DUBBLE	**Experiment title: Effect of the electrostatic forces on the crystallographic structure of artificial opal-like crystals grown onto conductive substrates: synchrotron ultra-small angle diffraction study**	**Experiment number**: **26-01-852**
Beamline: BM-26B	**Date(s) of experiment**: From: 10-12-2009 To: 14-12-2009	**Date of report**: 14-01-2010
Shifts: 9	**Local contact(s)**: Dr Giuseppe Portale	
Names and affiliations of applicants (* indicates experimentalists): W.G. Bouwman* (Delft), D. Byelov*, A. Petukhov (Utrecht), D. Chernyshov* (SNBL, ESRF), N. Sapoletova*, D. Gorozhankin*, K. Napolskii*, A. Eliseev* (Moscow), N. Grigorieva*, A. Mistonov*, A. Vassilieva*, S. Grigoriev* (St. Petersburg)		

Report:

The experiment was devoted to the study of structure and order of the colloidal photonic crystals prepared by the novel method based on vertical deposition in the presence of a DC electric field normal to the substrate. Deposition of negatively charged 530 nm PS spheres onto ITO glass vertically aligned electrodes was performed in a cylindrical glass cell (5 cm diameter) using a Solartron 1287 potentiostat. The distance between the electrodes was 3 cm. The concentration of PS particles in the colloidal solution was ~0.2 vol. %. Deposition of PS spheres has been carried out at constant voltage U ranging from 0.1 to 3 V for 24 h at 60±3 °C. A 12 keV X-ray beam (wavelength λ = 0.1 nm, bandpass $\Delta\lambda/\lambda = 2\times10^{-4}$, size 0.5×0.5 mm^2 at the sample position) was used. The beam was focused by the lenses, which were installed just before the sample. The data collection was performed by the CCD X-ray detector (Photonic Science VHR, 4008×2671 pixels of 9×9 μm^2) located at a distance of 8 m from the CR lenses. The colloidal films were first mounted perpendicular to the X-ray beam. Samples were then rotated around the vertical axis within the range $-75° \le \omega \le 75°$ and the diffraction patterns were recorded at each degree of rotation. The collected images represent sections of reciprocal space projected on the flat area detector. This allowed for the mapping of most of the three-dimensional reciprocal lattice of the crystal. It is worth noting that the curvature of the Ewald sphere in the small-angle experiments could be neglected due to the gigantic difference between the structure period and the X-ray wavelength. The background subtraction and reconstruction of reciprocal space from the data were performed by a in-house developed Mathcad code [1].

Figure 1a-d shows typical examples of microradian diffraction patterns measured for different orientations of a colloidal crystal, corresponding to lowest index zones of fcc structure, that is (111) at ω = 0°, (121) at ω = 19.5°, (101) at ω = -35.3° and (010) at ω = 54.7° (ω is the rotation angle around the vertical axis, which aligns with the [10-1] axis of the crystal). In the diffraction patterns one can clearly identify a large number of Bragg reflections, which can be assigned to the reciprocal lattice of the ideal fcc crystal structure with the cubic cell size of a_0 = 750 nm. Corresponding indexes are shown in Fig. 1.

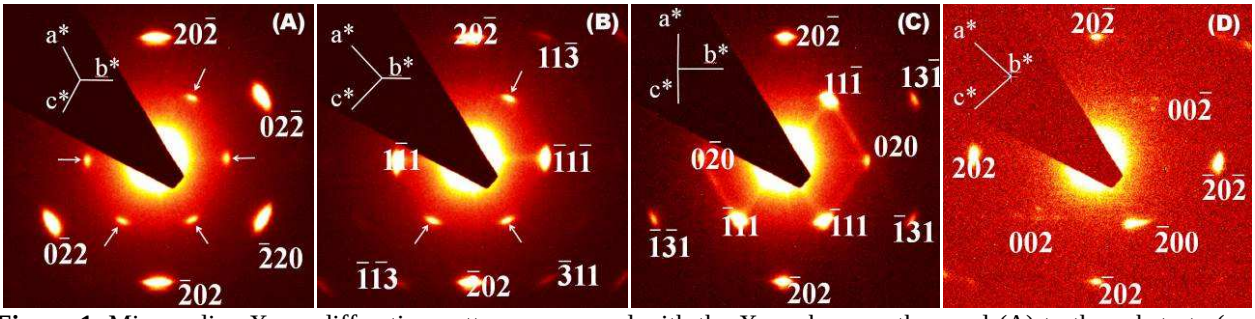

Figure 1. Microradian X-ray diffraction patterns measured with the X-ray beam orthogonal (A) to the substrate (ω = 0°) and after a sample rotation around the vertical axis by ω = 19.5° (B), ω = -35.3° (C) and ω = 54.7° (D). These patterns correspond to the index zones (111), (121), (101) and (010) of a fcc structure. The colloidal crystal is obtained on the cathode at U = 1.5 V. Peaks, which cannot be assigned to a fcc lattice, are marked by arrows in panels A and B.

