Laser diffraction study of inverse opals

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ABSTRACT

We discuss the experimental data on laser diffraction in photonic crystal films with an inverse opal structure. Two types of samples based on tungsten and manganese oxides were prepared by replicating colloidal crystals of 900 nm polystyrene microspheres. We scanned both colloidal crystals and inverse opals with a 532 nm laser beam and recorded symmetrical sixfold diffraction patterns for all samples studied. By using laser diffraction it is possible to calculate the period of photonic crystals and to examine their crystalline quality. This method allows monitoring evolution of the samples from colloidal crystals to inverse opals in a replicating process.

Keywords: photonic crystals, inverse opals, laser diffraction

1 INTRODUCTION

Over the last two decades, there is a constantly growing interest in materials with a periodic modulation of dielectric constant, also known as photonic crystals [1,2]. Many unusual phenomena, such as localization of light and control of spontaneous emission, were predicted for photonic crystals and may result in important technological applications, including high-performance light emitting diodes, low-threshold lasers, optical waveguides with sharp bends and all-optical microchips [1].

Self-assembly of submicron colloidal particles provides a suitable platform for the preparation of photonic crystals [3]. The materials thus formed are usually referred to as colloidal crystals or artificial opals, since they resemble corresponding natural gemstones. Due to easy and low-cost fabrication process, colloidal crystals were used as model objects in numerous studies of photonic crystals [4-6]. Nevertheless, opals are not expected to be employed in a wide range of commercial high-tech products since they do not meet several important requirements. First, opals are typically made of low refractive index materials, such as silica or polymers, while the use of materials with high refractive index would result in a tremendous enhancement of photonic crystals' optical properties [7]. Even more important restriction arises, when a particular optoelectronic device demands photonic crystals, in which unique optical characteristics are combined with additional functional properties (magnetic, electrical, mechanic, etc.).

Numerous recent studies have been focused on the preparation of inverse photonic crystals, which can be synthesized by filling the voids of opal templates with suitable structure-forming precursors and subsequent removing the initial microspheres to leave three-dimensionally ordered macroporous materials. This templating technique is very flexible and can be applied to the preparation of inverse photonic crystals based on a huge variety of materials, like metals, nonmetals, oxides, semiconductors and polymers [8]. Some of thus synthesized inverse opals possess high refractive index contrast and exhibit tunable functional properties promising for optoelectronic applications [9-12].

However, the use of inverse opals is strongly limited due to the preparation complexity of their well-ordered samples. Replicating procedure typically results in the shrinkage of photonic crystal framework, cracking, misalignment of different domains, etc. As a result, inverse opals are significantly less investigated than artificial opals. Typical tools for the structure analysis of inverse opals include scanning electron microscopy (SEM) and optical spectroscopy. Recent studies demonstrated that structural quality of photonic crystals can be verified by laser diffraction, though this method was mainly applied to colloidal crystals [13-16]. In the present work we compare laser diffraction data for colloidal crystals and inverse opals.

2 EXPERIMENTAL

Monodisperse polystyrene microspheres with an average diameter of 900 nm and relative standard deviation less than 5% were synthesized by emulsifier-free emulsion polymerization of styrene using potassium persulfate as initiator [17]. The size distribution of the spheres was studied by dynamic light scattering using ALV CGS-6010 instrument and 632.8 nm helium–neon laser as a light source.

Colloidal crystal films made of polystyrene microspheres were prepared using the vertical deposition method [18]. Glass microslides were thoroughly cleaned and immersed in an aqueous suspension of microspheres with a concentration ranging from 0.1 to 0.5 vol.%. The temperature of film growth was 50±1 ^{o}C.

Tungsten oxide was introduced into the voids of colloidal crystal as follows [12]. First, we prepared the dipping solution by dissolving metallic tungsten in the

mixture of hydrogen peroxide (30%) and glacial acetic acid at 0 °C for a few hours, filtering the solution and redissolving the sediment in absolute ethanol. Then, we infiltrated colloidal crystal voids with the dipping solution and dried the sample in air for a few minutes. We repeated the dipping-drying procedure 3-4 times in order to get more material into the voids. The resulting polystyrene-gel composite was heated up to 500 °C at the rate of 1 ºC/min and annealed for 1 h to remove the polystyrene template.

