ESRF	**Experiment title:** In-situ grazing incidence X-ray diffraction of growing the artificial opals. The kinetic of the growing crystal.	**Experiment number**: SC 3522
Beamline: ID10B	**Date of experiment**: from: 16/02/2013 to: 19/02/2013	**Date of report**:
Shifts: 9	**Local contact(s)**: Dr. Oleg Konovalov	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists): **A. Chumakova* (PNPI), A. Vorobiev* (ILL), E. Velichko*(PNPI), K. Napolskii* (MSU), D. Petukhov*(MSU).**

Introduction

It is well known that artificial opals (AO) consist of submicron monodisperse microspheres packed in a face-centered cubic structure. AO and materials on their basis are considered as good candidates for the creation of high quality Photonic Crystals (PhC). The latter have recently attracted great attention due to their unusual optical properties and promising applications in optical devices. The basic problem in creating AO is formation of defects at every stage of synthesis, which cause disorder of structure and subsequent deterioration of optical properties. There are several interactions which lead to crystal forming – Coulomb interaction between spheres or between substrate and spheres, capillary forces and gravity. Each of these interactions affects the quality of the AO structure. A separate impact of each driving force at different stages of the crystal formation is insufficiently studied.

Nowadays the vertical deposition technique is at the time being the most effective method for AO creation allowing synthesis of high quality defectless (fault-free) structures with an area of several centimetres. It was supposed that the vertical deposition technique suggests that the meniscus moves along the fixed vertical substrate and the crystal is formed in the area under meniscus [1]. Thus we can assign two specific directions in the AO structure. The first direction is the [111] axis, which is perpendicular to the substrate plane and along which the AO film grows layer by layer. The second direction is the [10-1] axis, which is displaced in the substrate plane and along which the meniscus moves. We are particularly interested in answering the following question: can the charged spheres form hexagonal layers in a bulk sample far from the meniscus or it is only possible in this triple gas-liquid-solid interface? How ordering of the spheres along the substrate depends on the distance from the gas-liquid interface?

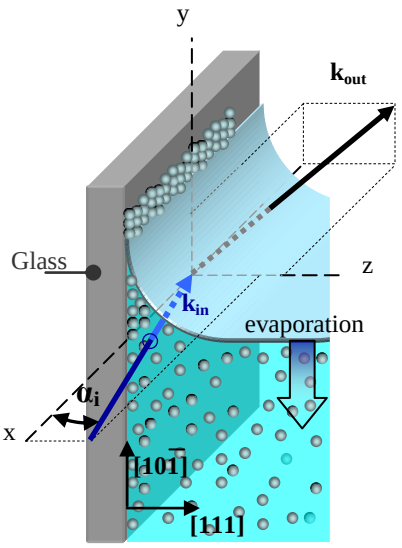

Fig.1. The scheme of the experiment

Samples and experimental techniques

In our experiments we have used several types of the suspensions of colloidal microspheres. Microspheres were PMMA and polystyrene with diameters (D) 200, 250 and 450 nm and dispersion (ΔD) of 5% in aqua or aqueous-alcoholic solvent. Substrates were glasses. Other samples were opal-like crystals, which were previous obtained and were used to check our experimental scheme.

We have applied grazing incidence X-ray diffraction (GID) method and small angle X-ray diffraction (SAXD) to study ordering of the charged spheres at the solid-liquid interface. We have used maximum energy available on ID10B (22 keV), which provides both reasonable penetrations through the suspension and angular resolution of the scattering. The positions of the substrate, container with suspension and radiation source were fixed during the experiment (Fig. 1). In such geometry the suspension evaporates and the meniscus moves along the fixed vertical substrate, thus the x-ray reflection was taken from the same spot

of the sample being under investigation. This spot of the sample was located 1) in depth of suspension at the early stage, 2) exactly under meniscus, 3) above meniscus, far away from suspension. The duration of such experiment was about 8-12 hours. The SEM measurements were carried out after the synthesis..

