Experimental report

20/06/2024

Proposal: **9-11-2100** **Council:** 10/2022

Title: Structural changes in the shell ofplasmonic core-shell microgels upon in-situ overgrowth of the gold cores

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: Poly-N-Isopropylacrylamide
gold

Instrument	Requested days	Allocated days	From	To
D22	1	0		
D33	1	1	27/06/2023	28/06/2023

Abstract:

We want to study the form factor of core-shell microgels before and after the wet-chemical overgrowth of the gold nanoparticle cores. Apart from other core-shell microgel systems known from literature, those ones containing single gold nanoparticle cores allow for the overgrowth of the core by a seeded growth protocol. This way the core can be increased in volume by almost 300 times. While following this growth is possible by rather standard analytical tools such as electron microscopy and SAXS, measuring and understanding the corresponding structural changes in the microgel shell has not bee done yet and will rely on small-angle neutron scattering. We propose to use gold-PNIPAM core-shell microgels with two differently cross-linked shells and for each of these two different sizes of the cores, i.e. the initial core size after the first synthesis and overgrown cores obtained after in-situ overgrowth. The scattering contrast will be varied by mixing D2O and H2O in order to perform measurements under full contrast as well as core matching conditions. The experimental results will also be used to complement the results from the proposed neutron reflectometry experiment (#88254).

SANS measurements in dispersion were conducted to study the form factor of various gold core – poly-*N*-isopropylacrylamide shell (Au-PNIPAM) microgels. The aim of the experiment was to analyze microgels with different crosslinker contents in the shell and cores of different sizes, as these can be overgrown *in situ* in the shell. Hence, we wanted to get information on the structural changes of the shell after the overgrowth. By probing temperatures below, close to and above the volume phase transition temperature (VPTT) of the microgel, we can compare the form factors in both the swollen and collapsed states. For our study, we investigated Au-PNIPAM microgels with core radii of 7 nm (before overgrowth) and 46 nm (after overgrowth) and crosslinker densities of 16.5 mol% and 8 mol%, respectively.

We had previously investigated the form factor of the cores before and after the overgrowth with small-angle X-ray scattering. Additionally, the Au-PNIPAM microgels were also intensively studied with temperature dependent dynamic light scattering (DLS) and extinction spectroscopy, providing a comprehensive overview of the temperature responsive behavior of the particles. However, these techniques offered only an overview of the overall microgels and did not provide detailed information about the internal structure of the polymer shell. Here, SANS provides us the opportunity to gain deeper insights into the shell. By adjusting the contrast of the dispersion medium to match the contrast of the core, we can effectively isolate the scattering of the polymer shell.

We could measure all four samples in D_2O at nine different temperatures ranging from 12 °C to 51 °C. The microgels with large cores were also measured in gold-core matched water. The data for the microgels with small cores have been fully analyzed, while the data analysis for the microgels with large cores is currently in progress.

In Figure 1a, the scattering curves of Au-PNIPAM microgels with small cores and high crosslinker density are shown at different temperatures. The Ornstein-Zernike contribution is visible at high q for the dark blue curve (12 °C). The form factor oscillations at low q can be attributed to the microgel. With increasing temperature (from dark blue to dark red), the first form factor minimum shifts to higher q, indicating a decrease in the size of the microgels. Furthermore, the Ornstein-Zernike contribution disappears at high temperatures. The scattering profiles were fitted using the exponential shell form factor model. The good match to the data can be seen in Figure 1a. From the model, we can extract the scattering length density profiles shown in

Figure 1b. The profiles reveal a transition from an exponential shell in the swollen state to a profile approaching homogeneous solid spheres in the collapsed state. The decrease in size with increasing temperature is also confirmed by the density profiles.

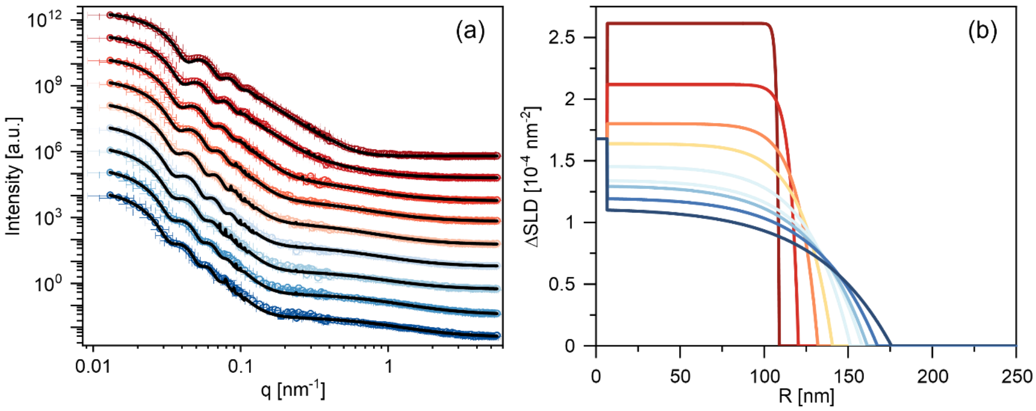

Figure 1: Au-PNIPAM microgels (R_{core} = 7 nm, crosslinker density = 16.5 mol%) in dilute dispersion at different temperatures. (a) Scattering profiles fitted with the exponential shell model (black line). (b) Scattering length density contrast profiles extracted from the exponential shell model. Temperature increases from dark blue to dark red.

Data analysis of the profiles measured from microgels with overgrown cores as well as profiles measured under core-matched contrast conditions is currently ongoing. Preliminary analysis suggests that there is a significant change in local polymer density close to the cores for the overgrown samples. If confirmed, this finding would be in agreement from observations of negatively stained samples investigated by transmission electron microscopy.

The D33 instrument was well suited for the proposed experiments. Thanks to the high flux, more temperature steps could be measured than initially planned. The q-range was well suited to resolve the form factor and the Guinier region of our microgels. Only for the swollen state measurements, where the microgels are largest in size, the Guinier plateau could not be fully reached at low q. For some samples containing 25 % H2O, i.e. with an increased incoherent scattering, data from the different panels did not correct properly, requiring to use an experimental water file acquired in the same configuration as a flat field. This points to a potential issue either in some instrument parameters or a parasitic background that depends on the incoherent level.