Experimental report

23/07/2019

Proposal: 1-10-38 **Council:** 4/2017

Title: Free-film sample environment for containment-free in-situ observationof CdS Qdot formation

Research area: Chemistry

This proposal is a new proposal

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Samples: D2O
PbS
CdS
EDTA - Ethylenediaminetetraacetate
CdCl2
Na2S

Instrument	Requested days	Allocated days	From	To
D11	1	1	06/06/2018	08/06/2018
D16	1	0		

Abstract:

The aim of the proposal is to provide a novel, containment-free sample environment for liquid samples for neutron scattering. The setup was previously established for X-ray scattering and will be optimized for sample volumes in neutron scattering as part of an ILL summer student placement project (Ref. SPECT_8). Although the main purpose of this beamtime request is instrumental, the proposal also pursues a timely scientific goal in the field of nanoparticle formation. We wish to investige the formation of CdS nanoparticles with respect to organic ligand shells and crystallization in aqueous solution. The role and size of the organic ligand shell made of ethylenediaminetetraacetate (EDTA) in the 2.5 mM solutions shall be observed for the precursor to particle transition and requires the high flux of D11. At D16 we wish to investigate the open question when and how CdS quantum dots transform from restructured precursors to crystalline particles. To this effect, the first Bragg peak of CdS at 1.9 A-1 needs to be observed. As a future perspective the sample environment can be used for corrosive liquid samples and also in spectrometers.

NEUTRONS FOR SCIENCE	**Experiment title:** **Free-film sample environment for containment-free in-situ observation of CdS Qdot formation**	**Experiment number:** 1-10-38
Beamline: D11	**Date of experiment:** from: 06.06.2018 to: 08.06.2018	**Date of report:** 23.07.2019
Shifts: 3	**Local contact(s):** Ralf Schweins	*Received at ILL:*

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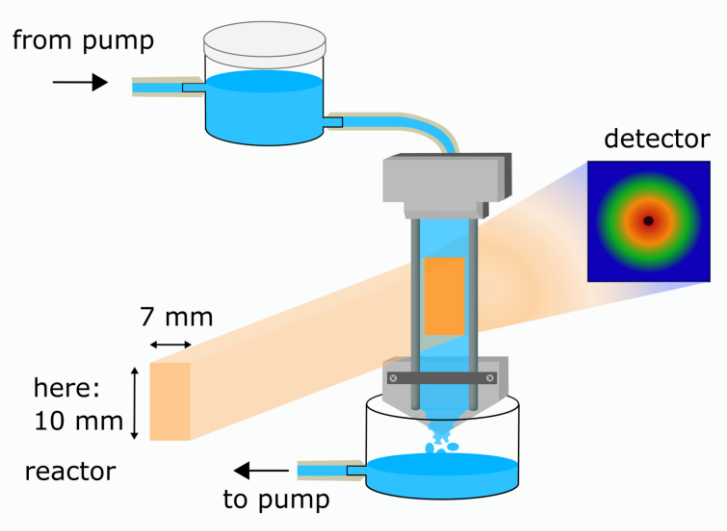
Report:

With this experiment we wanted to establish a containment-free sample environment for liquid samples. Every container in a neutron beam will give rise to undesired scattering. The aim of this work was to minimize the background by avoiding a container and at the same time providing a big sample volume in the beam. Therefore, a free-film setup was designed with a beam area of 7 x 10 mm^2 and a thickness of 0.5 mm (see Fig.). The principal aim of the experiment was to characterise the setup and prove its functionality for SANS experiments. Additionally, as a first in-situ experiment we watched the formation of CdS nanoparticles which were stabilised with ethylenediaminetetraacetate (EDTA, $C_{10}H_{14}N_2O_8Na_2$). Contrast matching experiments were carried out to learn about the properties and the influence of the ligand shell of the particles on the formation and agglomeration.

The proposed experiments were carried out using a wavelength of 4.6 Å and detector distances of 1.4 m, 5 m, 13 m and 39 m. For the experiment an upper reservoir of about 100 ml was used. This lead the fluid through a tube to the inlet of the free-film. The trapezoidally-shaped inlet spread the liquid between two metal wires which were separated by 9 mm. The height of the film can be adapted in the range of 1 cm up to 5 cm. Afterwards the fluid is collected in the lower reservoir



Schematic of the free-film setup. The orange rectangle indicates the neutron beam.

and transported back to the upper reservoir via a peristaltic pump.

In preparation for the experiment the setup was designed, custom-built and tested with the CdS nanoparticle solutions. The particle formation is a precipitation reaction between the two aqueous salt solutions $CdCl_2$, pre-mixed with EDTA, and Na_2S. For the SANS experiments, heavy water was employed. The salt concentrations in the final reaction volume were 3.0 mM $CdCl_2$, 3.1 mM EDTA and 7.7 mM Na_2S. At the beginning of the beamtime, we measured stable CdS nanoparticle dispersions with different D_2O concentrations in Hellma cells for the detector distances of 1.4 m, 5 m and 13 m to estimate measurement times. Afterwards the in-situ setup with a He protective atmosphere was installed on the beamline to prevent H-D-exchange of the heavy water with humidity from air. The nanoparticle formation was measured in-situ separately for the detector distances. All the samples were 100% D_2O solutions, just for 13 m there was time to also measure 70 % und 40 % D_2O solutions in the free-film.

By using the free-film instead of Hellma cells the background could be decreased on average by a factor of 37 %. The containment-free sample environment gives rise to a possible water exchange with the atmosphere. This changes the deuterium concentration slightly over time. The He atmosphere inside the jacketing with a glovebag supressed this effect by a factor of 5. The remaining exchange was 1% exchange over 10 h. The amount of water in the sample was determined via gravimetry and IR spectroscopy. The thickness of the free-film was determined to be 0.5 mm by the use of incoherent neutron scattering, normalised to experiments with the same D_2O concentrations in background subtracted Hellma cells.
In addition, the in-situ measurements of CdS nanoparticle formation showed an increasing structure at 0.03 nm^{-1} on the timescale of hours against our expectations. However, it was beyond the scope and proposal of this experiment to carry out sufficient contrast matching experiments to fully understand the CdS particle formation, for which we will submit a new proposal shortly.

All the results regarding the characterisation and implementation of the free-film setup were published in [1].

[1] Krauss, S. W., Schweins, R., Magerl, A., Zobel, M., *J. Appl. Cryst.* 52.2 (2019)