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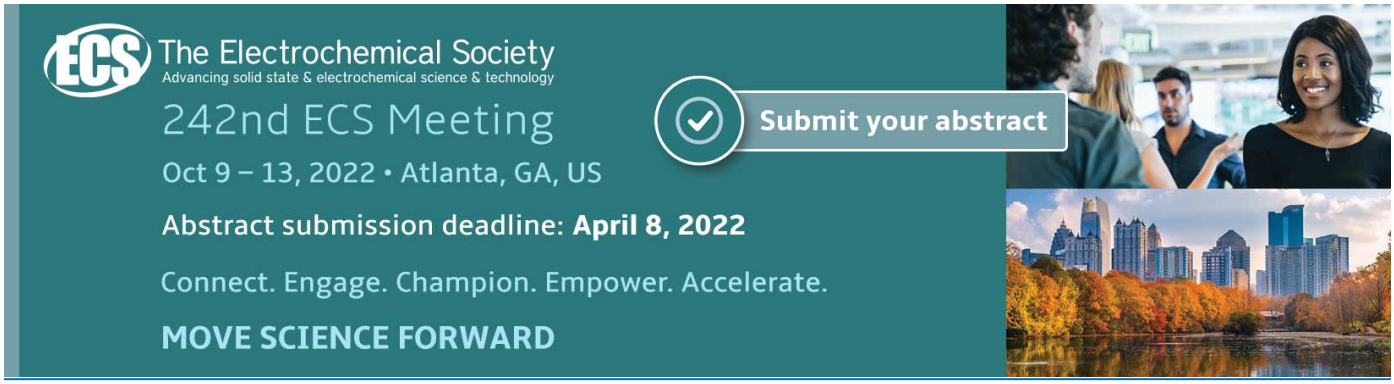

Manipulation of inverted and direct opals by a Focused Ion Beam Scanning Electron Microscope (FIB SEM).

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Abstract.

Focused ion beam (FIB) milling techniques are presented aiming at the manipulation of both tin dioxide (SnO_2) inverted opals and polystyrene (PS) direct opals. Different SnO_2 opals are considered in order to estimate the regularity of their bulk after the production. A SnO_2 mesoporous monolith is FIB micromachined to make it suitable for optical applications. PS direct opals are structured by FIB milling at different scales. Ordered arrays of PS opals are modified by selectively removing a single sphere. In performing this task, we discuss the effects on the FIB milling due to the gas-assisted enhanced etching and to the binding of the nearest neighbours. Techniques to achieve imaging of PS opals in absence of a conductive coating are also brought up. Furthermore, isolated PS spheres are drilled with or without enhanced etching in order to produce controlled defects on them. The FIB-assisted manipulations we show may find potential applications in the field of photonic crystals, (bio)sensors and lithography assisted by colloidal masks.

Keywords: Focused Ion Beam (FIB), micromachining, direct and inverted opals, colloidal PS microspheres, nanocavity.

1. Introduction

The Focused Ion Beam (FIB) is both a nanofabrication and a powerful inspection tool, especially when coupled with a Scanning Electron Microscope (SEM) [1; 2]. In recent years, FIB applications have greatly expanded, also invading the soft matter field [3; 4]. Ordered aggregates of colloidal spheres of different sizes or compositions are employed as building blocks in direct opals (DOs) photonic crystals (PhCs) or as masks in imprint contact lithography [5; 6]. Moreover, arrays of colloidal spheres are commonly used as templates for inverted opals (IOs), which can work as gas sensors or as PhCs as well. It is crucial for all these applications to check the regularity of such arrays and possibly to achieve controlled defects in the structure.

