Experimental report

21/12/2021

Proposal:	**9-10-1690**	**Council:**	10/2020

Title: Nanoparticle agglomeration inducedby temperature-driven phase transition of the stabilising ligand shell and preferential solvent de-mixing

Research area: Physics

This proposal is a new proposal

Main proposer: **Bjorn KUTTICH**

Experimental team:
Bart-Jan NIEBUUR
Andrea PYTTLIK
Anna ZIMMERMANN
Martin SIEBRECHT

Local contacts: Ralf SCHWEINS

Samples: Au nanoparticle stabilised by hexadecanethiol dispersed in decane

Instrument	Requested days	Allocated days	From	To
D11	2	1	21/06/2021	22/06/2021

Abstract:

Colloidal stability of non-polar metal nanoparticles is an important question in many industrial applications. However, it is not well understood because DLVO theory does not apply, making these systems also interesting from a fundamental point of view. Combined investigations by SAXS and MD simulation give strong evidence that under certain conditions a disorder to order phase transition within the ligand shell, stabilising the nanoparticles, promotes particle agglomeration. Due to the weak contrast in electron densities between ligand shell and surrounding solvent this cannot be addressed by X-ray scattering. We therefore propose SANS experiments on previously well characterised nanoparticle dispersions with different particle diameters and solvent compositions, exploiting different deuteration schemes to simultaneously access ligand shell structure and agglomeration properties of the systems.

Ligand-stabilized metallic nanoparticles (NPs) are a class of materials with a high potential for use in various applications, such as printed conducting structures, optical nanocomposites and quantum-dot enhanced sensors and displays. Their colloidal stability in organic solvents is an important property, which may be optimized for specific applications. It mainly depends on steric effects of the ligand shell, which provides a stabilizing effect, whereas van der Waals interaction between the (metallic) cores destabilize the system [1]. Furthermore, it has been shown that a disorder-to-order transition of the ligand shell may lead to nanoparticle agglomeration at low temperatures [2]. These interactions lead to a strong dependence of the used solvent on the agglomeration temperature of NPs, which can, therefore, be used to modify their colloidal stability. However, the use of binary solvents provides additional complexity, because not only solvent-solvent interactions may play a role, also the preferential interaction of either solvent with the particle influences the stability of the system.

From preliminary SAXS measurements we found, that hexadecanethiol-coated gold nanoparticles (Au-NPs) with a core diameter of 4 nm show a non-linear trend of the agglomeration temperature (T_{agglo}), in mixtures of cyclohexane and hexadecane with varying compositions (Figure 1a). In this work, small-angle neutron scattering (SANS) is applied to investigate the complex interactions involved in this effect.

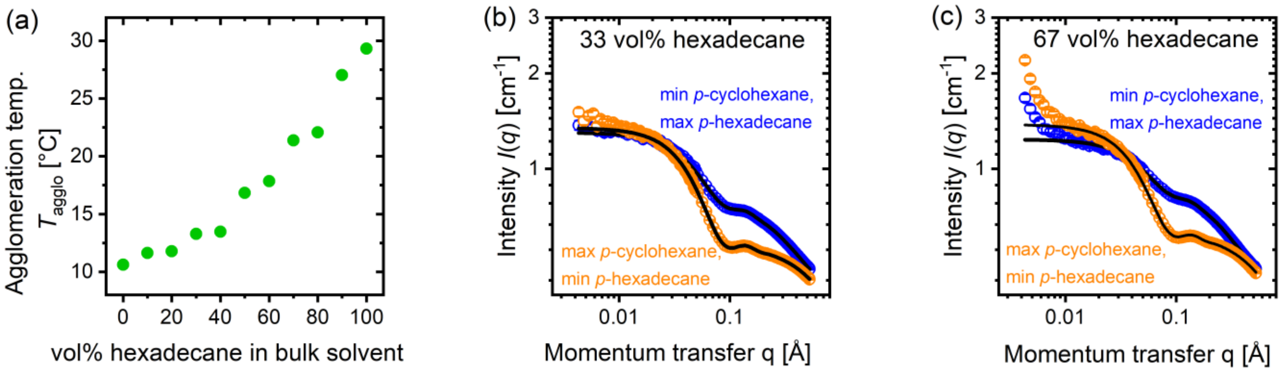

Figure 1. (a) T_{agglo} of hexadecanethiol-coated 4nm gold nanoparticles in mixtures of cyclohexane and hexadecane. (b) SANS patterns of hexadecanethiol-coated 4 nm gold nanoparticles dispersed in 33:67 v/v cyclohexane/cyclohexane, and (c), in 33:67 v/v cyclohexane/cyclohexane. Black lines are fits to the data as described in the text. In (b) and (c), the different contrast schemes are given in orange (amount of *p*-cyclohexane maximized) and blue (amount of *p*-hexadecane maximized).

