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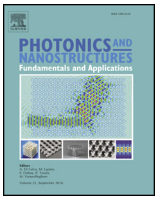

Angle-resolved reflection spectroscopy of high-quality PMMA opal crystal

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ABSTRACT

PMMA opal crystal was prepared by a simple hybrid method, which includes sedimentation, meniscus formation and evaporation. We investigated three surfaces of this crystal by angle-resolved reflective light spectroscopy and SEM study. The angle-resolved reflective measurements were carried out in the 400–1100 nm range. We have determined the high-quality ordered surface of the crystal region. Narrow particle size distribution of the surface has been revealed. The average particle diameter obtained with SEM was nearly 361 nm. The most interesting result was that reflectivity of the surface turned out up to 98% at normal light incidence. Using a fit of dependences of the maximum reflectivity wavelength from an angle based on the Bragg–Snell law, the wavelength of maximum 0° reflectivity, the particle diameter and the fill factor have been determined. For the best surface maximum reflectivity wavelength of a 0° angle was estimated to be 869 nm. The particle diameter and fill factor were calculated as 372 nm and 0.8715, respectively. The diameter obtained by fitting is in excellent agreement with the particle diameter obtained with SEM. The reflectivity maximum is assumed to increase significantly when increasing the fill factor. We believe that using our simple approach to manufacture PMMA opal crystals will significantly increase the fabrication of high-quality photonic crystal templates and thin films.

1. Introduction

Photonic crystals (PhCs) are attractive optical materials for fundamental research and practical applications in various fields of technology due to their outstanding properties. Among these properties the photon stop-band (or photonic band gap, PBG), light-wavelength selectivity and high-performance photoluminescence are of primary importance [1–8].

Structural periodicity in a PhC leads to light coherent scattering from a highly accurate, ordered structure that results in the formation of PBGs, which are optical analogues of electronic band gaps in semiconductors [9]. The PBG is known to be in agreement with light reflection from a periodic structure if the structure period is equal to half of the incident light wavelength [10]. Moreover, wavelength selectivity [4] and total reflection [11] take place entirely due to PhC periodic order.

PhCs have worldwide been investigated for their possible application in biological labeling [12,13], therapeutics [14,15], biodetection [15], bioimaging [15,16] and solar cells [17,18]. Based on their promising properties infrared quantum counter detectors, temperature sensors and three-dimensional displays [19] are feasible. There are some more attractive phenomena concerning PhCs, such as extraordinary optical transmission [20], low-loss transmission [21], enhanced absorption [22,23] and multi-functional and multi-responsive luminescence [24]. Some PhC devices are already in use. For example, PhC fibers [25], LED [26], no-loss waveguides [27,28], resonators [29] and compact solid-state lasers [30] have already been fabricated.

Among PhCs, opals (natural or artificial) are distinguished as a special class. Opals are three-dimensional periodic crystals of great interest [31], which derives from the fact that opals can be prepared using relatively simple and inexpensive production methods, and considerable surface area of three-dimensional, highly precise, ordered templates of opal can also be obtained. Obviously the most appropriate technique to fabricate colloidal crystal is the

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self-assembly approach [31], the most popular methods of which are gravity sedimentation, vertical deposition, electrophoresis, spin coating as well as the melt-shear organization technique [32,33] and crystallization in physically confined cells [31]. Nowadays a number of researchers [34–37] have concentrated on combining stimulus-responsive materials with the self-assembled PhCs.

Inverted or inverse opals (IOs) are a particular case of PhCs [38–40], commonly used in gas and liquid sensing [41–43], battery electrodes [44] and catalysts [45–47]. More recently, a series of works [48–50] have been devoted to so-called smart devices based on inverted opal structures. IOs are three-dimensional porous structures formed using sacrificial polymer[24] or silica [51] templates by filling the opal voids with a precursor. The original opal template is then removed by etching or annealing. As a polymer template, polymethyl methacrylate (PMMA) or polystyrene opal is conveniently used. To obtain a high-quality inverse opal, the most-ordered PMMA or polystyrene spheres in the opal template should be fabricated.

One of the main methods to check opal template quality is optical reflection and scanning electron microscopy (SEM). The reflection at normal incident light for an ideal opal template is 100% under certain wavelengths. Indeed, research works have confirmed high opal template reflectivity [3,52–54]. However, no studies have been identified in which the opal crystal reflectivity reaches 100% from a relatively large area. An analysis of articles on this topic showed that the highest reflectivity from a relatively large area of opal crystal was ~80% measured with incident light normal to the *hkl* = 111 crystal planes [55]. Thus, the purpose of this study was to produce a high-quality opal crystal with reflectivity reaching 100% from a relatively large area by using a simple and inexpensive method.

