Experimental report

08/02/2016

Proposal: 9-10-1442 **Council:** 4/2015

Title: Silver complex-modified CTAB micelles as precursors for nanoparticle formation

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: Tilo SCHMUTZLER

Experimental team: Torben SCHINDLER
Tilo SCHMUTZLER

Local contacts: Peter LINDNER

Samples: CTAB micelles

Instrument	Requested days	Allocated days	From	To
D11	3	1	22/09/2015	23/09/2015

Abstract:

Gold and silver nanoparticles (AuNPs, AgNPs) exhibit outstanding optical properties due to their plasmonic behavior. One common route of producing such nanoparticles is to transform the precursor salts (HAuCl4, AgNO3) in presence of the surfactant CTAB.[1] Our recent small angle X-ray and neutron scattering (SAS) experiments support the existence of CTA-Br-Au complexes as catalytically relevant components for AuNP formation. Upon the addition of the precursors and the ligands ascorbic acid and thiourea, we found drastic differences in the diffuse SAS signal with respect to the aqueous CTAB solution indicating significant structural differences in the formed gold complex-modified micelles. This effect is even more pronounced if AgNO3 is used instead of HAuCl4 as precursor. The proposed SANS experiments will allow us to compare our results of HAuCl4 containing CTAB solutions to that with AgNO3 as precursors for nanoparticles. It will be possible to locate the single components of the micelles via contrast variation by using different D2O/H2O mixtures. This work will help to understand the noble metal nanoparticle formation in general.

[1]T.K.Sau et al.,Adv.Mater.2010,22,1781-1804.

experimental report for 9-10-1442

Silver complex-modified CTAB micelles as precursors for nanoparticle formation

Introduction and State of Science

Silver and gold nanoparticles (NP) exhibit outstanding optical properties. The plasmonic behaviour of such particles is strongly dependent on their size and shape. Different morphologies are often synthesized in the presence of the structure directing agent and micelle forming surfactant hexadecyl-trimethyl-ammonium bromide (CTAB).[1]
One common route of producing gold NPs is to reduce the precursor $HAuCl_4$ in the presence of CTAB and $AgNO_3$. Although the synthesis of such NPs is highly investigated, the exact formation mechanism of different morphologies and the exact role of CTAB and $AgNO_3$ is still unclear.[2] $AgNO_3$ stays unreduced after the reaction whereas the concentration is crucially regarding the final morphology of the gold NPs. The common explanation for that effect includes the adsorption of silver complexes beside CTAB on certain facets of the gold nanocrystals. In that way the isotropic growth of the nanoparticles is avoided and e.g. rod-like shapes can be achieved.

To study the adsorption of silver containing complex compounds we used the combination of small angle scattering (SAS) with X-rays (SAXS) and neutrons (SANS) as well as transmission electron microscopy (TEM) to characterize gold nanorod containing solutions with various concentrations of additives. Therefore TEM was used to characterize the morphology of the used nanoparticles. Figure 1 shows the results of the quantitative TEM measurements. It is obvious that a rod-like fraction is dominant beneath a non rod-like fraction (denoted as aggregate fraction) that can be neglected in further SAS evaluation due to its low amount compared to the nanorod fraction.

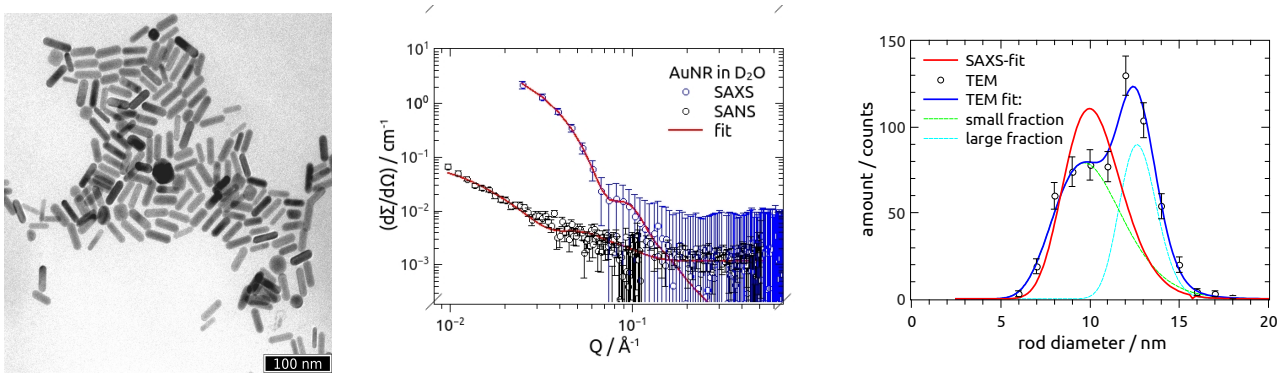

Fig.1: *TEM image (left) of the sample used for further SAS analysis showing gold nanorods and a small amount of non rod-like particles. Fitting the SAS data (of SANS @ D11 and SAXS @ our laboratory instrument) simultaneously is very sensitive to the rod diameter distribution and can be compared directly to the values gathered from quantitative TEM analysis (right).*

