



An alternative method to obtain direct opal photonic crystal structures

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ARTICLE INFO

Article history:

Available online 9 May 2009

PACS:

42.70.–a

42.70.Qs

78.55.–m

81.20.Fw

82.70.Dd

Keywords:

Spin-coating

Colloids

Reflectivity

Silica

ABSTRACT

We describe the protocol that we have elaborated in order to obtain monosize polystyrene spheres. Starting from these spheres a simple and effective method, based on spin-coating technique, was developed to realize colloidal photonic crystal structures. The process produces compact 3D arrays of polystyrene microspheres (opals) that are organized into crystalline lattices. This process offers the ability to rapidly form 3D photonic crystals using inexpensive instrumentation, which makes it attractive for an array of applications. Process parameters, fabricated structures, and their experimental characterization are presented.

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1. Introduction

Colloidal crystals, three-dimensional (3D) periodic structures formed by monodisperse colloids [1–3] have been extensively explored due to their important applications as diffractive optical devices, chemical and bio-sensor [4,5], and high-density magnetic and optical data recording materials.

Recently, they have attracted renewed interest, mainly because they provide a much simpler, faster, and cheaper approach than complex semiconductor nanolithography techniques to create 3D photonic crystals (PCh) working in the optical wavelength range [6–8].

A variety of methods, such as gravity sedimentation [9], electrostatic repulsion [10], capillary forces induced convective self-assembly [11,1], and electric field induced assembly [12], have been developed to create colloidal crystals in a time period from days to weeks.

In this contest one of the main obstacles for putting into practice the interesting optical and structural properties of colloidal crystals actual devices is the incompatibility of the time-consuming and unclean self-assembly crystallization techniques commonly used to make colloidal crystals with the fast and dirt free technology required to fabricate devices.

A new approach to colloidal crystallization of submicrometer diameter spheres that overcomes some of the obstacles mentioned above has been proposed by Jang and McFarland [13]. In fact it was shown that it is possible to obtain ordered colloidal structures by spin-coating technique reducing sensitively the deposition time. In particular, in these studies, the attention was focused to find the best conditions (nanoparticles concentration – solution and velocity of spin rotation) to obtain large self-assembled areas using silica spheres.

In this communication, we describe the protocol that we have elaborated to realize monosize polystyrene (PS) spheres and the condition used to obtain a crystalline submicrometer latex colloids structure using a spin-coating technique, starting from ours PS spheres just dispersed in water. The developed preparation protocol allows to obtain a strongly diffracting opal-like structure within few hours without further processing.

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2. Experimental

Latex spheres have been synthesized according to a single-stage polymerization process based on formation and growth of polymeric nuclei dispersed in an emulsion constituted by water, styrene, potassium persulfate (KPS) and sodium dodecyl sulfate (SdS).

The polymerization was carried out in all-glass reactors of 500 ml reaction volume. The reactor was equipped with a stirrer, a reflux condenser, a heating jacket to control the temperature. In particular two parameters have been controlled during the synthesis: temperature and impeller speed. Temperature was kept at 80 ± 2 °C along the emulsion through a heating jacket connected to a PID controller. The mechanical stirrer had a speed equal to 300 rpm with a variation estimated in 1 rpm. The standard procedure was as follows: water 190 g and styrene 20 ml, were pre-mixed in the reactor at the temperature of 80 °C for 2 min. To start the polymerization an amount equal to 0.70 g of KPS and 0.092 g of sodium dodecyl sulfate dissolved in 10 ml was injected. After 4 h the polymerization was completed and after cooling down the colloidal solution was purified by repeated centrifugation/redispersion cycles followed by dilution to the final volume fraction about 1 wt%.

Size distribution of latex spheres has been determined from TEM images acquired by high resolution transmission electron microscopy (HRTEM) JEOL 2010 FEG.