This study presents a high-quality opal surface with extrapolated reflectivity up to 98% at normal incidence, as well as bulk opal made from stacking uniform-sized particles into a face-centre cubic (fcc) array. The opal crystal was produced using a hybrid method, which includes sedimentation, meniscus formation and evaporation. This method is simple and allows relatively large high-ordered surfaces with high reflection. We have found that our hybrid method is similar to the methods specified in recent research [55,56]. However, different technological parameters were used here.

This study presents angle-resolved reflective measurements and an SEM study of opal PMMA crystal with three surfaces.

2. Experiment

2.1. Synthesis of PMMA spheres

Methyl methacrylate (MMA), distilled water and 2,2′-Azobis(2-methylpropionamidine) dihydrochloride initiator were used for synthesis of the PMMA emulsion. A necessary condition of the dispersion formation of submicron PMMA spheres with a narrow size distribution is a short phase of intense multiple nucleation, changing with slow controlled growth of the particles without changing their numbers. The chain radical polymerization process of methyl methacrylate can be divided into three stages: activation of the initiator, the reaction of the monomer with an initiator radical and the growth of the molecule and breakage of the polymer chain. When heated, the initiator decomposes with the formation of active radicals, which are the initiators of the polymerization reaction.

The emulsion polymerization procedure requires the heating of methyl methacrylate emulsified in water to 70 °C or 80 °C. In this study, the emulsion temperature was kept at 75 °C. We used 140 ml of MMA, 560 ml of distilled water and 0.3 g of initiator to make PMMA spheres of 360–370 nm. The mixer speed was fixed at 700 rpm. All polymerization procedures for mixing water and methyl methacrylate lasted about 2.5 h. During nanoparticle (NP) dispersion synthesizing, the IR spectra of the NP dispersion was recorded by using a FT-801 IR Fourier spectrometer with a fibre probe [57]. Thus, we were able to fully monitor the polymerization process using IR spectra. Before polymerization, we saw only MMA peaks. However, after the polymerization process, we saw only PMMA peaks. Peaks of MMA and PMMA were identified using the following articles [58–60]. Thus, we assume that all chemical reagents completely reacted.

The concentration of nanoparticles in water dispersion was estimated to be ~15 vol% (~6×10^{15} nanoparticles per one liter). The polydispersity of the nanoparticles was less than 3% according to SEM.

2.2. Preparation of PMMA opal-like structure

In this study, we used the hybrid method to form opal PMMA crystals. This hybrid method included sedimentation, meniscus formation and evaporation. Our method is slightly similar to Colvin's one [61], but there are a wide range of differences: materials of colloidal particles, cavities for crystallization, evaporation and sedimentation conditions, sample sizes. Hot emulsion of PMMA spheres was poured in a small bowl coated with polytetrafluoroethylene, which has hydrophobicity. Recent studies have shown that hydrophobicity plays a key role in the formation of high-quality opal crystals [55,56,62]. The bowl volume was near 100 ml, the diameter was 90 mm and the rounding radius between the bottom and the wall of the bowl was approximately 13 mm (meniscus-like area).

During opal manufacturing, the bowl was not covered and kept at room temperature. In addition, there was no shaking of the bowl with the emulsion. We waited 350 h until the water in the bowl was completely naturally evaporated. The humidity in the room was constant at 60%. Finally, the opal crystal was obtained. Thus, the use of a hydrophobic surface and a long duration of self-assembly led to the formation of an opal crystal with a high-quality surface.

2.3. Apparatus and analytical conditions

The FTIR-spectra were performed with a VERTEX 80 V spectrometer equipped with an A513 variable angle reflection accessory. The FTIR-spectra were obtained in 25000–8000 cm^{-1} with resolution 2 cm^{-1}. Morphology analysis was carried out with a Hitachi S-5500 field emission scanning electron microscope (FE-SEM) at 3 kV using secondary electron imaging. No metal films were coated on the sample surface prior to taking the SEM measurement in case of a dielectric sample. During deposition, sputter coater damages every polymer sphere and opal-like structure. That is why surface charging occurs despite using the charge suppression scan mode of the SEM.

3. Results and discussion

A bulk colloidal crystal with a high-quality surface was grown. A segment was taken from the colloidal crystal centre as shown in Fig. 1a. Places where samples were taken are shown in Fig. 1b.

Fig. 2 shows the SEM study of three surface types marked as Samples 1, 2 and 3. Sample 1 is the part of the bulk opal corresponding the bowl-opal interface. Sample 2 is obtained from a direct meniscus (sample-air interface). Sample 3 is the middle-part of the opal crystal (sample-air interface).

As shown in Fig. 2a, there is a short-range order in Sample 1, but disorder is mainly observed. The inset in the top right corner of Fig. 2a demonstrates that no ideal spheres are observed. Fig. 2b shows that there is a long-range order with high-ordered polymer