2. Materials and Method

In this paper, tin dioxide (SnO_2) IOs and small regular aggregates of PS spheres are considered as examples of characterization and manipulation carried out by a FIB/SEM device. SnO_2 IOs are produced by the monodispersion of PS spheres in a SnO_2 media, following a standard recipe for the preparation and the removal of the sphere template [5]. Portions of commercial PS spheres (Ø = 500 nm) self-assembled on a Si surface are considered as DOs. Different FEI DualBeam workstations have been

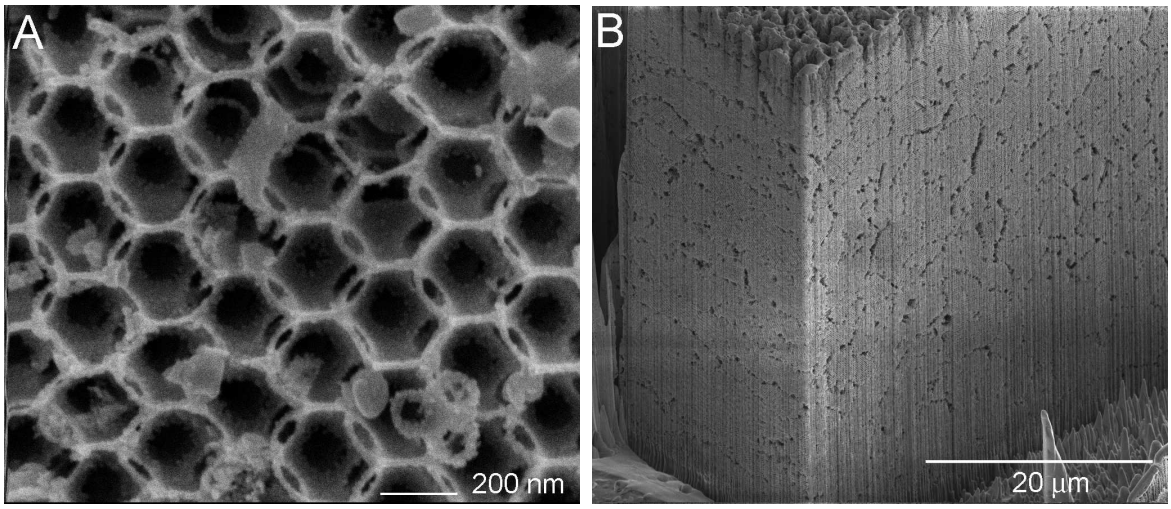

Figure 1. (A) SEM of tin dioxide inverted opals (Acceleration voltage 5 kV, thru-the-lens detector, magnification 200kX) (B) micromachining of SnO_2 mesoporous powder grain (SEM at 2.5 kV, E-T detector, magnification 5kX).

employed: a Strata 235, a Nova NanoLab 400 (both coupling a FIB with a SFEG-SEM) and a Quanta 3-D 200 (coupling a FIB with an Environmental SEM – ESEM).

3. Results

The quality of SnO_2 IOs is assessed by means of a FIB/SEM system, disclosing their morphology from micro-scale to nano-scale (Fig. 1A). Electron imaging reveals a complex morphology formed by regular, periodic structures organized in adjacent blocks of few micrometers and with different orientations. The IO regular structure characterized by spherical shells (Ø $\sim$200 nm) and nanopores (Ø $\sim$20 nm) can be seen in Fig. 1A. An investigation of the inner portion of an inverted opal is also carried out by a FIB milling, proving the existence of these periodic structures beneath the surface.

FIB micromachining of a SnO_2 mesoporous powder grain was prepared in order to fabricate a monolith suitable for photonic applications (Fig. 1B). The milling started at a nominal current of 7 nA at the standard ion acceleration voltage (30 kV). The polishing was carried out by lowering the current at each step. The final step was the polishing at 500 pA.

The next quest is to prove the possibility of a FIB-assisted micromanipulation of regular aggregates of PS particles, since they are employed directly as colloidal PhCs or as templates for IOs. This is challenging because it frequently means facing non-conductive elements with charged particle beams. The deposition of a conductive layer is the standard solution to both electron imaging and FIB milling operations [7]. The use of an ESEM is a way to avoid this countermeasure for imaging, as shown in Figs. 2A-B. Alternatively, we have experienced good resolution SE images by adopting the FIB as a primary beam and the lowest current (1 pA) (cf. Figs. 3A-B).