The rod diameter distribution analysed by TEM shows two fractions whereas the SAS analysis leads to an averaged value over the whole sample and could be used in all following fits.

The rod solutions are low concentrated (0.3 mmol/L which is equal to 0.006 wt% in aqueous CTAB solution). To study the influence of different silver complexes on gold nanorod containing solutions we added $AgNO_3$ (0.1 mol% compared to gold) in gold nanorod solutions (1mM CTAB in D_2O) in presence of different ligands which are known to form complex compounds with silver ions. In CTAB solutions Ag^+ should form the complex anion $[AgBr_4]^{3-}$ or $[AgBr_2]^-$, whereas in presence of thiourea (tu) the formation of the complex cations $[Ag(tu)_x]^+$ (x=1,2,3,4) is more likely due to the higher complex formation constant.[3] Additionally ascorbic acid (AscH) is known to act as ligand

[1] T.K. Sau *et al.*, *Adv. Mater.* **2010**, *22*, 1781-1804.
[2] F. Hubert *et al.*, *Langmuir* **2008**, *24*, 9219-9222.
[3] S. Ahmad *et al.*, *Trans. Metal Chem.* **2002**, *27*, 782-785.

for metal cations (e.g. Cu^{2+}) and can also be considered to form complex molecules like $[Ag(AscH)_2]^+$ or $[Ag(Asc)_2]^{2-}$.[4] We investigated the influence of these different ligands on the interaction behaviour between gold nanorods and silver complex compounds by adding $AgNO_3$ (0.3 mmol/L) to a 1mmol/L CTAB solution of gold nanorods (0.3 mmol/L) in water with 0.01 mol/L of ligand (tu or AscH).

