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Preparation and Properties of Silica Inverse Opal via Self-Assembly

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Abstract. The bottom-up colloidal synthesis of photonic band gap (PBG) materials or photonic crystals (PC) has attracted considerable interest as compared to so-called top-down lithographic approaches due to the simple processing steps involved and the prospect of the economically viable production of complex 3-dimensional optical materials from simple colloidal particles. To date self-assembly techniques constitute the most popular approach to fabricate 3D photonic crystals from colloidal particle suspensions. Based on the natural tendency of monodisperse colloidal particles to organise into ordered arrays, this method represent the best option due to the ease of fabrication, ability to produce larger area samples and cost. Here we report on the fabrication of long range three-dimensional (3D) ordered poly (methyl methacrylate) (PMMA)-silica PC structures and the subsequent fabrication of robust silica inverse opals using self-assembly methods. The optical properties of these materials are described and discussed in terms of potential applications of these materials.

Introduction

Photonic crystals (PC) are periodic structures that exhibit a spatial modulation in their dielectric function, with the periodicity of this modulation being comparable to the wavelength of light usually in the ultraviolet, visible or infrared region of the electromagnetic spectrum. Such materials are currently of high fundamental and technological interest owing to their ability to confine and control the flow of light [1]. The complex light-matter interactions in these materials produce modified wave propagation when the periodicity of the PC goes from one or two dimensions to three dimensions, where it is possible to create optical phenomena similar to those seen in natural opal gemstones, which are made from the natural assembly of colloidal silica particles. As such 3-D colloidal photonic crystals made in the laboratory are often referred to as artificial opals. The transport of electromagnetic waves in photonic crystals is determined by the so-called photonic band gap [2], which is the optical analogue of a directional band gaps for electrons that exist in semiconductors and insulators. The unique properties of photonic crystals (PC) has attracted enormous interest as they could lead to a wide range of new or improved devices including decorative coatings, sensors, photovoltaic, solar concentrators, passive optical components (filters, splitters), negative refractive index media devices such as cloaking devices, perfect (aberration free) lenses and optical interconnect technologies [3-8].

So-called 'inverted opals' are known to exhibit more complete photonic band gaps than conventional opals [9]. These materials are the negative replicas of direct opals and could be seen as an ordered array of communicating voids in a solid matrix. Preparation of their inverted structures has therefore been envisaged as an alternative way to investigate further the optical properties of such 3D structures. Unfortunately it is often the case that successful experimental investigations of inverted structures are hampered due to the difficulty in manufacturing robust 3D inverted PC structures with long range order. Infilling a second material into the interstitial lattice voids between the colloidal spheres of the opal followed by removal of the spheres is one popular way of creating the inverted structure. In order to achieve this, techniques such as chemical vapour deposition [10] and atomic layer deposition [11, 12] have been employed with a reasonable degree of effectiveness, yet these methods often require the use of potentially expensive specialist equipment. In this present

work we highlight the use of an alternative approach for the infilling of the voids in the parent material which is both simple and easy to perform, requiring no specialist equipment other than laboratory glassware.

One useful method for the reliable production of colloidal silica based photonic crystals was first performed by Jiang et al. in 1999 [13]. This method employed a suspension of the silica particles in contact with a vertical substrate onto which the particles assembled as the solvent in the suspension evaporated. The method is often called "controlled-evaporation", "vertical deposition" and even the "Colvin" method, after the head of the group at Rice University in the USA who demonstrated the particular approach. Easy and cheap to perform, this technique has rapidly attracted a huge amount of attention. The quality of the opal obtained with the controlled-evaporation method depends on many parameters such as the sphere size and their size distribution, the volume fraction of particles, the relative humidity, the evaporation time and drying temperature [13-15]. The control of these parameters allows the control of the film thickness and quality. Films prepared in this manner form as a result of close packing which results in a face-centred cubic structure, similar to that found in natural opals, the alternative hexagonal close packed arrangement being much less commonly observed.

