Experimental report

05/03/2019

Proposal: 9-10-1514 **Council:** 4/2017

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

Research area: Materials

This proposal is a continuation of 9-12-498

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Samples: PbS and oleic acid in d14-hexane

Instrument	Requested days	Allocated days	From	To
IN6	2	0		
IN5	2	2	11/04/2018	13/04/2018
IN16B	1	0		

Abstract:

We propose to continue the investigation of the organic surfactant shell's adsorption on colloidally stable semiconductor nanocrystals in hexane-d14 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 time-of-flight (TOF) and backscattering (NBS) 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 already measured by SANS and NBS in proposal 9-12-498, respectively. This experiment becomes feasible due to the previous complimentary characterization 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 9-10-1514 on IN5

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The purpose of this experiment was to explore the vibrational spectrum of colloidally stable PbS NCs in d_{14}-hexane. At IN5, we performed neutron time-of-flight (TOF) measurements between 300 – 2 K at a wavelength of 5 Å (2.5 Å for T = 2 K) to derive the generalized density of states (GDOS). We carried out individual scans for (1) the PbS NCs surface-functionalized with oleic acid in d_{14}-hexane in a specified empty measurement can (PbS/OA/d_{14}-hex/EC), (2) OA/d_{14}-hex/EC, (3) d_{14}-hex/EC, (4) OA/EC, (5) EC. **Table 1** summarizes the temperatures at which scans were taken for all samples.

Table 1. Summary of performed measurement scans at IN5. "+" means that a measurement at the specified temperature for the sample of that column has been taken.

Temperature / K	PbS/OA/d_{14}-hex/EC	OA/d_{14}-hex/EC	d_{14}-hex/EC	OA/EC	EC
2	+	+			
100	+	+	+	+	+
150	+	+	+	+	
183	+	+	+	+	
200	+	+	+	+	+
239	+	+	+		
300	+		+	+	+

Figure 1 displays the generalized density of states (GDOS) at 183 K and 150 K for PbS/Oleic acid in d_{14}-hexane, oleic acid in d_{14}-hexane and pure d_{14}-hexane. The temperatures are chosen to be below and above the melting point of d_{14}-hexane (178 K). Above the melting point, the GDOS spectrum is dominated by vibrations of the solvent (**Figure 1a**). For frozen d_{14}-hexane, the GDOS exhibits several convoluted bands, which are mostly due to vibrations of solid d_{14}-hexane (**Figure 1b**). However, for some energies the scattering intensities of PbS/OA/d_{14}-hexane or OA/d_{14}-hexane are significantly larger than that of pure d_{14}-hexane, e.g. at 6-8 meV. We integrate the GDOS of OA/d_{14}-hexane as well as pure d_{14}-hexane from 0 – 20 meV energy transfer and display the difference at 150 K and 183 K in **Figure 1c**. As expected, above the melting point of d_{14}-hexane no distinct bands are obtained. In contrast, for 150 K we find a broad peak at 6-8 meV and several smaller bands at 11 meV, 13 meV as well as 15-16 meV. To verify that these bands originate from oleic acid, we also measure the GDOS of pure oleic acid and display the result in **Figure 1c** for comparison.

In **Figure 1d**, we analyze the difference in the integrated GDOS spectra of PbS/Oleic acid/d_{14}-hexane against the pure d_{14}-hexane matrix. Again, the ΔGDOS remains featureless for the liquid solvent, but reveals several distinct bands for the frozen matrix at 1-4 meV, 8-11 meV and 14-16 meV.

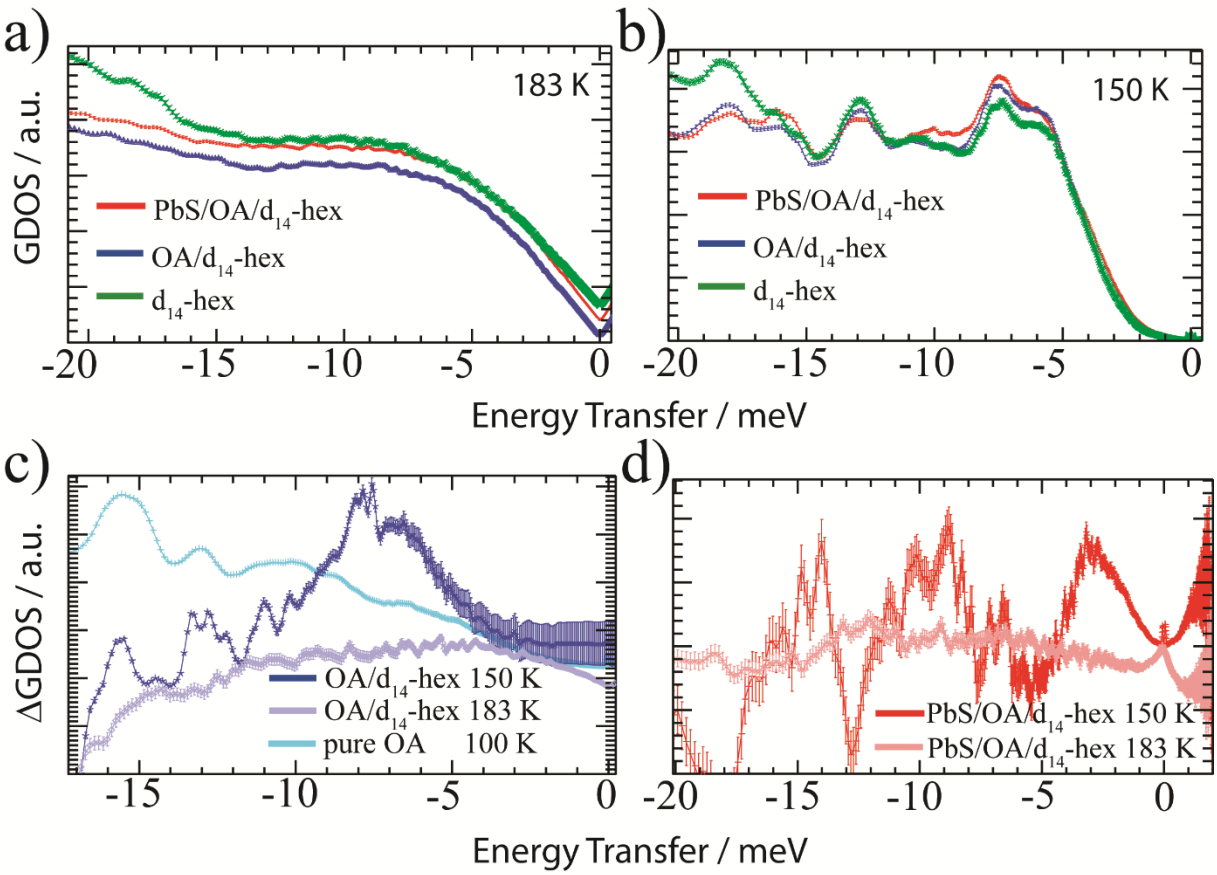

Figure 1. a) Generalized density of states (GDOS) of PbS/OA/d_{14}-hexane, OA/d_{14}-hexane and d_{14}-hexane for a momentum transfer of 0 – 20 meV at 183 K and ***b)*** at 150 K. ***c)*** Difference GDOS of OA/d_{14}-hexane vs. d_{14}-hexane at 150 K and 183 K as well as the absolute GDOS of pure OA. ***d***) Difference GDOS of PbS/OA/d_{14}-hexane vs. OA/d_{14}-hexane at 150 K and 183 K.