Experimental report

12/10/2016

Proposal:	**9-10-1413**	**Council:**	10/2014

Title: Crystal structure and core alignment in colloidal crystals of gold-nanorod@polymer core-shell particles

Research area: Chemistry

This proposal is a new proposal

Main proposer: **Matthias KARG**

Experimental team:
Paul MULVANEY
Sarah JABER
Matthias KARG
Astrid RAUH
Nico Oliver CARL

Local contacts: Ralf SCHWEINS

Samples:
Au
$(C_6H_{11}NO)_n$

Instrument	Requested days	Allocated days	From	To
D11	3	3	15/05/2015 12/11/2015	17/05/2015 13/11/2015

Abstract:

Plasmonic nanostructures represent promising components for new optical and non-linear optical devices in many advanced applications. However for most of these devices the nanostructures need to be assembled into 2D and 3D superstructures with high order and defined lattice constants. We face this challenge by using gold nanorod/polymer core/shell colloids and their crystallization at high volume fractions. Knowledge of the crystal structure, inter-particle separation, domain size and potential alignment of the anisotropic cores is crucial for understanding the optical performance of these materials and to make them suitable for the realization of new, functional devices. Small angle neutron scattering is the only technique capable of measuring hard-core/soft-shell colloids at high volume fractions in large sample containers, which are required for controlled crystallization into highly ordered crystals with cm dimensions.

EXPERIMENTAL REPORT

EXPERIMENT N° **9-10-1413** INSTRUMENT **D11**

DATES OF EXPERIMENT **14/05/2015-18/05/2015 and 12/11/2015**

TITLE

Crystal structure and core alignment in colloidal crystals of gold-nanorod@polymer core-shell particles

EXPERIMENTAL TEAM (names and affiliation)

Matthias Karg, Astrid Rauh, Nico Carl: University of Bayreuth, Physical Chemistry I, Universitätstr. 30, 95440 Bayreuth, Germany (current address, M. Karg: Heinrich-Heine-University Düsseldorf, Physical Chemistry I, Universitätstr. 1, 40204 Düsseldorf, Germany)
Paul Mulvaney, Sarah Jaber: University of Melbourne, Bio21 Institute & School of Chemistry, 30 Flemington Rd, 3010 VIC, Australia)

LOCAL CONTACT Ralf Schweins

Date of report 12/10/2016

The aim of this experiment was the structural analysis of hydrogel encapsulated metal nanoparticles at high volume fractions. SANS was used to analyze the form factor of dilute dispersions and the structure factor of concentrated systems.
In the past we have successfully shown that seeded precipitation polymerization can be used to encapsulate surface functionalized nanoparticles (seeds) by chemically cross-linked hydrogel shells composed of poly-*N*-isopropylacrylamide (PNIPAM).[1] Thorough analysis of such core-shell particles by means of dynamic and static light scattering, SAXS and SANS was applied to study the particle morphology in the non-interacting concentration regime ($S(q) = 1$) at different states of swelling.[2] The degree of swelling was simply changed by temperature profiting from the lower critical solution temperature (LCST) beahiour of PNIPAM. In contrast, at high volume fractions $S(q) = 1$ is no longer valid and crystallization can occur above a certain threshold concentration. Depending on the overall particle size, crystalline samples show strong Bragg peaks in the visible wavelength range. Until now it was unclear whether the presence of the gold cores influences the crystallization behaviour (hard core/soft shell) of the hydrogel particles and whether the gold cores affect the photonic properties of the material due to the pronouncd absorption cross-section. To study the influence of the gold cores systematically, we synthesized two batches of core-shell particles with gold cores of approximately 18 nm in diameter and PNIPAM shells with two different degrees of cross-linking (10 and 25 mol-%). For each system a fraction of the material was exposed to aqua regia, a strong acid, in order to etch away the gold cores. This way we were able to prepare PNIPAM colloids with and without gold cores with exactly the same hydrogel morphology and dimensions.