Grazing incidence x-ray diffraction and small angle x-ray diffraction

We present the results of the first in-situ grazing incidence X-ray experiment on monitoring of the artificial opals growing process during the vertical deposition of the monodisperse spherical PMMA particles from the aqueous solution on the glass substrate. The main idea of the experiment was to reveal the exact location of the crystallization process by measuring the X-ray scattering from the dynamic meniscus area. However, we have to recognize that the most of the results were carried out ex-situ. We suppose that it happened because of number of reasons. The first one - a thermodynamic control of crystal growth is complex problem. The second one - we observed radiation damages on the substrate surface, the focused beam (energy E ~ 21.85 keV) burns out the crystal film during 8 hours. Nevertheless, our results indicate that the particles adjusted by the substrate are concentrated mainly under the meniscus (Fig. 2a) but not deep in the suspension. This leads to the outset of the ordering process in the meniscus top. We suggest that the spheres ordering starts at the gas-liquid-solid boundary and continues at the air-solid boundary above the meniscus. The final crystal formation occurs during the drying process and its driving force is the solvent evaporation from the crystal voids (Fig.2b).

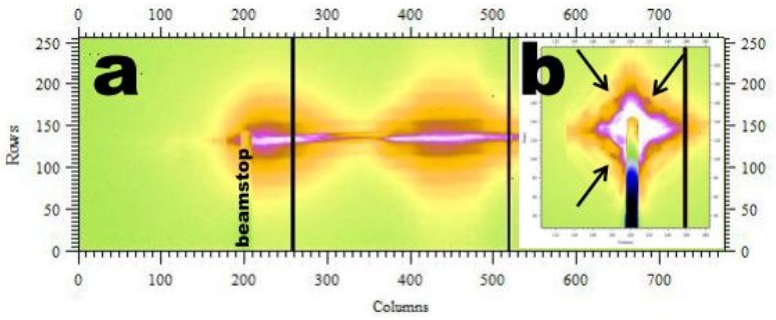

Fig.2. Diffraction patterns taken for colloid with PMMA particles (a) during in situ experiment and (b) after synthesis

To control our in-situ experiment we have obtained diffraction patters for opal-like crystal which was synthesized by PS particles with diameter 450 nm at usual conditions. It should be noted, that earlier we have tried to study this sample at this beam line, but we were observing only the form-factor distribution from the spheres. However, after upgrading the beam line has became better and we have obtained magnificent diffraction pattern (Fig. 3a). One can see the eight orders of diffraction peaks, while as we usually observed four or five orders by μXRD on the same samples [2]. The five diffraction orders have been observed after dipping the prepared opal-like crystal into the solution. Therefore we can conclude that the used experimental setup enables to resolve nanostructures with periodicity about 500 nm and proposed experiment can be successful at the defined conditions of the synthesis.

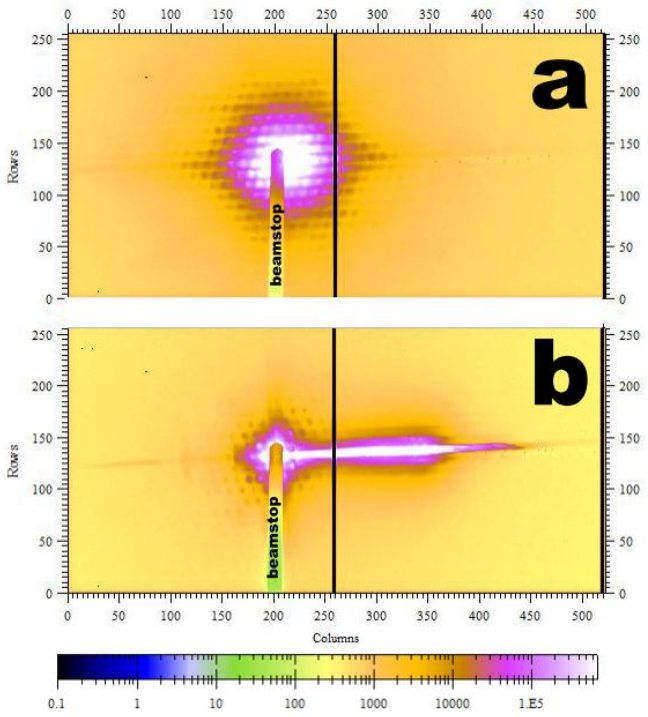

Fig.3. Diffraction patterns taken for opal-like crystal (a) on the air and (b) into the solution

References

[1] M.G. Nikolaides et al., Nature, 420, 299 (2002)

[2] K. S. Napolskii, N. A. Sapoletova, D. F. Gorozhankin et. al., Langmuir. **26**, 2346 (2010)