In order to reach a controlled fabrication, one needs to determine the pattern shape, the milling time and the ion beam current as main control parameters to completely remove a single sphere. Many tests have been arranged on isolated PS spheres (Ø = 500 nm). Ion beam current was set at 1 pA; a circular milling pattern with a diameter of 500 nm was able to remove a sphere in a milling time longer than 400 s. In this case, results were not completely reproducible since sometimes charging built up on the milled sphere causing a drift of the incoming ions.

The Selective Carbon Etching (SCE), which consists in locally delivering H_2O vapour on the milling site, is adopted to enhance the milling rate. SCE also contributes in shortening the milling time by increasing the pitch of the patterning. It is worth noticing that this also means a lower ion dose and hence

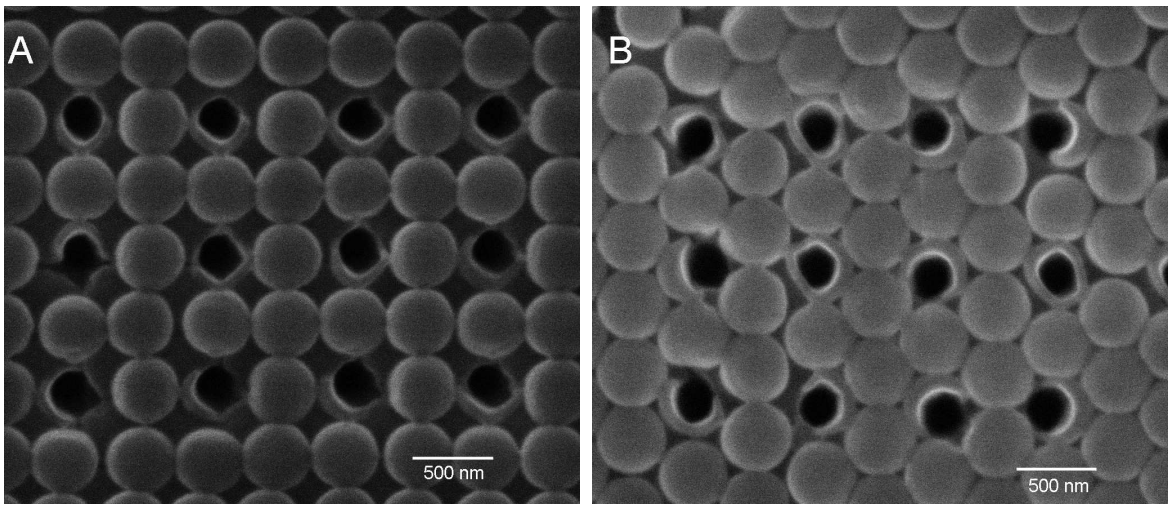

Figure 2. Selective removal of a sphere: (A) in a square array; (B)in a hexagonal array. (ESEM at 15kV, chamber pressure 2 hPa, magnification 70kX for both images)

a less consistent charging. The removal of a 500 nm PS sphere is achieved by a circular pattern with a diameter of 190 nm and a milling time of 50 s, obtaining a greater advantage than in the previous case.

Results of periodic removals on a square array and a hexagonal one are displayed in Figs. 2A-B. SCE is employed with the milling parameters we reported above. A comparison between the square and the hexagonal array is useful to understand that the presence of the nearest neighbours is not negligible in the removal operation. The packing configuration due to six nearest neighbours (Fig. 2B) instead of four (Fig. 2A) causes an incomplete milling of the spheres for the case B, which may require a further polishing in the zone of the debris.

Isolated PS spheres are FIB drilled, by performing circular patterns with smaller radii than before. Holes with nominal diameters of 60, 90, 120 nm are obtained inside the colloidal spheres (Fig. 3A). Nanocavities in silica nanospheres have been previously obtained by Woldering *et al.* [7]. These authors report that enhanced etching by iodine vapour has a negligible effect on the FIB drilling. As a difference from their work, we note that on the contrary SCE introduces an interesting widening of the drilled hole due to the chemical action of the H_2O vapour on the PS sphere (Fig. 3B). The SCE gives rise also to a deformation of the sphere which departs from the circular shape, in a way similar to the production of nanoholes on PS colloidal spheres by means of Reactive Ion Etching (RIE) [8].

