

Presenting Author: Max Burian
E-mail: max.burian@unileoben.ac.at

Preferred Format: (Oral)

In-situ Synchrotron Studies of Colloidal Crystallization and the Influence of the Nanocrystal Shape

Max Burian,^a Heinz Ammenitsch,^b Gerhard Fritz-Popovski,^a Maksym Yarema,^{cd} Wolfgang Heiss,^c Maksim Kovalenko,^e Oskar Paris,^a Rainer T. Lechner^a

^aInstitute of Physics, Montanuniversität Leoben, Franz-Josef-Str. 18, 8700 Leoben (Austria)

^bInstitute of Inorganic Chemistry, TU Graz, Stremayrg. 9/4, 8010 Graz (Austria)

^cInstitute of Semiconductor and Solid State Physics, JKU Linz, Altenbergerstr. 69, 4040 Linz (Austria)

^dDepartment of Information Technology and Electrical Engineering, ETH Zurich, Gloriastr. 35, 8092 Zurich (Switzerland)

^eDepartment of Chemistry and Applied Biosciences, ETH Zurich, Wolfgang-Pauli-Str. 10, 8092 Zurich (Switzerland)

Colloidal crystals using crystalline nanoparticles (NCs) as building blocks offer the opportunity for designing artificial solids with tailored properties [1] used e.g. for nanoelectrodes [2]. The assembly of colloidal crystals is not only influenced by the NC-size, but also by the shape of the individual NC. One reason for the deviation of the spherical shape is the crystallographic facet formation on the NC surface, in order to minimize the total free surface energy. The recently achieved control of the synthesis process [1, 3] of these NCs results in size distributions below 5%. This allows the use of SAXS methods to retrieve the mean shape of a large ensemble of inorganic NCs.

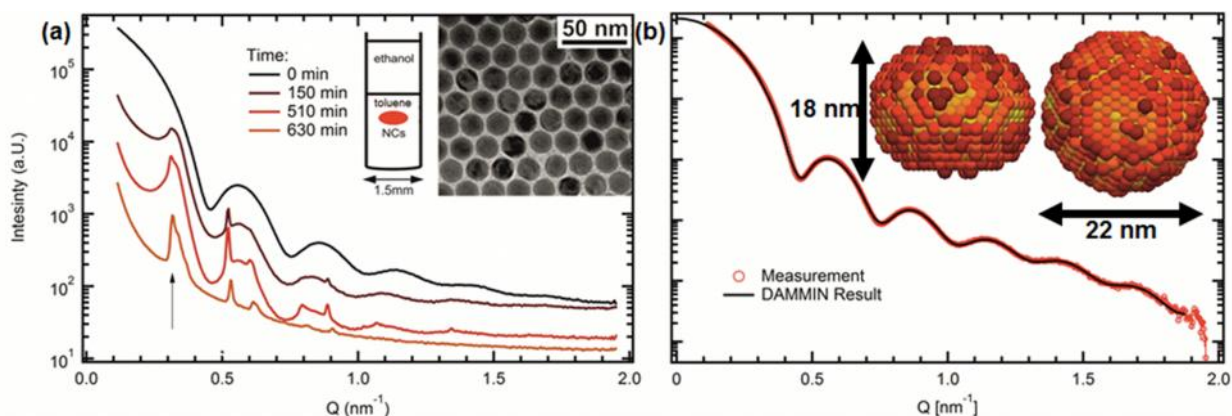


Fig. 1: (a) Time resolved *in situ* SAXS patterns of the formation of self-assembled colloidal crystallization of Bi-NCs shown in the inset. (b) SAXS pattern (red spheres) compared to the calculated fit (black line) for the faceted shape using a dummy atom model of around 1 nm shown in the upper inset. (both measurements were performed at the Austro-SAXS beamline at ELETTRA.)

We studied by in-situ SAXS/WAXS the template free self-assembled colloidal crystallization by diffusion of a non-solvent into the colloidal dispersion [3]. The SAXS patterns of the NC ensembles were recorded below the NC-solvent/non-solvent interface at the SAXS beamline at ELETTRA. Hence, we can follow the crystallization process in short time steps as a function of the non-solvent concentration.

Furthermore, we revealed that the 22 nm Bi NCs are nearly monodisperse, but deviate significantly from a spherical shape. A good correspondence between SAXS data and fit was found for an elliptical shape with two main axes of 18 nm and 22 nm (see Fig.1), which could not be detected with previous TEM studies. A nearly perfect fit was achieved by using the ATSAS software package developed originally for the shape retrieval of monodisperse protein structures [4]. The obtained mean shape clearly reveals the faceted NC surface (see Fig. 1). Further investigations show a correlation between crystal size and aspect ratio of the main axes. It can be shown, that the NC approaches spherical shape with decreasing radius. We are currently testing the application of this method for experimental laboratory setups. In the future we will affirm the reliability for more complex shapes, e.g. core-shell structures, and applying small but finite size distributions. We cross-check the results using an alternative new software package (2D-GIFT) [5].

1) D.V. Talapin, MRS Bull. 37, 2012, 63-71.

2) M. Yarema, S. Pichler, D. Kriegner, J. Stangl, et al., ACS Nano 6, 2012, 4113.

3) M. Yarema, M.V. Kovalenko, G. Hesser, D.V. Talapin, W. Heiss, JACS 132, 2010, 15158-15159.

4) D.I. Svergun, Biophys J., 1999, 2879-2886.

5) G. Fritz-Popovski, J. Appl. Cryst. 46, 2013, 1447-1454.