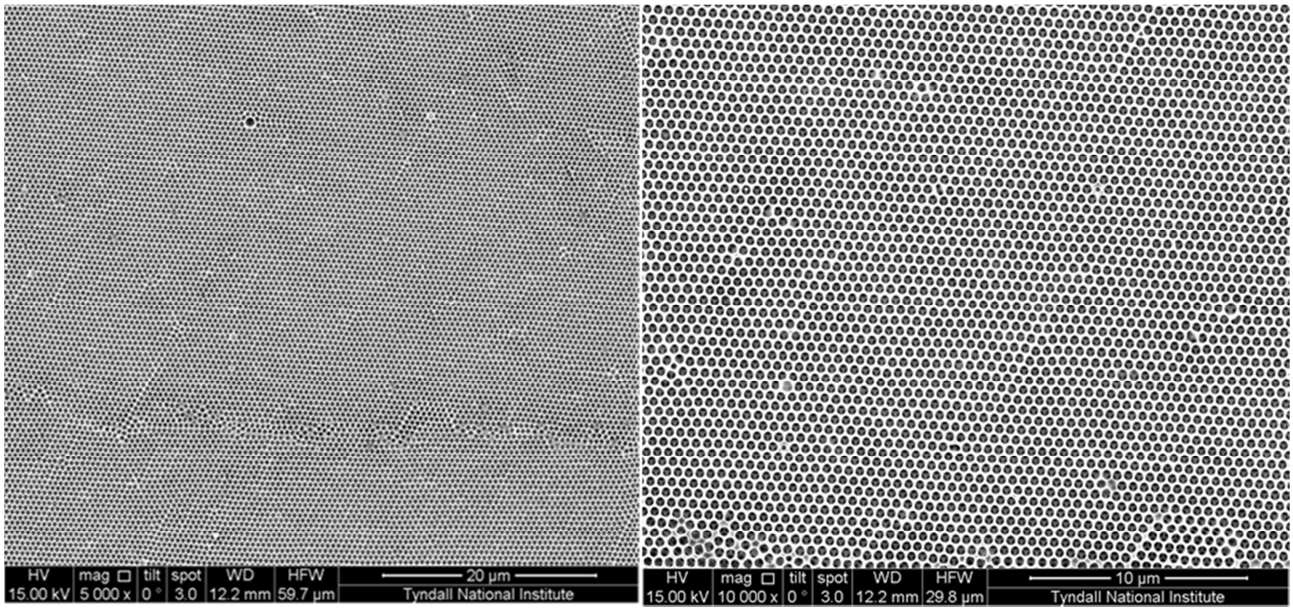
By borrowing from a concept for the fabrication of large area 3D ordered colloidal arrays of nanoparticles reported elsewhere [16], we have infiltrated PMMA colloidal particles (475nm) with hydrolysed TEOS to form composite silica PMMA material. Following this the PMMA crystal template was removed by solvent dissolution to produce a robust silica inverse opal. This approach promises to yield high quality, large area samples that could be used in the fabrication of many types of optical devices.

Experimental Section

PMMA colloidal spheres (475 nm) were synthesised using a procedure that we have reported previously [17]. The composite silica-PMMA was prepared via controlled evaporation self-assembly from an aqueous colloidal suspension containing the two components, namely poly(methyl methacrylate) (PMMA) spheres and tetraethylorthosilicate (TEOS) solution (Sigma Aldrich). A 0.15 volume percent PMMA suspension of the particles in Millipore water was prepared containing 0.12 ml TEOS sol. The sol made up from the hydrolysis of the TEOS in solvent medium (using ethanol : HCl (0.1 molar) : TEOS with ratio 8:1:1; respectively). A cleaned glass substrate was tilted in the mixture of the suspension (PMMA+TEOS). The addition TEOS was important as it acts as the 'cementing component' that holds the PMMA together in the PC backbone. The PMMA template was removed by using acetone and further calcined at 450^{o}C on a hot plate to form a silica inverse opal. This film exhibited opalescence confirming the successful formation of a PC film. The morphology of the resulting films was studied using scanning electron microscopy (SEM). The optical properties of the 3D silica inverse opals were measured using an optical bench set-up for wavelengths, λ, ranging from 450 to 1600 nm. Collimated un-polarized white light from a tungsten lamp was focused onto the sample using an 8 cm focal length lens and the transmitted light was collected through an optical fibre to the spectrometer (Ocean optics) and the data processed by SpectraSuite software. In both the reflectance (R) and transmittance (T) mode the baseline correction was done with a bare glass substrate to eliminate the effects such as light reflection at the air-glass interface and substrate absorption, if any. For angle resolved transmission data collection, the sample mounted onto a rotational stage was rotated at angles, theta, ranging from 0 to 65^{o}, measured from the surface normal of the (111) hexagonal plane grown parallel to the substrate surface. For reflectance measurements, the unit was rotated to collect the reflected signal at a range of angles from 10 to 65^{o}.

Results and Discussion

SEM images of the fabricated 3D silica inverse opals are presented in Fig. 1. The SEM top view images reveal the consistency of inverse opal formed over large domain sizes, >20 μm. The efficiency of the method can be appreciated from fact that the three-coordinate interconnects from the second layers of the (111) planes of the PC can also be observed.



a. b.

