Experimental report

01/03/2017

Proposal: 9-12-467 **Council:** 4/2016

Title: Adsorption of silver thiourea complexes on gold nanorod surfaces

Research area: Chemistry

This proposal is a continuation of 9-10-1442

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Samples: H2O
D2O
Gold nanoparticles Au
CTAB organic surfactant C,H,O

Instrument	Requested days	Allocated days	From	To
D11	3	2	06/07/2016	08/07/2016

Abstract:

The adsorption of silver complexes on gold nanoparticles seems to play a crucial role in gold nanorod (AuNRs) formation. We were able to detect the adsorption indirectly using the combination of SAXS, SANS and TEM. The AuNRs are stabilized with a bilayer of CTAB. The replacement of CTAB by silver thiourea complexes leads to a transformation of the CTAB molecule arrangement to micelles that can be detected easily by SANS. The change of the electron density of the stabilizing layer on top of the AuNRs is accessible via simultaneous SAS fitting. There we observed an unexpected behavior where the amount of transformed micelles and the electron density of the AuNR shell decreases as the silver ion concentration in solution was increased. We are convinced that we will understand this effect using titration-like experiments where each step will be characterized by SAXS and SANS, respectively. Analyzing this data will help us to evaluate the amount of CTAB and silver complexes per AuNR surface. This will lead to a deep understanding of the stabilizing effect of CTAB on noble metal nanoparticles in general and the catalytic behavior of silver complexes in the case of AuNR synthesis.

experimental report for 9-12-467

Adsorption of silver thiourea complexes on gold nanorod surfaces

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 role of CTAB and $AgNO_3$ is still not fully understood.[2] $AgNO_3$ stays unreduced after the reaction whereas the concentration is crucial 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.

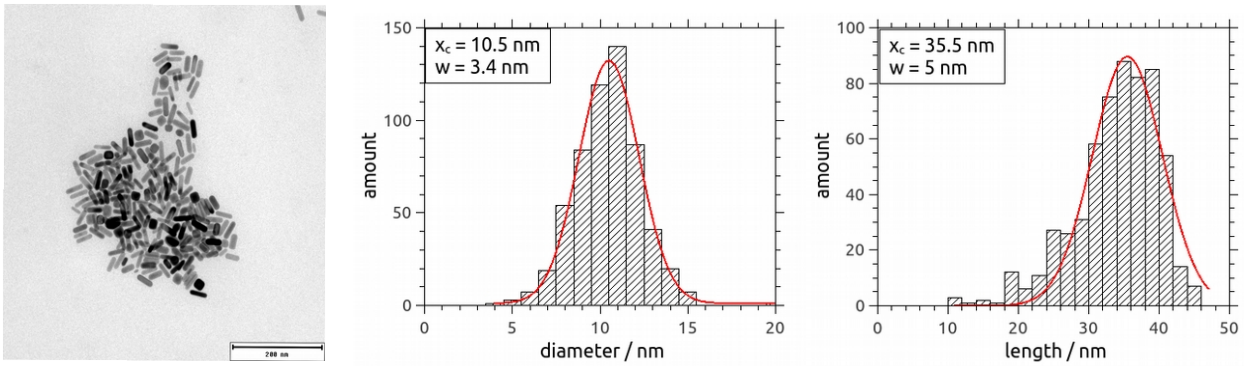

Fig.1: *TEM image (left, scale bar is 200 nm) of the sample used for further SAS analysis showing gold nanorods and a small amount of non rod-like particles. TEM analysis and fitting reveals the gaussian distribution around 10.5 nm for the diameter (middle) and 35.3 nm for the length (right). These parameters can be used for further SAS analysis of the same sample.*

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) UV-Vis-NIR absorption spectroscopy and transmission electron microscopy (TEM) to characterize gold nanorod containing solutions with various concentrations of the additives $AgNO_3$ and thiourea (tu). UV-Vis-NIR spectroscopy was used to show that the adsorption of silver-thiourea complexes modifies the absorption belonging to the longitudinal surface plasmon resonance of AuNRs. TEM was used to characterize the morphology of the used AuNRs (Fig.1). The rod-like fraction is dominant beneath a non rod-like fraction that can be neglected in further SAS evaluation due to its low amount compared to the nanorod fraction. Anyway, the TEM analysis reveals gaussian distributions for both: the diameter (around 10.5 nm) and the length (around 35.5 nm). Since SAS is not very sensitive to the lengh compared to the diameter of the AuNRs, the distribution for the length was neglected in further SAS analysis to decrease the amount of parameters. Therefore, the length was set to 35.5 nm in all fits.