Figure 1 shows UV-Vis extinction spectra of the sample with 10 mol-% nominal cross-linker content with and without gold cores measured at two different volume fractions.

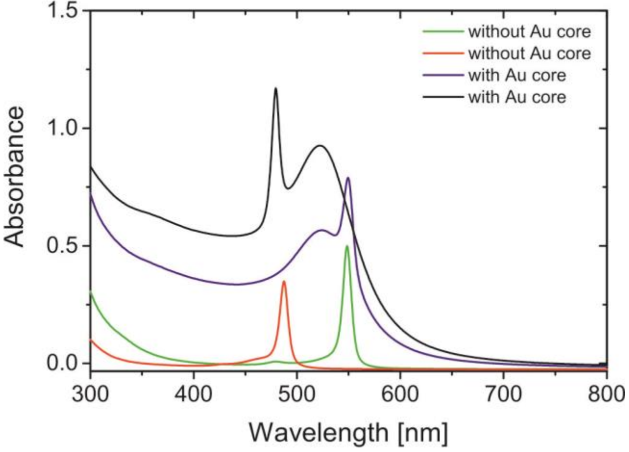

Figure 1: Extinction spectra of PNIPAM hydrogel particles at high ($\phi = 0.92$; purple and green) and medium volume fraction (black and red) as measured in heavy water at 25°C by UV-Vis spectroscopy. The purple and blck trace correspond to particles dispersions of core-shell colloids with gold cores.

All samples show narrow Bragg peaks indicating the high degree of crystalline order. In case of the core containing gold-PNIPAM colloids, the absorbance is significantly higher and the localized surface plasmon resonance is visible at approx. 525 nm. The samples of PNIPAM particles without cores show only the Bragg diffraction and some weak scattering contribution at lowest wavelngths. Surprisingly, the Bragg peak position and FWHM is not affected by the presence or absence of the gold core at a given concentration. This indicates that the gold cores neither affect the photonic properties nor the structural properties. To ultimately proof this hypothesis we used the reported beamtime for SANS measurements on the D11 instrument to analyze the structure factor of our samples. Only neutrons provide the sufficient contrast for the highly swollen PNIPAM shells against heavy water. Furthermore the D11 instrument offers the required large q-range with access to very low q. Figure 2 shows 2D detector images of the same samples as used for the measurements shown in figure 1.