Inverse opals based on manganese oxide were synthesized by infiltrating colloidal crystal template with water-alcohol solution of manganese acetate, drying the sample in air, heating the resulting composite at the rate of 1 ºC/min up to 500 ºC and annealing for 1 h [19].

SEM images of the samples were recorded using LEO Supra VP 50 instrument. Prior to imaging the samples were coated with a thin gold layer to reduce surface charging.

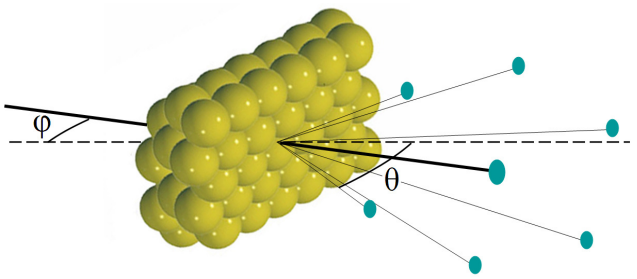

Figure 1: The scheme of laser diffraction experiment. Dashed line represents normal to the surface of the sample; φ and θ are angles of incidence and diffraction, respectively. The setup was adjusted so that angles φ and θ belong to horizontal plane.

The geometry of the experiments on laser diffraction is shown in Fig. 1. Laser diffraction patterns were recorded using a weakly focused frequency doubled Nd:YAG laser (λ = 532 nm). The diameter of the laser beam spot on the sample was 0.1 mm, corresponding to the spot area of 8000 μm^2. Photonic crystals were placed on a special stage allowing micrometer adjustment of the in-plane position of the sample with a precision of 10 μm. The setup allowed varying the angle of incidence of the laser beam so that the same area of the sample was illuminated while rotating.

3 RESULTS AND DISCUSSION

SEM image of colloidal crystal film prepared by vertical deposition of 900 nm polystyrene microspheres is shown in Fig. 2. The particles are ordered in a close-packed arrangement, and it is possible to find areas of at least 35×35 μm^2 with no cracks and only a few point defects. The samples similar to that shown in Fig. 2 were used for the synthesis of inverse photonic crystals.

High quality of colloidal crystals is partially inherited by inverse opals. SEM images of macroporous tungsten and manganese oxides are shown in Fig. 3. The average center-to-center distance d between the spherical voids is 860 nm for WO_3 and 885 nm for MnO_x. Since the average size of the polystyrene microspheres used for template preparation was 900 nm, the shrinkage of the samples during the sintering could be estimated as 5% and 2%, respectively. This shrinkage occurs due to the removal of volatile components (mainly water and carbon oxides).

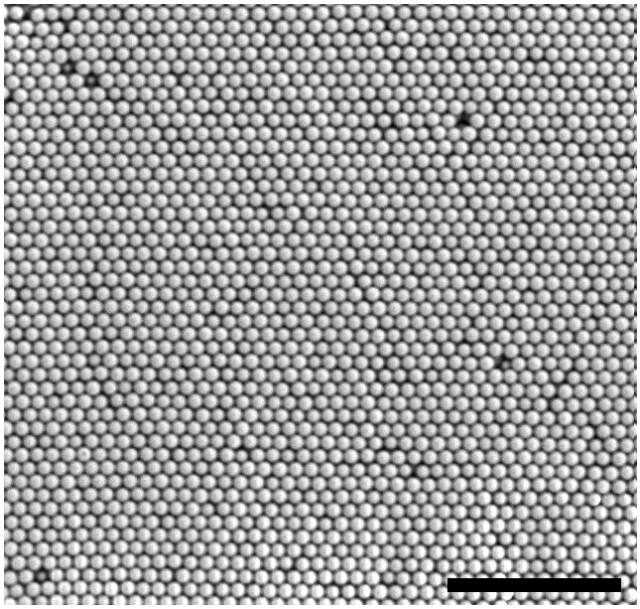

Figure 2: SEM image of a ca 35×35 μm^2 area of the colloidal crystal film composed of 900 nm polystyrene microspheres. Scale bar is 10 μm.