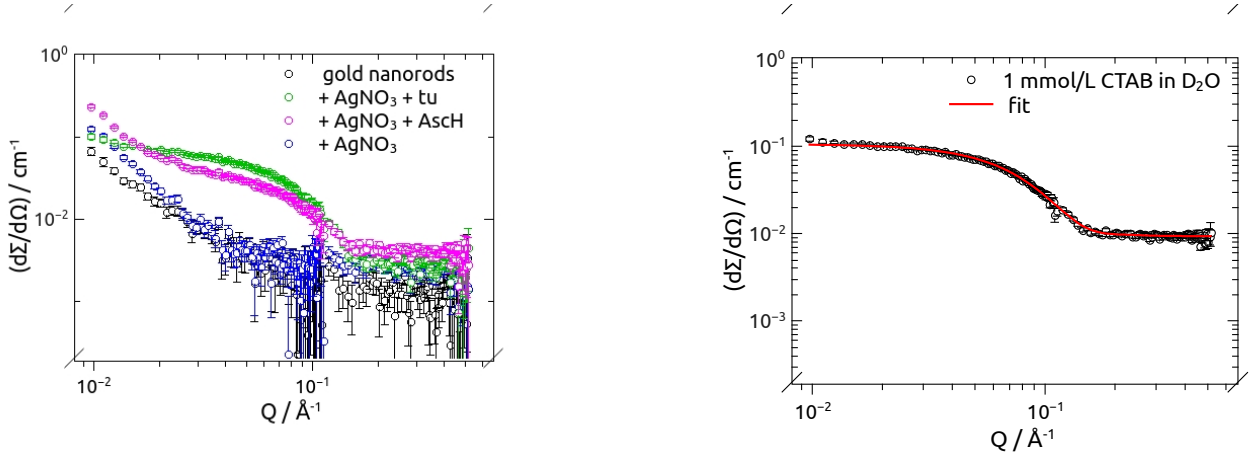

Fig.2: *left: SANS data of gold nanorod solutions (1mmol/L CTAB in D_2O): without any additives (black circles), with 0.3 mmol/L $AgNO_3$ (blue circles), 0.01 mol/L ascorbic acid (AscH) and 0.3 mmol/L $AgNO_3$ (magenta circles), 0.01 mol/L thiourea (tu) and 0.3 mmol/L $AgNO_3$ (green circles). Additionally to the gold nanorod signal a strong scattering related to CTAB micelles is appearing in the samples where tu and AscH are present. CTAB micelles can be characterized by fitting the scattering of a pure solution of CTAB in D_2O (1 mmol/L) using a spherical particle fraction with a radius of 2.20(45) nm. These micelles can not be detected in the samples without further ligand which indicates that the whole amount of CTAB is located at the nanorod surface whereas addition of ligands leads to a replacement of CTAB by the silver complex compounds. In this cases, the scattering related to CTAB micelles is clearly visible.*

The addition of ligands seems to initiate a stronger adsorption of the silver complex compounds compared to the CTAB molecules. This leads to a partial transition of the CTAB stabilizing layer into micelles which becomes visible due to the formation of a strong scattering in SANS that is characteristic for dispersed CTAB micelles in aqueous solution (figure 2). As the concentration of the silver complex molecules at the gold nanorods facets increases, the electron density of the nanorod shell should be significantly enhanced.

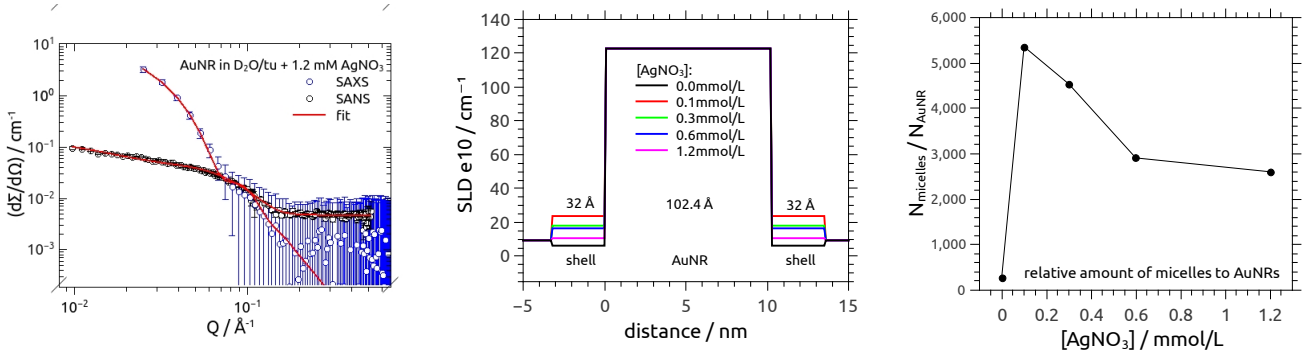

Fig.3: *left:* simultaneous fit of SAS data (blue: SAXS, black: SANS) *of gold nanorod solutions (1mmol/L CTAB in D_2O): with 1.2 mmol/L $AgNO_3$. Middle: scattering length density (SLD) profile of the fitted model for the case of X-ray scattering. The model includes 102.4 Å thick gold nanorods (the length was 388.2 Å) a 32 Å shell with a decreasing SLD by increasing the $AgNO_3$ concentration. This is consistent with the decreased amount of micelles (right) in solutions with a higher amount of $AgNO_3$ (right).*

This effect can be detected by fitting the SAXS data of the different solutions (figure 3). Using the morphologic distribution (analysed by TEM) and the shell thickness of 32 Å determined by SAXS

[4] M.B. Davies, *Polyhedron* **1992**, *3*, 285-321.

and SANS[5] it is possible to fit the SAS data simultaneously to analyse the electron density of the nanorod shell and the amount of released micelles. The fitted parameters were therefore the amount of gold nanorods and micelles and the scattering length density (SLD) of the shell for X-ray and neutron scattering, respectively.The fit results indicate the partial transition of the stabilizing CTAB double layer due to the adsorption of silver thiourea complexes on the gold nanorod surface. This leads to a formation of CTAB micelles in aqueous solution. In contrast what we expected, the highest SLD was observed at the lowest concentration of $AgNO_3$. At the same time as the SLD of the AuNR shell decreases the amount of CTAB micelles is also reduced. At this moment we have no sufficient explanation for this observation. We plan to do some further SAS experiments to fully understand the adsorption process of the silver complexes. For that we intend to do titration-like experiments to clarify the role of silver and ligand concentration.

[5] S. Gómez-Grana et al., *Langmuir* **2012**, *28*, 1453-1459.