SANS measurements were performed at 35 °C, i.e., in the dispersed state of the NPs, in mixtures of cyclohexane and hexadecane with a 100:0, 67:33, 33:67 and 0:100 v/v composition ratio. To isolate scattering from the shells during the SANS experiments, contrast matching has been applied. For measurements in pure cyclohexane and pure hexadecane, the ratio of deuterated and protonated solvents was chosen such, that the scattering length density (SLD) of the solvent matches that of the NPs gold core. To be able to isolate the contributions from cyclohexane and hexadecane to the scattering at the shell, two different contrast schemes were used for the solvent mixtures. In the first sample, the amount of *d*-cyclohexane is maximized, whereas in the second sample, the amount of *d*-hexadecane is maximized. A particle concentration of 10 mg ml^{-1} was chosen to ensure good statistics. In addition, all solvent mixtures were measured in the absence of NPs.

The neutron wavelength was chosen at $\lambda = 6$ Å. A q range from 0.004-0.5 Å^{-1} was covered with sample-detector distances of 1.7 m and 16.5 m. The sample thickness was 2 mm. The signal of the empty pressure cell was subtracted from the data. H_2O was measured to determine the detector sensitivity, and dark current was measured using boron carbide. The software MANTID was used to perform the data reduction.

In Figure 1b and c, exemplary SANS patterns are shown. In all cases, the scattering curves feature a shoulder at ~0.02 Å^{-1}, which results from scattering at the particle shells. At high q-values, a second decay is present at q-values that match with those of the decays observed in the pure solvent mixtures. Therefore, this decay results from scattering at the solvent molecules on the molecular length scale. Additionally, weak forward scattering is observed, pointing to weak aggregation of the NPs. To account for these contributions, the scattering curves were modelled using the expression

$$I(q) = I_{\mathrm{pCS}}(q) + I_{\mathrm{OZ}}(q) + I_{\mathrm{bkg}} \tag{1}$$

which combines a form factor of polydisperse core-shell particles, $I_{\mathrm{pCS}}(q)$, and an Ornstein-Zernike structure factor, $I_{\mathrm{OZ}}(q)$, to account for scattering by the solvent molecules. I_{bkg} is a constant background, which accounts for incoherent background scattering.

The shell thickness, t_{s}, resulting from the fits, is shown in Figure 2a in dependence on hexadecane content of the bulk solvent. In all cases, it amounts to ~20 Å, independent of solvent composition, which corresponds roughly to the length of stretched hexadecanethiol molecules. Therefore, the size of the ligand determines the shell thickness, i.e., a layer of solvent molecules of one specific type at the ligand chain-ends, increasing the effective size of the shell, does not exist.

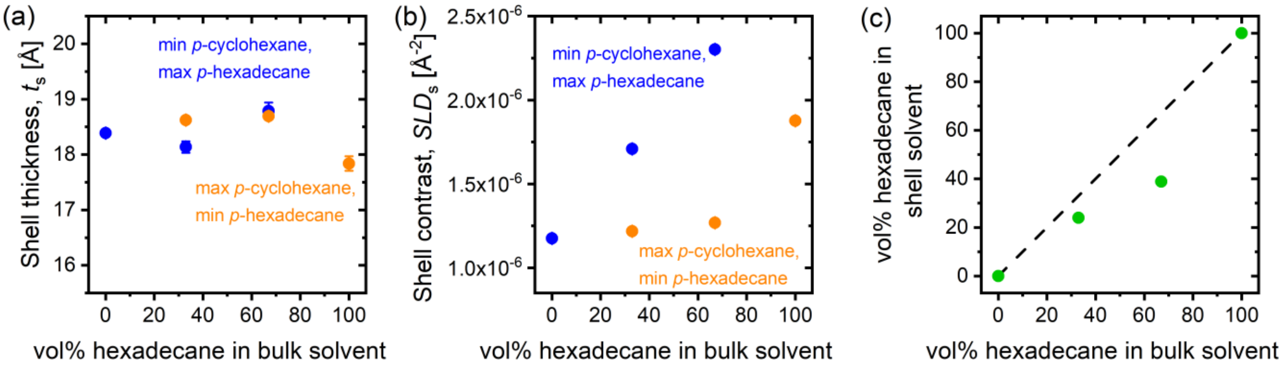

Figure 2. Results from fitting the SANS patterns. (a) shell thickness t_{s}, (b) shell contrast SLD_{s}, and (c) vol% hexadecane in shell solvent. In (a) and (b), the different contrast schemes are given in orange (amount of *p*-cyclohexane maximized) and blue (amount of *p*-hexadecane maximized). In (c), the dashed line indicates the nominal amount of hexadecane.

