflectance measured for dry opal (■) and opal filled with various iodine-ethanol solutions: ●, $C = 0$% w/w; ▽, $C = 7.89$% w/w; ◇, $C = 9.97$% w/w; ◁, $C = 15.89$% w/w; ▷, $C = 30.05$% w/w; (b) reflectance spectra measured for dry opal: before (□), and after 7th (○), 10th (△), 13th (▽), 16th (◇) filling with iodine solution and washing procedure.

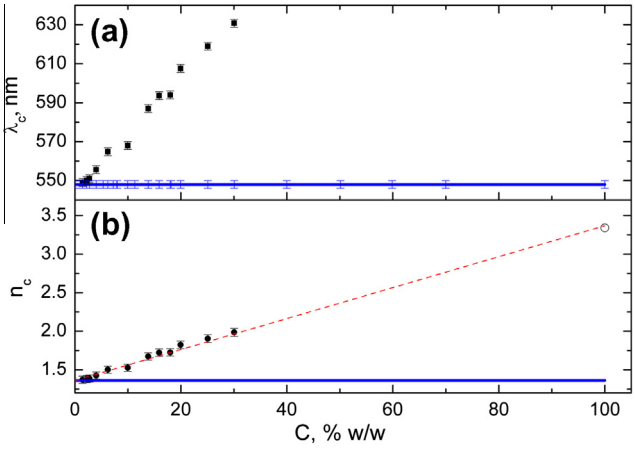

Fig. 5. Spectral positions of Bragg's peaks registered for opal filled with iodine solutions (■, a) and refractive indices (obtained using formulae (3)) of iodine solutions (●, b) vs. their weight percentage concentrations; ○, refractive index of crystalline iodine [14]; dashed line represents the least square fitted dependence (5). The fitted value of the refractive index increment is given in the text; horizontal lines represent averaged wavelength of Bragg's peaks registered for opal infiltrated with pure ethanol before each investigation of iodine solution (a) and refractive index of ethanol (b), respectively.

established, e.g. from the λ_c position of Bragg's peak using an opal. In this case, Eq. (5) can be converted to the form:

$$C = \frac{n_c - n_{\text{solvent}}}{a} \tag{6}$$

Uncertainty of this value can be also very easily calculated using total differential method:

$$\Delta C = \frac{1}{a}(Cp\Delta a + \Delta n_c) \tag{7}$$

where Δn_c and Δa represent uncertainty of the refractive index for the iodine solution, the concentration of which is C, and uncertainty of the refractive index increment respectively. Uncertainties of the weight percentage concentration of iodine solutions investigated in this work are in the range $\Delta C \in (2.3 - 3.2)\%$ w/w.

Due to different polarity and surface energy, the different solutions can have very different contact angles with the opal template, and thus significantly affect the filling factor. However, for a given solution concentration (C) effective filling factor should be always the same, which should result in the same change in Bragg's peak position (λ_c). Therefore knowing the relationship between λ_c and C (marking curve (Fig. 5)) for the solution filling opal in a manner appropriate for a given C one can determine the unknown concentration of the iodine solution in ethanol.

4. Conclusions

Simple procedure of determining refractive indices for different weight percentage concentration of iodine solution has been presented. This technique is convenient and reliable. It has allowed determining dependence of the refractive index on the concentration of the iodine solution. This procedure requires optically homogeneous opal with known parameters (diameters of silica spheres and filling factors). It is based only on the determining the wavelengths of Bragg's peaks in the reflectance spectra measured for known opal infiltrated with the investigated medium. The significant advantage of this method is possibility of determining iodine solutions of even high concentration, which is not possible in the case of transmission methods. The next one is that the optical reflectance can be measured in arbitrary units. The uncertainties of the determined values of refractive indices are very simple for reliable determining. The presented method of investigations does not require sophisticated apparatus and cumbersome theoretical calculations. The opal is not destroyed during the measurements and can be used repeatedly. The disadvantage may be the difficulties in obtaining good quality opal with a sufficient area.

The same measuring techniques can be applied for determining refractive indices and concentrations of other solutions.

Acknowledgements

The authors wish to thank Professor Marian Nowak for stimulating advice and helpful discussions.

This paper was partially supported by the NCN (Poland) under Contracts No. NN507250140.

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