Fig. 1. Silica inverse opal structure with different magnifications. Scale bars are a. 20 μm, and b. 10 μm

Transmission spectra recorded for the bare PMMA opal as a function of angle of incidence are shown in Fig. 2. The absolute reflectance and transmission spectra recorded from a silica inverse opal consisting of 3D air spheres supported by an SiO_2 dielectric backbone are presented in Fig. 3. The presence of a reflection band, or so-called 'stop band' and a corresponding transmission dip centred at 864 nm reveals the formation of a PBG. The bare PMMA opal shows a stop band centred at 1108 nm. The PBG of silica inverse opal thus exhibits a blue shift in the position of the stop band of 244 nm as compared to that of the bare opal. This shift may be attributed to a combined effect of a small reduction in the effective refractive index of the material n_{eff} (composite SiO_2: air as compared to composite PMMA: air) and a slight reduction in the lattice spacing between the layers of voids in the strucutre as compared to the spacing between the spheres in the parent strucutre, that arises because of the finite thickness of the SiO_2 layer grown between the spheres.

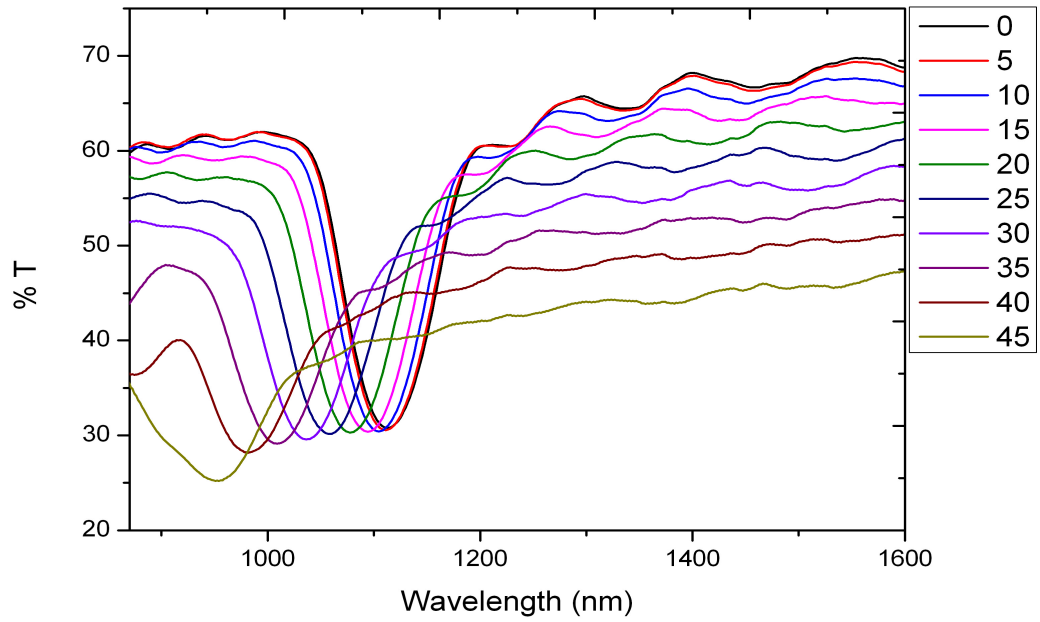


Fig. 2. Transmission spectra of the bare PMMA opal recorded as a function of angle of incidence

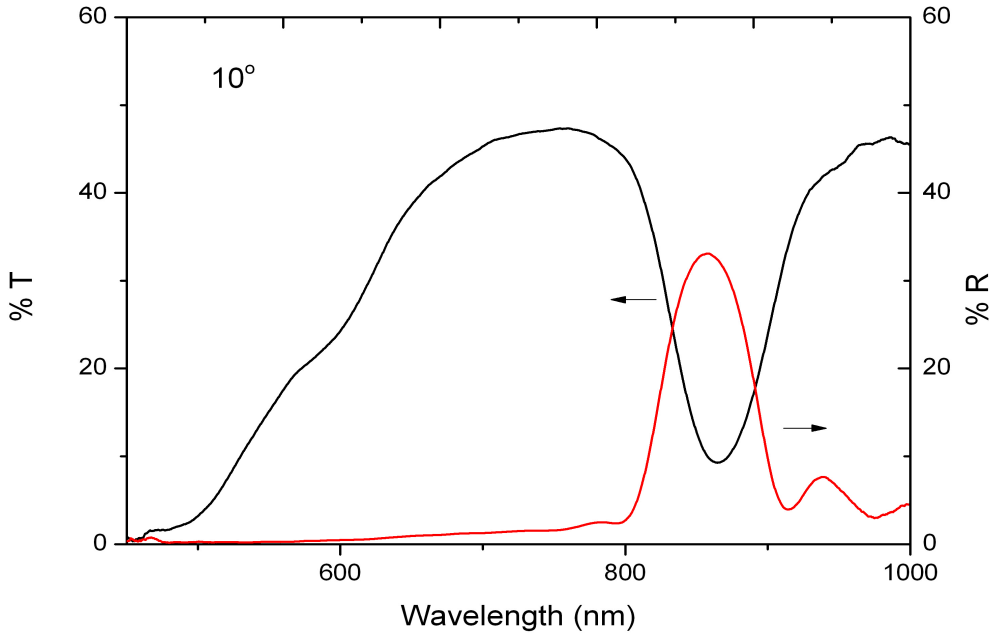


Fig. 3. Reflectance and transmission spectra recorded from the silica inverse opal at an angle of 10°