The formation of PCh was achieved from a drops (about 400 μ l) of the above colloidal solution spread onto a square glass substrate, previously treated to make the surface hydrophilic and subsequently 'spinned' using the following parameters: speed of 200 rpm with a spinning time of 90 min.

Structural characterizations of the opals were performed using the AFM NT-MDT P47H apparatus. Optical properties and quality of the opal structures were evaluated by transmittance and reflectance measurements at different angles, using a double beam Varian spectrophotometer.

Moreover, in order to prove the good quality of the direct opals realized by spin-coating technique, these structure were infiltrated with a silica solution [14] and inverse opals structures were obtained using the same protocol previously described [15].

3. Results

In Fig. 1 we present a TEM image of the PS spheres.

The diameter of the PS spheres was calculated analyzing HRTEM images determining an average dimensions of 236 nm with a polydispersivity of about 3%.

In Fig. 2, we report an AFM image from the top surface of an opal obtained by spin-coating technique, moreover Fig. 3 shows the Fast Fourier Transforms' (FFT) image, calculated from Fig. 2.

Fig. 4 shows the normalized reflectance spectra collected along the normal (1 1 1) plane of the opal.

Transmittance spectrum is reported in Fig. 5(b) together with the Photonic Band structure, Fig. 5(a), calculated using numerical methods [16], corresponding to direction in the reciprocal space, namely $\Gamma-L$, for the [1 1 1]-oriented crystals, considering an ideal opal made of PS sphere with a diameter of 236 nm.

Fig. 6 shows a typical SEM image of the inverse structure that we have obtained starting from direct opal structures realized by spin-coating technique.

4. Discussion

As shown in Fig 1, by means single-stage polymerization process, that it's based on the dispersion of monomer in water [17,18] it's possible to obtain nanospheres with low polydispersity.

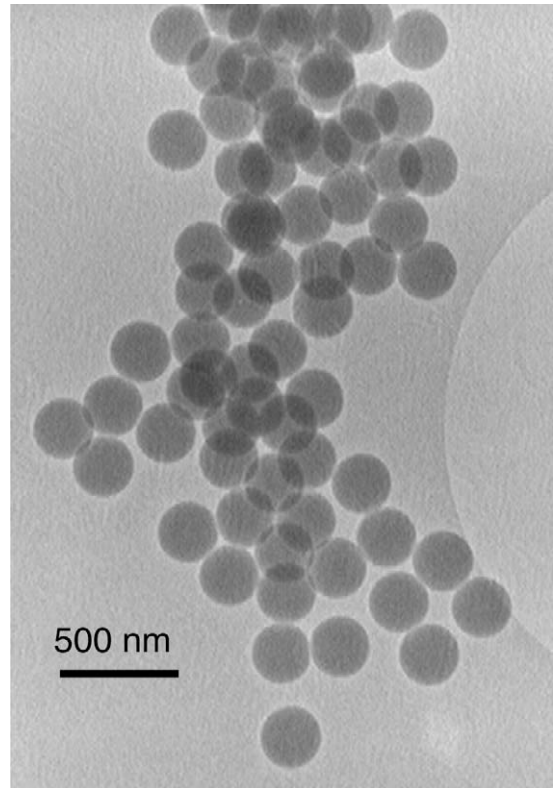


Fig. 1. HRTEM characterization of latex spheres synthesized by microemulsion, where an average dimensions of 236 nm with a polydispersivity of about 3% is determined.

In fact this method exploits the formation of long polymeric chains due to reaction with the initiator (KPS in our case). Moreover we added in the emulsion an anionic surfactant as SdS in order to improve the dispersion of monomer in water. The presence of surfactant in aqueous dispersion results in formation of micelles, which act as reservoirs for monomers. Thus, the reaction between the monomers dissolved in water and free radicals from the initiator generates nuclei-oligomers in the form of tiny particles. The nucleus grows into large chains until all monomers encapsulated into the micelles have been eliminated. The final result consists of the formation of latex spheres with a narrow size distribution.