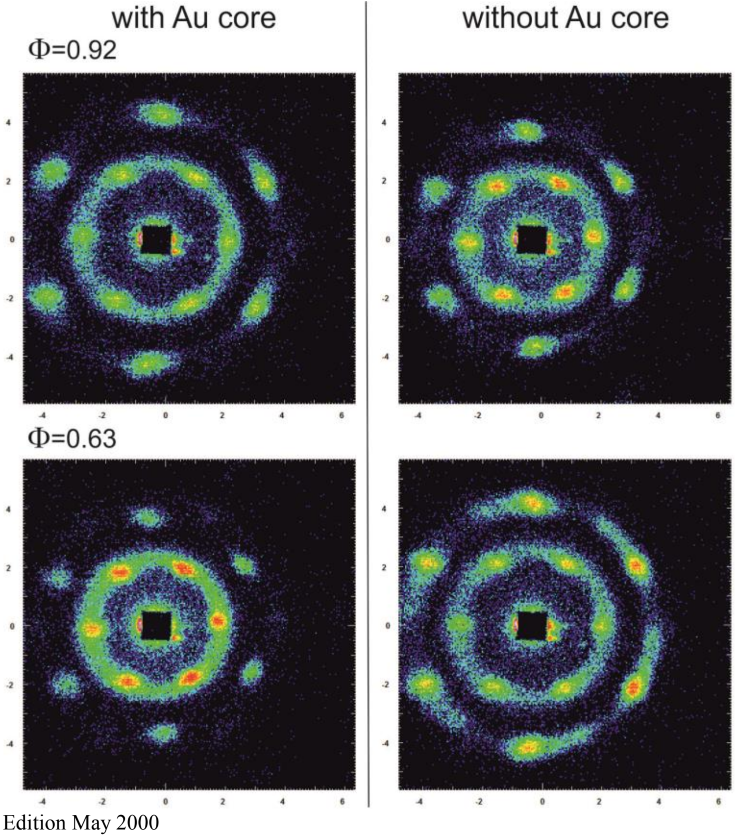

Figure 2: 2D detector images from SANS measurements using the D11 instrument. PNIPAM hydrogel particles with gold cores (left column) and without cores (right column) were measured at $\phi = 0.92$ (top row) and $\phi = 0.63$. The sample-to-detector distance was 39 m.

All detector images recorded at the largest sample-to-detector distance possible (39 m) show pronounced Bragg peaks of several orders. These can be clearly asigned to FCC type structures. As expected the peaks appear closer to the beamstop (lower q) for the lower concentrated sample (larger inter-particle distance). In very good agreement with the results from extinction spectroscopy one finds that scattering pattern and hence the crystal structure is nearly unaffected by the presence or absence of the gold cores. This is also illustrated by figure 3 where the radially averaged data (merged for different sample-to-detector distances) are shown.

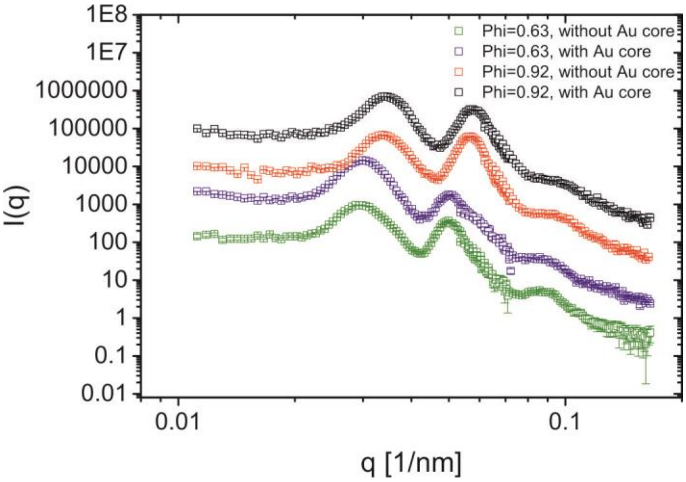

Figure 3: Scattering profiles of the crystalline samples with and without gold core merged from measurements at 28 and 39 m sample-to-detector distance. The colour code is the same as in figure 1.

Figure 3 shows two pronounced structure factor peaks for each sample. At each concentration nice agreement between the peak positions of crystals prepared from particles with and particles without cores is found. This ultimately proofs that the presence or absence does not influence the crystallization behavior and the structure factor. This however is valid for our core-to-shell size ratio that this small due to the relatively small core sizes with respect to the large PNIPAM shell. Whether the same results are found for particles with significantly larger core-to-shell size ratios is currently under investigation.

In conclusion, our experiments have shown that SANS is the perfect tool to study the form and structure factor of complex colloidal particles with dimensions in the range of several hundred nm. Due to the macroscopic size of our crystalline samples used for extinction spectroscopy (approx. 0.8 cm x 2 cm with 0.1 mm thickness) and because of the huge X-ray contrast mismatch between gold and PNIPAM, SAXS is rather unsuited for our investigations. The D11 instrument combining high neutron flux and a very broad q-range is ideally suited for our studies.

We would highly appreciate use of the D11 instrument for our future SANS investigations.

[1] A. Rauh, T. Honold, M. Karg, *Colloid & Polymer Science,* **294**(1), 37-47 (2016)

[2] M. Dulle, S. Jaber, S. Rosenfeldt, A. Radulescu, S. Förster, P. Mulvaney, M. Karg, *PCCP*, **17**, 1354-1367 (2015).