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DUBBLE	**Experiment title:** **Quantitative determination of disorder in colloidal photonic crystals.**	**Experiment number**: **26-02-376**
Beamline: BM26B	**Date(s) of experiment**: From: 16-06-2007 To: 21-06-2007	**Date of report**: 07-08-2007
Shifts: 9	**Local contact(s)**: Dr. K. Kvashnina	

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Report: (max. 2 pages)

As explained and motivated in our beam time application, our research is concerned with using colloidal crystals as photonic crystals. Although colloidal crystals are quite suitable for use as photonic crystals, their optical properties suffer from disorder and defects in the colloidal crystal, which in turn stems from either fabrication method or building block properties. Colloidal particles, usually made trough a wet-chemical synthesis, display a certain size polydispersity (standard deviation of the size distribution relative to the mean). It has been calculated (Koenderink *et al.*, Phys. Rev. B, **72** (2005), 153102) that current state-of-the-art polydispersities, which are 2-5% for micron-sized SiO_2 colloids, would limit control over photons to some 50 lattice parameters, and would impede application of colloidal crystals in situations where large photonic crystals are needed. However, we have recently been able to synthesize spherical SiO_2 colloids which we believe to have a size polydispersity of the order of 0.5%, i.e. nearly an order of magnitude smaller than what is found in literature. We would like to show quantitatively that using these colloids as building blocks, we can produce colloidal crystals with significantly smaller defect densities, owing to this extremely low polydispersity.

As a first step, we therefore need to accurately establish the size and the polydispersity of our colloids. Conventional ways of doing this include Static or Dynamic Light Scattering (SLS/DLS) and Transmission Electron Microscopy (TEM). However, none of these methods is suitable to measure polydispersities that are very small (Megens *et al.*, Langmuir **13** (1997), 6120). We therefore turn to SAXS. The vast q-space available with this method, and the high quality monochromaticity of the X-rays, allow us to very accurately establish particle size as well as polydispersity in situ. For this, the same set-up was used as described in further detail in the report on experiment 26-02-384 (Petukhov). With this, using the Be lens allowed us to measure particle formfactors at very small scattering angles. Without the Be lens, but refocussing with the bending mirror, we were able to do similar measurements at larger scattering angles, in total measuring scattered intensities ranging over at least 6 orders of magnitude and establishing ~40 minima in the particle formfactor. This in itself is a scientific record as far as we are aware, but foremostly indicates the ultra-low-polydispersity. If we plot the formfactor data in a Porod plot, we can clearly see a beating superposed on the $\cos^2(qR)$ form. This is expected, as we know that the electron density is likely not homogeneous over the particle volume. This is caused by the synthesis method, which consists of a number of successive growth steps of the so-called Stöber synthesis, starting from SiO_2 core particles produced in a micro-emulsion of only 50 nm in size. These cores are expected to have a lower density than subsequent shells. We have also measured the formfactors of the particles at their different stages after each shell growth, which we hope will allow us to model the behaviour seen in the Porod plot in a satisfactory way, or at least help us establish an upper limit of the polydispersity. Moreover, these data may form a unique proof of (relative) density

differences in silica resulting from different types of synthesis (micro-emulsion vs. Stöber). Lastly, these measurements were done at different particle volume fractions. Concentrated samples allowed us to measure intensity profiles at higher scattering angles with short exposure times, while diluted samples allow us to avoid effects of the structure factor. This is illustrated in Figure 1.