From Fig. 2(A) a well-ordered close packed structure is evident and at the same time a triangular arrangement is observed, that can be attributed to planes $\langle 111 \rangle$ of a face centered cubic (fcc) system [19]. Moreover FFT's image displays sharp peaks confirming the presence of long-range crystalline order.

From Fig. 4, it is possible to identify the stop bands in the visible region and observe that increasing the angle of incidence the stop band position shifts to shorter wavelengths [15]. This behavior can be expressed by the modified form of Bragg's law [20]:

$$\lambda = 2 \cdot 0.816 \cdot D \cdot \sqrt{(n_{\text{eff}})^2 - (\sin \theta)^2}, \quad (1)$$

where λ is the wavelength of the light reflected by the PCh, D is the dimension of PS spheres, n_{eff} is the effective refractive index and θ is the angle measured from the normal to the planes.

Substituting in Eq. (1) D with the value determined by TEM images (236 nm), assuming that the reflection occurs from the (1 1 1) planes of an fcc structure, and fitting the wavelength of the peak of the stop band as a function of the incidence angle, θ , it was estimated a value of $n_{\text{eff}} = 1.436$.

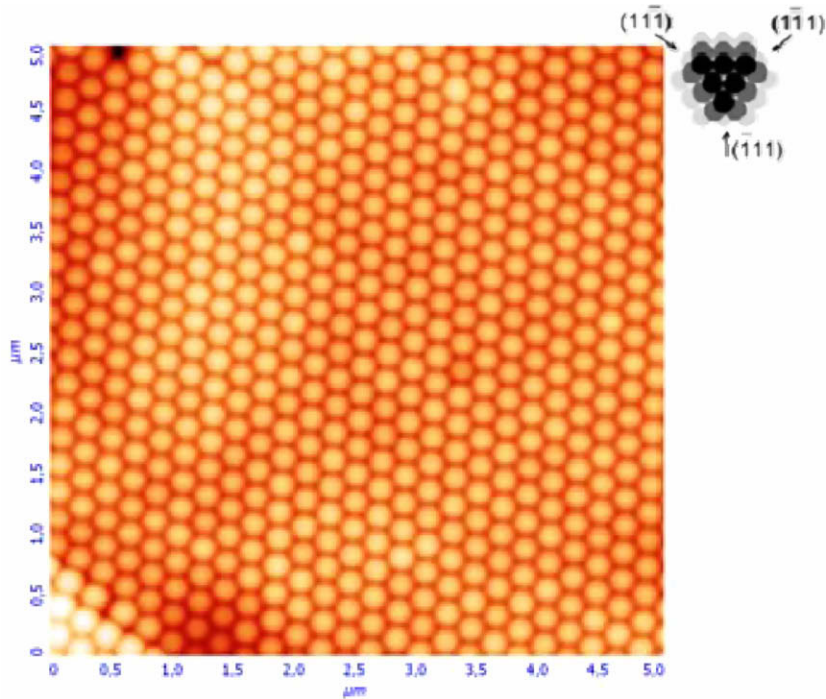


Fig. 2. AFM image of the top surface of the opal formed by spin-coating technique of 236 nm diameter polystyrene spheres. The inset displays the triangular arrangement of the PS spheres.

Furthermore, it's well known, that the effective refractive index can be determined by the following equation [21]:

$$n_{\text{eff}}^2 = n_p^2 \cdot V_p + n_m^2 \cdot V_m = 0.74 \cdot n_p^2 + 0.26 \cdot n_m^2. \quad (2)$$

Here, n_p and n_m are refractive indices of the PS microspheres and the surrounding medium, respectively; V_p and V_m are the volume fractions of the PS microspheres and surrounding medium (air), and are 74% and 26%, respectively. $n_p = 1.55$ (PS microspheres) and $n_m = 1$ are used in the calculation. The value is calculated to be 1.427 that is very close to the experimental value indicating the good quality of the realized direct opals structures.