The rod solutions were low concentrated (0.3 mmol/L which is equal to 0.006 wt% in aqueous CTAB solution). To study the influence of silver complexes on gold nanorod containing solutions we added $AgNO_3$ (0.3 or 0.4 mmol/L) in gold nanorod solutions (1mM CTAB in D_2O) in presence

[1] T.K. Sau *et al.*, *Adv. Mater.* **2010**, *22*, 1781-1804.
[2] F. Hubert *et al.*, *Langmuir* **2008**, *24*, 9219-9222.

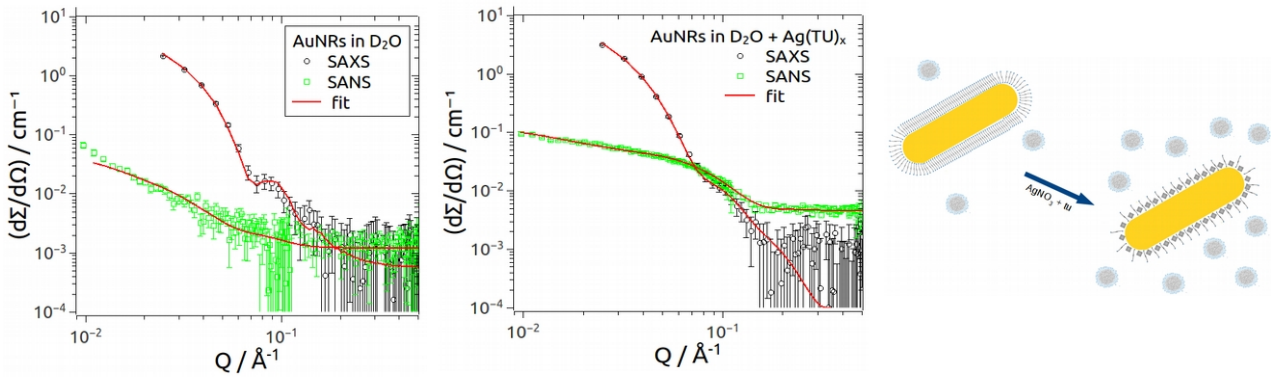

Fig.2: *Combined SAXS and SAS analysis by simultaneous fitting of gold nanorods (AuNRs, leftt) using the morphological parameters known from TEM analysis (Fig.1). The addition of silver-thiourea complexes leads to the formation of scattered intensity at higher Q in SANS. This scattering is related to the formation of spherical CTAB micelles. The proposed mechanism is shown on the right hand side: the stabilizing CTAB double layer transforms into micelles due to the replacement of CTAB molecules of the AuNR surface by molecules of silver-thiourea complex.*

of thiourea (tu) (1.2 up to 20 mmol/L) which is known to form several silver complexes $[Ag(tu)_x]^+$ (x=1,2,3,4).

The addition of ligands seems to initiate a stronger adsorption of the silver complex compounds compared to CTAB molecules. It is known that CTAB forms a double layer on the AuNRs which stabilize them against aggregation.[5] The adsorption of silver-thiourea-complex leads to a partial transition of the stabilizing CTAB bilayer into micelles which becomes visible in SANS due to the formation of a strong scattering signal at around 0.1 $Å^{-1}$ that is characteristic for dispersed CTAB micelles in aqueous solution (Fig.2, middle).