The period of photonic crystals can be independently determined from the diffraction experiments. The angle at which the diffraction spots are observed can be analyzed by considering each layer within the photonic crystal as a two-dimensional diffraction grating [13], the pitch of the grating D is equal to d/2. Following simple diffraction theory we can write

$$\sin\theta = \sin\varphi + \frac{\lambda}{D}, \qquad (1)$$

where λ is the laser wavelength, φ is the angle of incidence of the laser beam, and θ is the angle of diffraction (Fig. 1).

In angle-dependent diffraction experiments we mounted colloidal crystal or inverse opal film on a stage and then by in-plane moving the sample we scanned it with the laser beam until sixfold diffraction pattern with no diffuse ring linking the spots has been observed (see the inset of Fig. 4). Then the sample was rotated around the axis of laser beam to make two of six diffraction spots horizontal, ensuring that angles of incidence and diffraction belong to horizontal plane. Finally, we rotated the sample around the vertical axis and monitored diffraction angle as a function of angle of incidence.

It should be stressed that sixfold diffraction pattern shown in the inset of Fig. 4 is typical of single crystals and indicates that illuminated area of 8000 μm^2 contains close-packed domains with the same crystallographic orientation

[20]. Such patterns were recorded from numerous spots of both opal and inverse opal films, confirming that the well-ordered close-packed structure of colloidal crystals was preserved during replicating process.

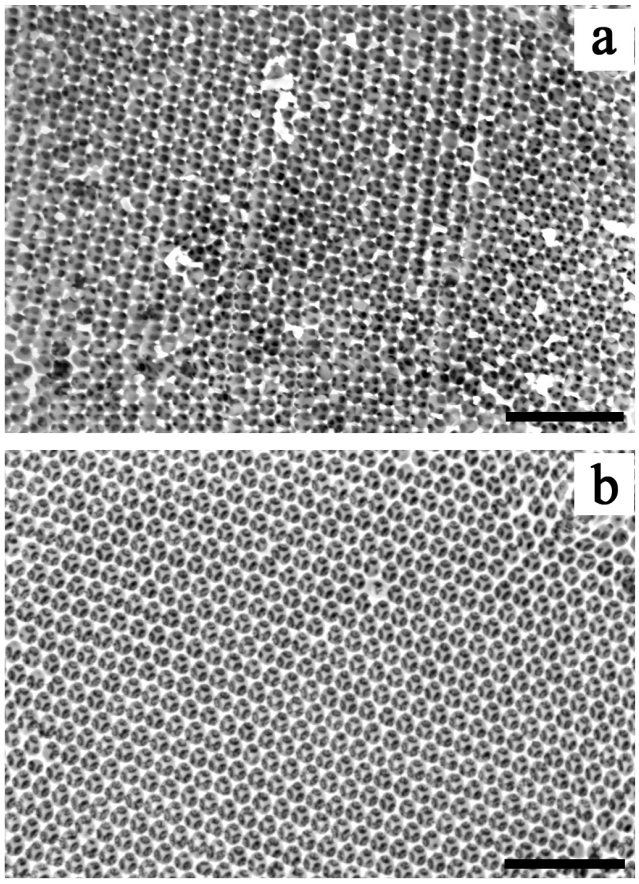

Figure 3: SEM images of inverse opals based on tungsten oxide (a) and manganese oxide (b). Scale bar is 5 μm.