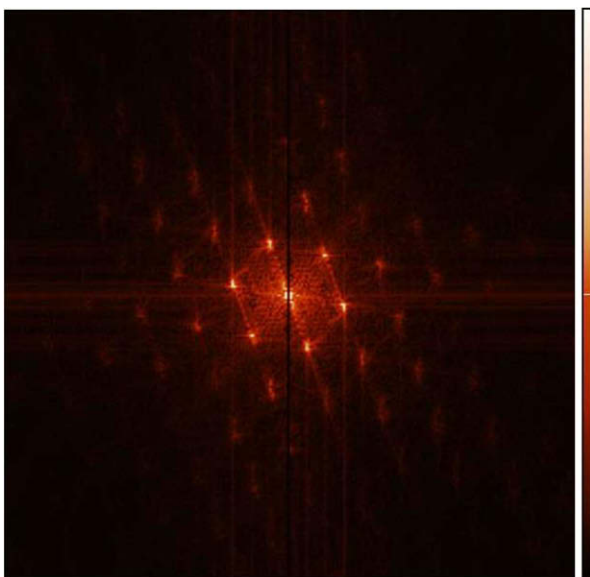


Fig. 3. FFT's image, from the samples realized, displays sharp peaks confirming the presence of long-range crystalline order.

Fig. 5(b) [1 1 1]-oriented crystals transmittance shows a clear minimum centered at the frequency $a/\lambda = 0.6$ due to the opening of a pseudobandgap at the L point of the first Brillouin zone in the spectral region (Fig. 5(a)). In order to estimate the quality of the fabricated photonic crystal we have determined the peak broadening effects (p.b.e.). In fact the peak broadening effect at normal incidence, defined as $\Delta\lambda/\lambda_c$, where $\Delta\lambda$ corresponds to the full width at half height of the transmittance spectrum and λ_c is the position of the transmittance minimum peak, gives a normalized measure of the photonic stopband [1]. From Fig. 5(b) a value of stop band depth of about 40% and a value of p.b.e = 0.09 are determined. These values confirm the good quality of the opals realized.

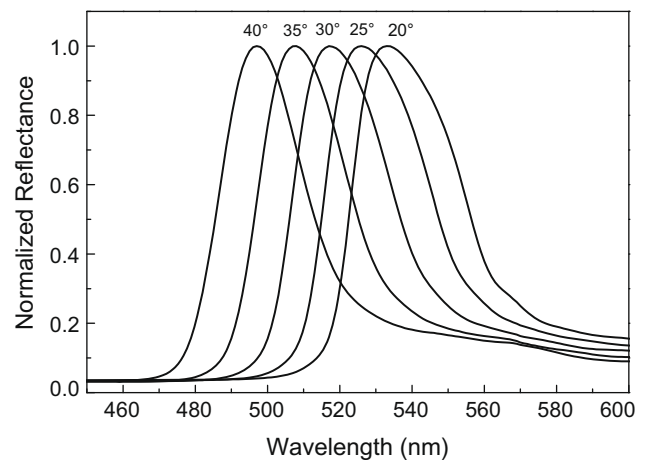


Fig. 4. Reflectance spectra at different incidence angles performed on the direct PS opal along the normal of the (1 1 1) plane of the sample.

