Experimental report

10/02/2017

Proposal: 9-12-498 **Council:** 10/2016

Title: Structure, temporal fluctuation and vibrational spectrum of the surfactant shell of PbS nanocrystals in solution

Research area: Materials

This proposal is a new proposal

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Samples: PbS nanocrystals an oleic acid in d8-toluene solution

Instrument	Requested days	Allocated days	From	To
D11	1	1	31/01/2017	01/02/2017
IN5	1	0		
IN16B	2	3	31/01/2017	03/02/2017

Abstract:

We will investigate the organic surfactant shell's adsorption on colloidally stable semiconductor nanocrystals in toluene-d8 solution, the softness of this organic layer and its influence on the vibrational spectrum of the nanocrystals. PbS nanocrystals coated with oleic acid as the surfactant are technologically relevant for quantum dot-based solar cells and subject to long-term investigations by several research groups including our collaboration, utilizing electron microscopy, X-ray scattering, optical/NIR-spectroscopy, Raman spectroscopy, etc. We propose a combined approach using small-angle scattering (SANS), backscattering (NBS) and time-of-flight (TOF) spectroscopy on the same PbS nanocrystal solution to elucidate the dependence of the vibrational spectrum (using TOF) on the volume and dynamics of the oleic acid shell measured by SANS and NBS, respectively. This experiment becomes feasible due to the previous complimentary characterization mentioned above as well as the extremely high flux available at ILL, which is of paramount importance considering the relatively low volume fraction of the surfactant shell (approx. 1 monolayer on PbS with a diameter of 50 (±3) Å).

Structure, temporal fluctuation and vibrational spectrum of the surfactant shell of PbS nanocrystals in solution

Experiment 9-12-498 on IN16B and D11

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The purpose of this was to explore the structure and dynamics of the surfactant shell of colloidally stable PbS NCs in toluene-d8 and hexane-d14. At D11, we utilized small-angle scattering (SANS) to determine the dispersion and thickness of the surfactant shell in these two solvents (**Fig. 1, left panel**). We found that hexane-d14 is a better solvent than toluene-d8 at these high concentrations (~140 µM), as the upturn at low q-values in the toluene solution indicates beginning agglomeration. This tendency could neither be removed by diluting the solution (1:10) nor by short sonication (10s).
We continued to explore the temperature-dependence of the well-dispersed NCs in hexane-d14 in the temperature regime 268 – 298 K (**Fig. 1, center and right panel**). We found a small but significant trend to larger scattering intensities for lower temperatures.

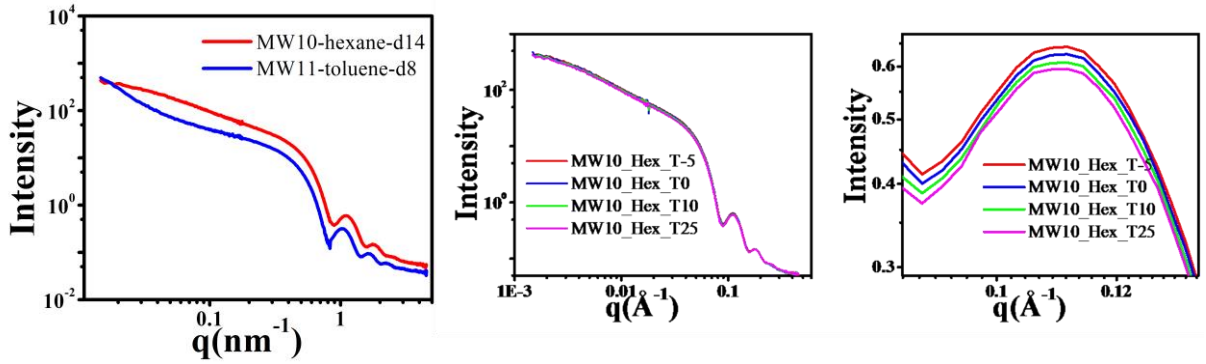

Figure 1. (left) *SANS of two almost identical PbS NC samples in hexane-d14 or toluene-d8 with a concentration of ~140 µM. (**center**) Temperature-dependence of the SANS signal of the PbS NC sample in hexane-d14. (**right**) Zoom into the q-region of the first-order correlation peak of the PbS NC sample in hexane-d14.*

At IN16B, we performed Quasi Elastic Neutron Scattering (QENS) and Elastic and Inelastic Fixed Window (E/IFW) scans between 300 – 183 K. **Figure 2a** shows an exemplary QENS scan at 239 K. The results show that at this temperature, free oleic acid diffuses faster than the instrument range (30 µeV, ~0.1 ns). Therefore, the broadened QENS signal from the NC sample can be tentatively attributed to slowed-down surfactant on the surface of the NC, diffusing on a nanosecond relaxation time scale.
EFW scans (**Fig. 2b**) illustrate the temperature-dependence and different behavior of free oleic acid and oleic acid immobilized on the NC surface in hexane-d14. At ~235 K, a phase transition occurs in the free oleic acid / d-hexane reference with notable hysteresis, indicating major dynamical changes in solution. In the NC sample, this phase transition is not observed. Instead, we note a gradual increase in the scattering intensity for various q-values below the transition temperature, which may potentially be linked to a gradual adsorption of the oleic acid to the NPs and subsequent surface diffusion, or a dynamic equilibrium of attached and free oleic acid molecules. The latter two possibilities will be tested by a fit of the q-dependence of the QENS spectra with various models.

The q- and temperature-dependence of the increased scattering from the NC sample was further studied by IFW scans in **Fig. 2c**. At ~200 K (22 K above the freezing point of d14-hexane) the q-dependence of the IFW scan changes distinctly, indicating a change of the confinement geometry of the diffusion process.

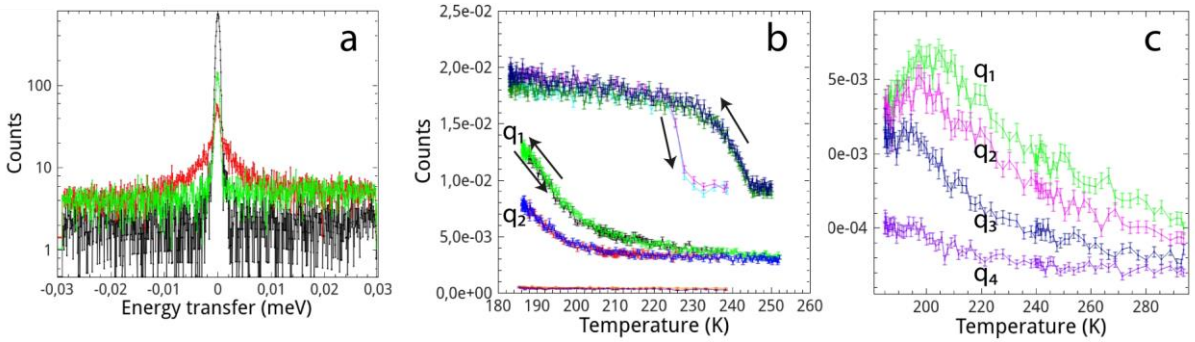

Figure 2. a) *Single-detector (2Theta=33deg.) QENS of the PbS-Oleic acid sample in hexane-d14 at 239 K (**red**). For comparison, the QENS signal of free oleic acid in d14-hexane (**green**) and the vanadium reference (**black**) are also displayed. **b**) EFW scans of free oleic acid (**top**) and PbS NCs in d14-hexane (**bottom**). **c**) IFWS at 1.3 µeV offset, showing the quasi-elastic amplitude at this offset for different q.*