In addition to the assigned Bragg peaks the diffraction patterns also show features, which cannot be assigned to the fcc structure (marked by arrows in Fig. 1a and b). They can be truly Bragg's reflexes (for example, corresponding to an hcp structure co-existing with fcc), or can be sections of diffuse objects in the reciprocal space. The later can be related to the finite film thickness and/or to the presence of stacking faults along <111> cubic directions [2]. Complete information on this type of disorder could be inferred from the distribution of diffracted intensity in the three-dimensional (3D) reciprocal space. The latter is reconstructed from the collected diffraction data. An example of 3D maps in reciprocal space are shown in Fig. 2 for the colloidal crystals formed on the anode (A) and cathode (B) at U = 1.5 V. One clearly sees the presence of the extended rods of diffuse scattering and of localized reflections with well-defined round shape. This reciprocal lattice is typical for a close-packed structure with stacking faults [2].

One can see that for the crystal grown on the cathode the width of the diffraction maxima is lower than one for the sample obtained on the anode. Thus, increase of a cathode polarization leads to the improvement of crystal quality but, at the same time, the thickness of a film decreases. In future the analysis of the distribution of the diffracted intensity along the Bragg rod with help of Wilson's theory [3] will be performed. We believe that collected data will help us to evaluate colloidal crystal quality as a function of applied potential.

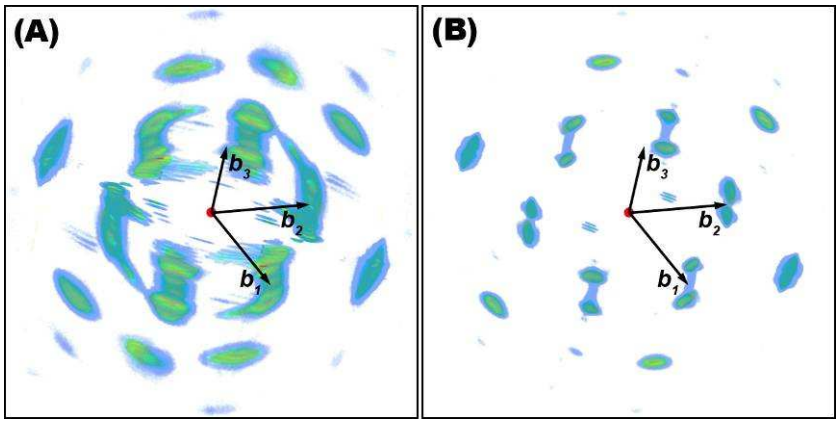

Figure 2. 3D reconstruction of the reciprocal space for the colloidal crystals obtained on the anode (A) and cathode (B) at U = 1.5 V. The reflections only within q < 0.03 nm^{-1} are shown. The hexagonal basis is depicted by the vectors $\boldsymbol{b}_1$, $\boldsymbol{b}_2$ and $\boldsymbol{b}_3$, where $\boldsymbol{b}_3$ corresponds to normal to the film surface.

In the conclusion we would like to stress that progress in SAXS instrumentations and computing techniques make 3D reconstructions of the reciprocal space routinely available. This method provides extremely valuable information on a real structure of mesoscopic materials, which cannot be easily obtained by other analytical approaches.

We should stress that for the 3D reconstruction of reciprocal space on the basis of diffraction images the precise alignment of the sample is required. Otherwise rotation of the sample along the vertical axis leads to movement of the X-ray footprint through the sample surface. In order to improve experimental setup on DUBBLE for such experiments the installation of the long-focus camera to the vertical axis at sample position is very desirable. Finally, we would like to thank our local contact Dr Giuseppe Portale for the excellent support.

References:

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[3] A.J.C. Wilson, *Proc. R. Soc. London Ser. A* **180** (1941**)**, 277-285.