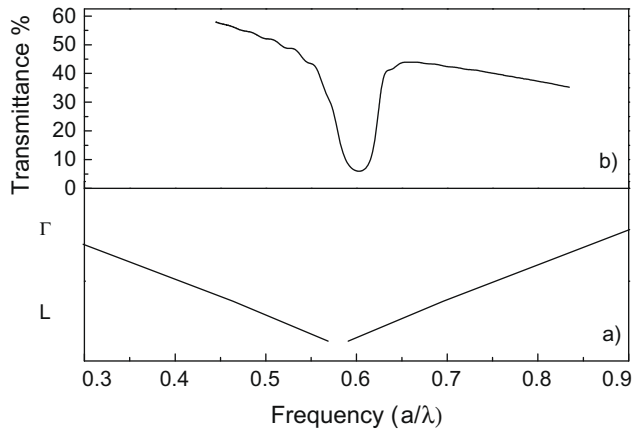


Fig. 5. (a) Photonic band structure of an fcc sphere crystal in the Γ – L direction. (b) Transmittance spectrum of spin-coated PS colloidal crystals with their (1 1 1) planes parallel to the substrate. From figure (b) we can notice a minimum in frequency centered at $a/\lambda = 0.6$, where a is defined as $a = \sqrt{2} \cdot D$ and D corresponds to the dimension of the spheres.

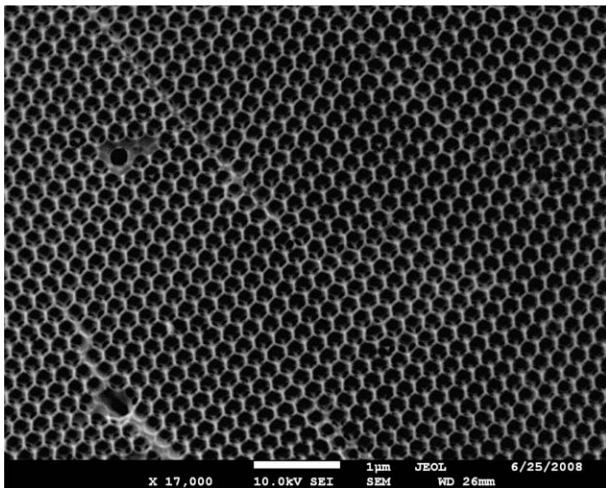


Fig. 6. Scanning electron microscopy image related to (1 1 1) facet of inverse silica opal.

Fig. 6 reveals that the hollow regions of the air spheres are well ordered in a triangular lattice corresponding to the (1 1 1) planes of a fcc crystalline structure [22].

The average dimension of the air-hollows is ~ 200 nm. This value is smaller than the diameter of the latex spheres (236 nm) used to form the template, which demonstrates that a shrinkage occurs during the sintering process. This fact is not surprising given that the latex spheres are mesoporous and, in the early stages of calcination, probably decrease in size as water vapor is released from the pores [23,24].

5. Conclusions

High quality synthetic opal photonic crystals were formed by controlled self-organization of colloidal silica spheres. A sol-gel fabrication protocol was elaborated obtaining polystyrene microspheres of 236 nm diameter with a polydispersity less than 3%. We have demonstrated that large well-ordered crystals of syn-

thetic opal can be produced in few hours starting from these spheres, employing spin-coating technique, without further processing.

From reflectance measurements at different angles we have estimated the effective refractive index n_{eff} and the diameter D of the spheres. These values are compatible with the dimension obtained by TEM measurements and with the n_{eff} estimated considering theoretical one.

Moreover the results indicate that the structure is a well-ordered 3D face centered cubic order structure. Transmission measurements permit to estimate the peak broadening effect $\Delta\lambda/\lambda_c = 0.09$ and the value of stop band depth of about 40%. Besides the large domains observed from SEM image related to the inverse structure obtained starting from opals prepared by spin-coating are a further indication of the high quality of the template realized.

Finally, we believe it will be possible to extend this technique, using particles of different sizes, to fabricate 3D PhCs functioning in different parts of the electromagnetic spectrum, including the IR and THz.

Acknowledgements

Authors acknowledge the financial support of PAT FaStFAL 2007–2010, CNR-GRICES 2007–2008, and COST MP0702: Towards Functional Sub-Wavelength Photonic Structures, L.M. Fortes acknowledge FCT (Fundação para a Ciência e Tecnologia) for the fellowship: SFRH/BPD/34754/2007.

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