4. Discussion & Conclusions

This work has presented FIB/SEM techniques in characterizing and in manipulating inverted opals, single colloidal PS microspheres and some aggregates of them. The advantages of FIB milling in the bulk characterization and the preparation of some SnO_2 IOs are provided (Fig. 1B). Although it is a destructive technique, FIB milling can provide a direct imaging of the inner shells and pores, paving the way for their statistical estimation [9] or their 3-D reconstruction [10], reaching e.g. a higher precision than standard mercury porisimetry. After a proper milling and polishing, a SnO_2 monolith is ready for a good injection or extraction of light from the flat surfaces minimizing the scattering due to a rough surface.

The controlled FIB cutting of well-organized DO domains in order to produce e.g. suitable templates for IOs is possible and their lift-out was already suggested. Here, we have presented the issue of manipulating the DO array at the level of a single colloidal sphere. This has been previously obtained by different electron beam lithographies [11; 12] or by femtosecond-laser machining [13]. A straightforward imaging of the modified PS spheres can be achieved in absence of coating by means of an ESEM as well

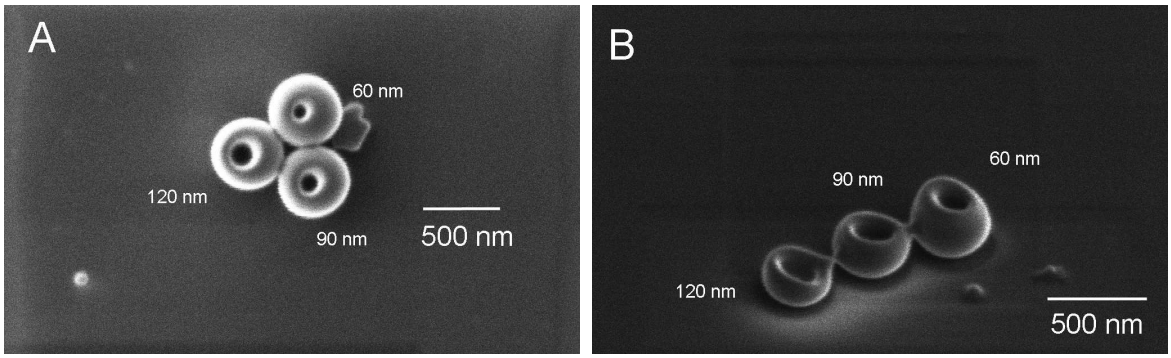

Figure 3. Nanocavities induced by FIB drilling at 30 kV with 1 pA nominal current. (A) Milling with a circular pattern with a diameter of 60 nm, 90 nm and 120 nm respectively. (B) Same operations but with Selective Carbon Etching (tilted view by 52°). (Ion images, accelerating voltage 30kV, nominal current 1pA, E-T detector, magnification 80 kX for A and 100 kX for B)

as by a FIB imaging. A dramatic enhancement is introduced by SCE on the controlled FIB milling and can be regarded as a sort of RIE on the PS spheres [8], but with a different local effect owing to the 'point' interaction characteristic of the FIB.

Colloidal spheres are drilled or selectively removed by FIB milling, suggesting interesting applications for these controlled defects. The selective removal can give rise to a monolayer of spheres with a new geometry (Fig. 2A-B), usable as a mask in optical applications or as a template in imprint contact lithography. Moreover, the missing of a sphere or of a row of them can be used respectively as optical cavity or as optical waveguide inside a PhC. The drilled holes (Fig. 3A-B) can set up optical nanocavities inside the DO or selective sites for large molecules in a biosensor mock-up. If non-through holes are generated, these can be used as microvials for biochemical microanalysis. Furthermore, one can fabricate composite functional colloidal spheres by injecting different particles inside the nanocavity.

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