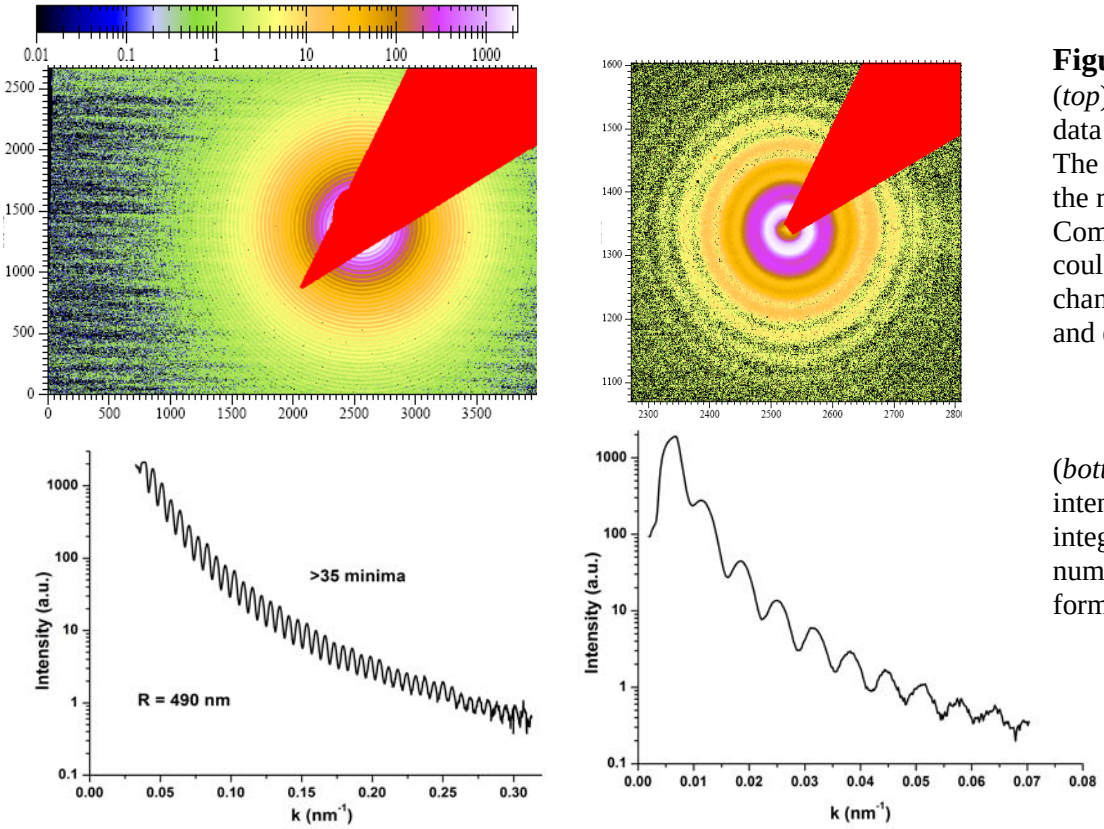

Figure 1.
(*top*) Two examples of SAXS data obtained at DUBBLE. The beamstop is masked by the red polygon. Complementary q-ranges could be investigated by changing beamstop position and exposure time.

(*bottom*) Corresponding intensity profiles (radially integrated) where a huge number of minima in the formfactor can be seen.

One type of lattice defects we investigated involves stacking disorder in the hexagonal planes of a colloidal crystal made with a popular technique called controlled drying. Often, a vertical stripe pattern is observed in such colloidal crystals that can easily extend over centimeter sizes, when the crystal is illuminated with visible light (Figure 2a). We speculated that these patterns stem from a difference in stacking sequence (J.H.J. Thijssen, PhD thesis, Utrecht University, 2007). With our set-up we were able measure rocking curves of individual stripes. Figures 2b,c show diffraction patterns at angles of +19.5 and –19.5, respectively. From the strength of the $(1\,\bar{1})$ reflection it is seen that both twins exist, but in each stripe one is more prevalent than the other. We are presently analyzing the widths of the two rocking curves to determine the number of layers in each twin.

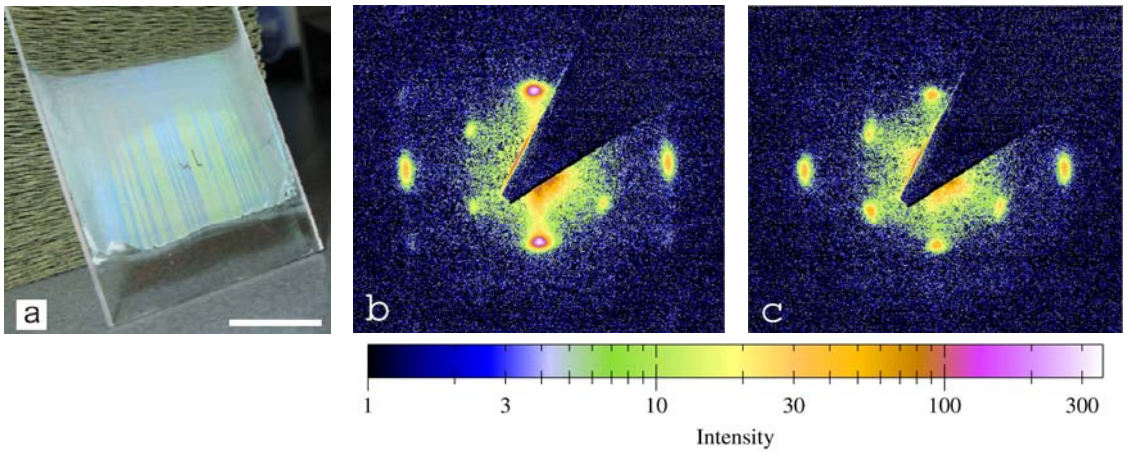

Figure 2. (a) Photograph of stripe pattern in colloidal crystals made by vertical drying. (b), (c) Diffraction at sample rotation of +19.5 and –19.5 with respect to the normal, respectively. The scalebar in (a) is 1 cm.

We would like to thank NWO and the DUBBLE staff for making these experiments possible, and in particular Dr. K. Kvashnina and D. Detollenaere for their assistence on site.