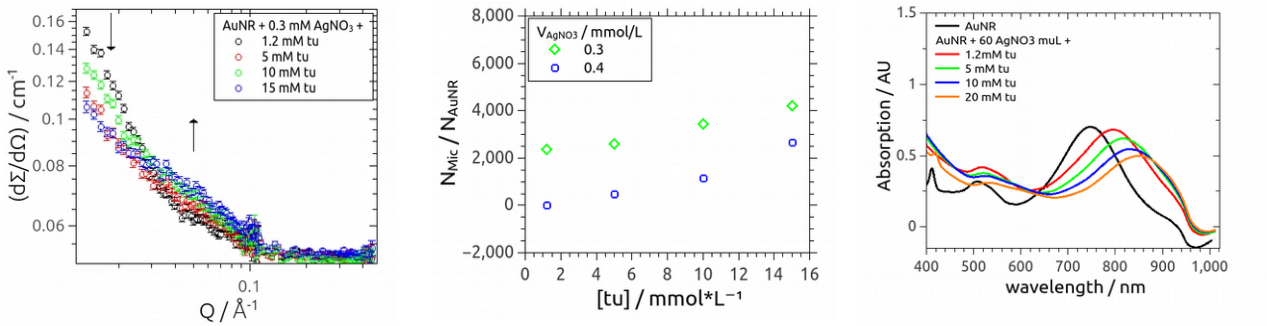

Fig.3: *The scattering in the SANS (left) signal at low Q is related to AgBr particles that are formed if the concentration of Ag^+ is to high relative to the tu concentration. Hence, is signal is decreasing by the addition of tu due to the formation of stable silver-thiourea-complexes. Since this is accompanied by a higher amount of adsorbed silver-thiourea-complex on the AuNR surface, the amount of formed micelles is also increased. The absorptaion ban position in the UV-Vis-NIR sprectrum is systematically shifted due to the adsorption of silver-thiourea-complex and thus can be tuned by the amount of silver and tu in the solution.*

Using the morphologic distribution (analysed by TEM) and the shell thickness of 32 Å determined by SAXS and SANS it was possible to fit the SAS data simultaneously to analyse the electron density of the nanorod shell and the amount of released micelles. 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.

In this experiment we analysed the dependency of CTAB micelle formation with respect to the concentration of Ag^+ and tu, respectively. We noticed that the amount of adsorbed silver-thiourea-complex and CTAB micelles decreases if the concentration of silver ions is increased. We learned from the SANS measurements that this is related to the formation of AgBr particles within the

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

solution as soon as the Ag^+ concentration is to low relativ to the tu concentration. If the tu concentration is high enough, all silver ions are bound to silver-thiourea-complexes and can not form AgBr precipitates.
The amount of adsorbed silver-thiourea-complex can be analysed indirectly by the shift of the absorption peak in the UV-Vis-NIR spectrum towards higher wavelengths (Fig.3, right). This enables us to tune the absorption of AuNRs by adding more tu (red-shift) or Ag^+ (blue-shift).
This experiment was absolutely necessary to understand the results we gathered from 9-10-1442.

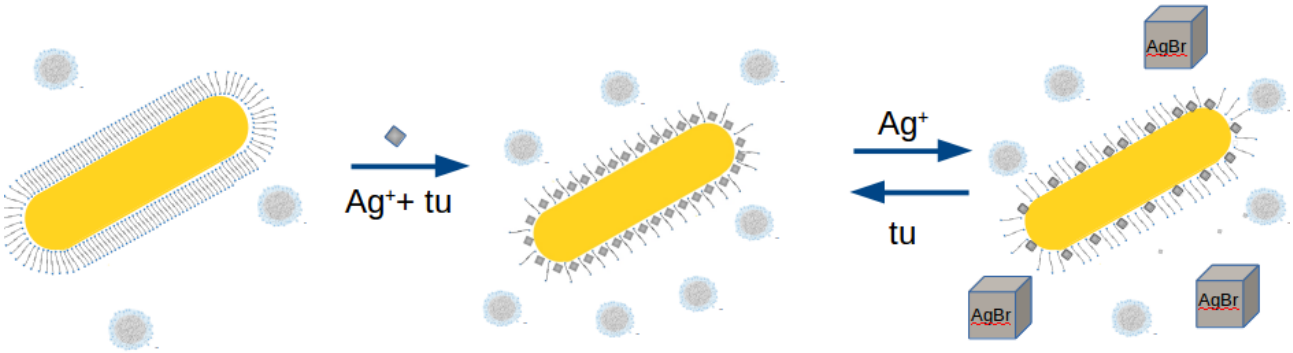

Fig.4: *proposed mechanism: the adsorption of silver-thiourea-complexes (grey diamonds) on gold nanorod surfaces leads to a partial transformation of the CTAB bilayer into micelles. Using high concentrations of $AgNO_3$ relative to tu leads to the formation of KBr crystal, whereas the adsorption of complexes is lowered and thus the amount of micelles decreased due to a reformation of the CTAB bilayer.*