We recorded dependencies of diffraction angle θ versus angle of incidence φ for all synthesized samples, including polystyrene colloidal crystals and inverse opals based on tungsten and manganese oxides. Accordingly to Eq. 1, the plot of $\sin\theta$ against $\sin\varphi$ is linear with a gradient of 1 and an intercept of λ/D (Fig. 4). It should be noted that the laser diffraction data are in a good agreement with the SEM results. The lowest linear fit corresponds to colloidal crystal, which possesses maximum lattice period among three samples studied (accordingly to SEM, the average size of microspheres d = 900 nm). The highest line describes diffraction data for WO_3 inverse opal with the average center-to-center distance between the spherical voids d = 860 nm, while the line corresponding to manganese oxide inverse opal (d = 885 nm) lies in between. The absolute d-values calculated from diffraction data are 899, 882 and 862 nm for polystyrene, manganese oxide and tungsten oxide photonic crystals, respectively. This method to determine the period of photonic crystal is nondestructive and thus has an advantage over SEM, which requires the use of vacuum and often employs coating the samples with conductive gold or carbon layers.

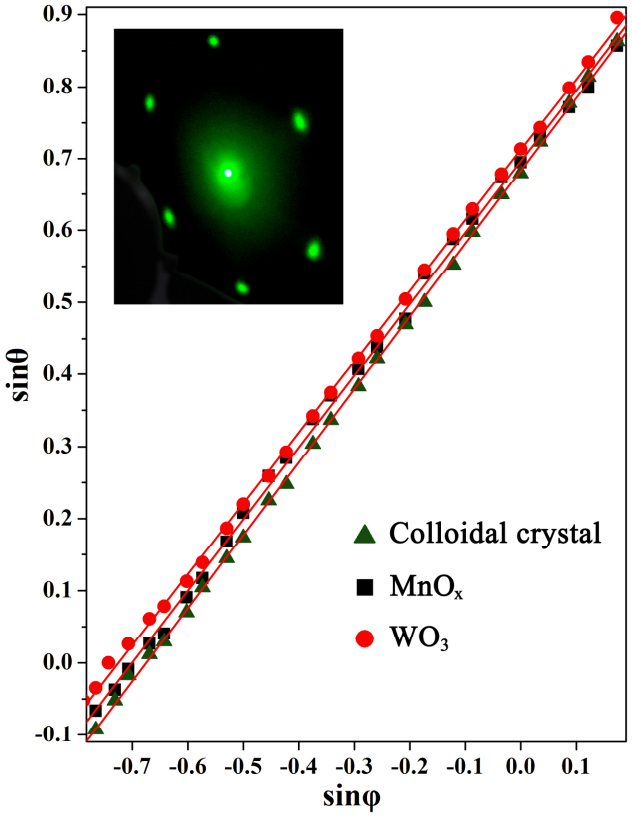

Figure 4: Angle-dependent laser diffraction data for polystyrene colloidal crystal (triangles) and inverse opals based on manganese oxide (squares) and tungsten oxide (circles). The solid lines are linear fits to the data from which the photonic crystal lattice periods can be determined. *In the inset:* Sideview photograph of diffraction experiment on WO_3 inverse opal. The sample holder can be distinguished in the left bottom corner of the photograph.

It should be stressed that laser diffraction can also be employed for constructing domain maps of photonic crystals, demonstrating for a macroscale area of the sample both regions where all domains have the same crystallographic orientation and disordered regions. [20].

4 CONCLUSIONS

In the present work we demonstrated that structural changes occurred in photonic crystal samples during their transformation from colloidal crystals to inverse opals can be monitored by laser diffraction. Bright sixfold diffraction patterns recorded from numerous spots of inverse opal films testify to their high structural quality. By using angle-dependent laser diffraction data we calculated the period of photonic crystals and visualized the shrinkage of inverse opals in a replication process due to the removal of volatile

components. This method of analysis takes on special significance for inverse photonic crystals, which are much less investigated than conventional opals. Since diffraction patterns can be recorded in a reflection mode, this method can also be applied for the study of bulk inverse photonic crystals. The significant limitation of this method is that the diffraction patterns can be observed only if the laser wavelength is less than photonic crystal lattice period. Therefore, the method is difficult to apply to photonic crystals for visible range, typically composed of structural units less than 300 nm in size.

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