The reflectance spectrum of the silica inverse opal was also found to exhibit a shift in the position of the stop band as a function of angle of incidence, as expected for a PBG material. This observation is consistent with the expected behaviour for a photonic crystal in terms of the Bragg-Snell relationship. By altering the angle of incidence (θ), the effective refractive index (n_{eff}) and the inter planar spacing (d) can be determined by the following equation [2, 18]:

$$\lambda = 2d\sqrt{(n^2{}_{eff} - \sin^2\theta)}. \quad (1)$$

This equation is found to apply to most colloidal photonic crystals and their inverse analogues since the stop band is formed as a result of the diffraction resonance for light incident on the material surface arising from the (111) family of planes of the structure combined with refraction effects arising at the interface between the air and the material's surface.

The correlation with the Bragg-Snell relationship was further confirmed by fitting the data points obtained to a plot of the square of the wavelength maximum (λ^2_{max}) for the stop bands recorded at varying angle of incidence angle, θ, against $\sin^2\theta$, Figure 4. The linear fit shown in Figure 4 is in complete agreement with the Bragg-Snell relationship prediction for photonic crystals. Using the plot shown in Fig. 4, n_{eff} can be measured and silica inverse opal was found to have reduced from 1.36 to 1.24 due to influence of filling fraction and change in materials.

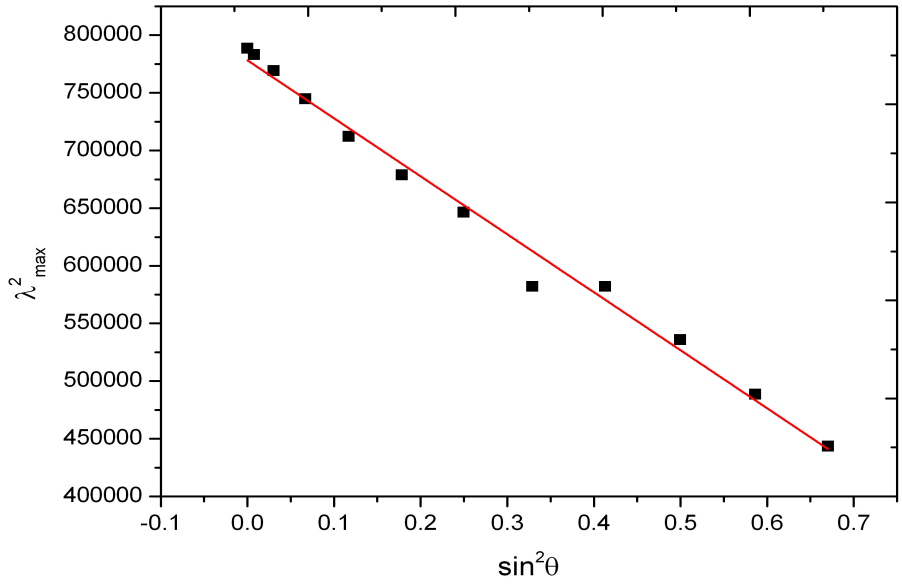


Fig. 4. Plot of λ^2max vs $\sin^2\theta$ showing a linear fit based on silica inverse opal reflectance measurenment.

The SiO_2 inverted structures were found to be quite robust and easy to handle, which suggests that the method presented here might make such materials genuinely accessable for applications where increased refractive index contrast is desirable. Such applications could include passive components such as mirrors and filters, or active components such as optical sensors where a high degree of discrimination between various wavelengths of light is required.

Conclusion

A simple and easy method for the infiltration of TEOS and its subsequent reaction to SiO_2 in the interstitial voids of a PMMA opal is reported. The infiltration was carried out using the one-step method involving co-crystallization of both TEOS and the PMMA spheres during self-assembly via a controlled evaporation process. The silica inverse opal exhibits a blue shift in the stop band as compared to that of the bare PMMA opal which we attribute to a reduction in effective refractive index and a reduction in the effective lattice spacing of the layers of voids in the inverted structure as compared to that of the layers of spheres in the bare PMMA structure. Optical reflectance measurements were made at various angles of incidence show good correlation using Bragg-Snell equation.

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