Experimental report

28/01/2020

Proposal: EASY-485 **Council:** 10/2018

Title: EDTA-directed CdS nanoparticle formation and agglomeration

Research area: Chemistry

This proposal is a new proposal

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Samples: CdS nanoparticles

Instrument	Requested days	Allocated days	From	To
D11	24	24	09/09/2019	10/09/2019

Abstract:

In-situ experiments of nanoparticle (NP) formation have been in the focus of research over the last decade to track particle size, shape, structure and properties. For long-term stability of NPs in applications, ligands are added. However, most studies of nucleation and crystallization were carried out without ligands.
In earlier studies on the formation of CdS NPs from aqueous solutions of CdCl2 and Na2S, it was found, that two steps occur. First, 1 nm precursors form in < 100 µs, which then assemble to particles of ca. 2.5 nm in diameter, further growing over time. In presence of the ligand EDTA (ethylenediaminetetraacetate), the nucleation and growth process is altered. While SAXS and TEM data indicate the existence of ca. 6 nm particles only, recent in-situ SANS measurements showed an increasing structure with ca. 120 nm diameter on the timescale of hours against our expectations. We hypothesize that the EDTA molecules create agglomerates of 120 nm which yet seem to be stable in dispersion over hours or days. With this proposal we want to investigate the evolution and kinetics of these EDTA-CdS-agglomerates and use contrast matching to highlight the CdS cores and ligand shells.

NEUTRONS FOR SCIENCE	**Experiment title:** **Free-film sample environment for containment-free in-situ observation of CdS Qdot formation**	**Experiment number**: EASY-485
Beamline: D11	**Date of experiment**: from: 09.09.2019 to: 10.09.2019	**Date of report**:
Shifts:	**Local contact(s)**: Ralf Schweins	*Received at ILL:*

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Report:

With this experiment we want to investigate the interparticle dynamics of CdS nanoparticles with an average diameter of 5 nm. In previous in-situ SANS experiments[1] with this system, we had first insights into the formation of superstructures on a characteristic timescale of ca. 6 hours. The aim of the measurements of this experiment is to complement the preliminary results by revealing the formation of structures on a timescale of days, provide insight into the composition by contrast matching and explore a broader concentration regime of the reactants. The proposed experiments were carried out using a wavelength of 5.5 Å and detector distances of 1.4 m, 8 m and 39 m.

The nanoparticle formation is a precipitation reaction between the two salt solutions $CdCl_2$ together with EDTA as a stabilizing ligand on the one side and Na_2S on the other side. In preparation for the experiment there have been SAXS and TEM measurements of these nanoparticles showing a particle size of 5 nm, but the superstructures had been inaccessible. The concentrations were tuned to be 6.25 mM of $CdCl_2$, EDTA and Na_2S in the final reaction volume. The employed EDTA had two of the four carboxylic groups protonated, while the other two were saturated with sodium. EDTA with different protonation levels were not used because of a corresponding change in the pH value which results in fast agglomeration. To start the reaction, the Na_2S solution was added to the $CdCl_2$ solution.

We started the measurement with equimolar salt and EDTA concentrations and repeated this experiment with a stepwise increase of the EDTA amount (25%, 50%, 75%). Afterwards we measured samples which have already been prepared several days before the experiment to get insight into the aging dynamics and long-term existence of the superstructures within the system. Then, contrast matching was done to selectively match the nanoparticles or the ligand shells. We used six samples with deuteration levels between 20 % and 80 %, each with the respective background measurement. In the final experiments, the overall concentrations of the salts and the EDTA were changed (keeping

their ratio equimolar) to 3.13 mM and 1.61 mM. Further, we reproduced the concentration of our preliminary experiment of 3.0 mM $CdCl_2$, 3.1 mM EDTA and 7.7 mM Na_2S, so that we can compare our current measurements with our earlier study, which was slightly outside the ideal stability windows of the CdS suspension.

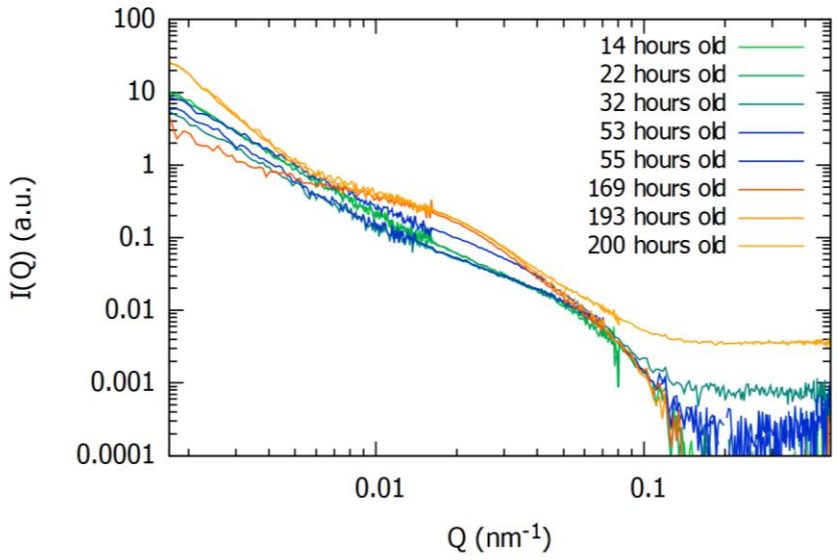

Fig 1: Merged SANS data of CdS nanoparticles in different aging states

All data was normalized and radially averaged to receive a one-dimensional scattering curve. The analysis of the aged samples revealed an increase in the scattering intensity at 0.02 nm^{-1} on a timescale of approximately 4 days (see Fig. 1). This suggests ongoing interparticle dynamics, leading to superstructures on a timescale of days. The contrast matching experiments showed a drop in the scattering intensity by hydrogen-deuterium ratios above 50 %. This could be explained by an intrinsic heterogeneity in the structure, if it is composed of nanoparticles, ligands and water. An increase of the EDTA concentration enhanced the formation of superstructures. These findings indicate that there is just a small concentration regime where EDTA leads to an effective particle-particle repulsion. This would indicate that a too big or a too small EDTA concentration leads to agglomerates. It was not possible to resolve the single nanoparticles based on the scattering curve as we would expect them on the basis of TEM and SAXS results of this system. Further analysis is still ongoing.

[1] Krauss, S. W., et al., *J. Appl. Cryst.* 52.2 (2019)