In Figure 2b, the scattering length density of the shell, SLD_{s}, is shown. Large variations are observed, which shows that the chain solvation strongly depends on the type of solvent used. For both solvent mixtures (33 and 67 vol% hexadecane), SLD_{s} of the sample with a maximized amount of *p*-cyclohexane is lower than for the sample with a maximized amount of *p*-hexadecane. The absolute values of SLD_{s} allow for a quantitative determination of the shell composition. The number fractions of ligands (l), cyclohexane (c) and hexadecane (h) molecules inside the shell can be determined from SLD_{s} according to the expression

$$SLD_{\mathrm{s}} = \frac{l\sum b_{\mathrm{i,L}} + c\sum b_{\mathrm{i,C}} + h\sum b_{\mathrm{i,H}}}{lV_{\mathrm{m,L}} + cV_{\mathrm{m,C}} + hV_{\mathrm{m,H}}} \tag{2}$$

with $b_{\mathrm{i,L}}$, $b_{\mathrm{i,C}}$ and $b_{\mathrm{i,H}}$ the scattering lengths of all atoms inside one ligand, cyclohexane, hexadecane molecule, and $V_{\mathrm{m,L}}$, $V_{\mathrm{m,C}}$ and $V_{\mathrm{m,H}}$ their respective molecular volumes. Therefore, the calculation of the number fraction of each component involves solving for three variables: the coefficients l, c and *h*. For the solvent mixtures, the values of SLD_s determined for the two contrast schemes (varied by the different ratios of protonated and deuterated molecules of the two solvent types) provide two relations between *l*, *c* and *h* by means of eq. 2. Together with the constraint that the number fraction of all components combined equals 1, a set of three equation is obtained, which allows for the calculation of each coefficient separately. Here, it is assumed that the adsorption of neither protonated nor deuterated molecules is preferred. For Au-NPs dispersed in pure cyclohexane, the shell may consist only of cyclohexane and ligands. Using eq. 2 with $h = 0$, the number fractions of both components can be related to the determined value of SLD_s. Together with the constraint that the number fraction of both components combined equals 1, the number fractions of both components can be calculated. Also here, it is assumed that neither the protonated nor the deuterated solvent is preferentially adsorbed by the shell. In the case of pure hexadecane, the equivalent procedure is applied.

The determined number fractions of the components inside the shell were converted to volume fractions. Figure 2c shows the volume fraction of hexadecane in the shell, normalized by the number fraction of both solvent types in the shell combined, i.e., it shows the volume ratio hexadecane/cyclohexane in the shell. At 0 vol% hexadecane in the bulk solvent, no hexadecane is present inside the shell. At 33 and 67 vol% hexadecane in the bulk solvent, however, the volume fraction of hexadecane inside the shell deviates from the composition of the bulk solvent. In both cases, it is lower than the nominal ratio, which implies that cyclohexane preferentially solvates the shell. With increasing volume fraction of hexadecane in the bulk solvent, the volume fraction of hexadecane inside the shell increases, but much slower than the volume fraction of hexadecane in the bulk solvent. Therefore, the imbalance between the presence of both solvent types inside the shell increases with increasing volume fraction of hexadecane in the bulk solvent. Towards 100 vol% hexadecane inside the bulk solvent, cyclohexane becomes increasingly scarce, and the nominal amount of hexadecane inside the shell is again achieved at 100 vol% hexadecane inside the bulk solvent.

The preferential solvation of the shell by cyclohexane may be at the origin of the non-linear trend of T_{agglo} in dependence on hexadecane volume fraction in the bulk solvent. As has been shown previously, cyclohexane is a better solvent for hexadecanethiol-stabilized Au-NPs than hexadecane [2]. The enrichment of cyclohexane inside the ligand shell suppresses the disorder-to-order transition and, therefore, lowers the temperature at which this transition takes place. Consequently, also T_{agglo} is lowered, leading to its non-linear trend.

We thank Dr. Ralf Schweins for excellent support during the measurements

[1] Kister, T.; Monego, D.; Mulvaney, P.; Widmer-Cooper, A.; Kraus, T. *ACS Nano*, **2018**, *12*, 5969-5977
[2] Monego, D.; Kister, T.; Kirkwood, N.; Doblas, D.; Mulvaney, P.; Kraus, T.; Widmer-Cooper, A. *ACS Nano*, **2020**, *14*, 5278-5287