Experimental report

08/03/2016

Proposal: **9-10-1407** **Council:** 10/2014

Title: In situ study of the passivation of ZnO nanoparticle surfaces

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: ZnO

Instrument	Requested days	Allocated days	From	To
D11	3	1	03/07/2015	04/07/2015

Abstract:

ZnO semiconductor NPs (NPs) are of high importance in research due to their promising opto-electronical properties. This makes them favorable for the integration into e.g. solar cells. For these applications a layer of organic molecules is needed to passivate the NPs electronically. In a previous study, we detected the acetate layer surrounding the ZnO NPs directly using a combined approach of SAXS and SANS. The analysis of the simultaneous SAXS/SANS fits showed that the acetate layer had a thickness of about 1nm, which is increased for higher temperatures and longer ripening times. In this study we want to investigate the exchange of this acetate layer by two different catechol molecules which passivate the NP surface and make them suitable for the integration in solar cells. The surface coverage of catechol molecules attached to ZnO NPs could already be determined, however only by ex situ measurements. To gain inside into the passivation of ZnO NPs surfaces by the binding of catechol molecules we want to perform SANS measurements to study the shell characteristics for different amounts of added catechol in situ. Therefore we propose for three days of beamtime at D11.

Experimental Report for proposal 9-10-1407: *In situ* study of the passivation of ZnO nanoparticle surfaces

ZnO semiconductor NPs (NPs) are of high importance in research due to their promising opto-electronical properties which change for small NPs due to the quantum size effect. This makes them favorable for the integration into *e.g.* electronic devices and solar cells.[1] For these applications a layer of organic molecules is needed to passivate the NPs electronically.[2] Thus, beneath the knowledge of the size and shape of the ZnO core information about the surface modification is of high interest and necessary to prepare NPs with desired properties. For the direct investigation of the organic molecules which passivate the NP surface in solution, SANS is superior to other techniques as the structure of the stabilizing layer and thus thickness and density of this layer can be deduced *in situ*. For a better passivation of these NPs different stabilizer molecules are used *e.g.* catechol molecules.[2] In this study we studied the changes of the stabilizing layer upon the addition of varying amounts of a catecholic molecule which is depicted in figure 1.

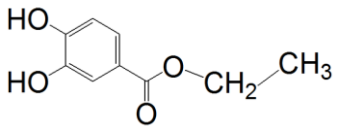

Figure 1: Structure of the used catechol molecule (ethyl-3,4-dihydroxybenzoat).

The ZnO NPs are prepared using a standard routine which includes the formation of a zinc precursor under solvothermal conditions in ethanol (EtOH) which is stabilized by six acetate molecules.[3] ZnO is immediately formed after the addition of an ethanolic solution of LiOH. The NPs can further ripen in dependence of time and temperature.

In a previous study, we detected the acetate layer surrounding the ZnO NPs directly using a combined approach of SAXS and SANS. The core properties were determined using SAXS and the shell was detected mainly by SANS, as the influence of the shell on the SAXS pattern is small. The analysis of the simultaneous SAXS/SANS fits showed that the acetate layer had a thickness of about 1 nm, which is increased for higher temperatures and longer ripening times. In addition to these findings, the concentration of acetate within this layer is decreasing during the ripening process with increasing shell thickness.[4] After washing, the size of the shell is decreased to the monolayer size of acetate (~0.47 nm).

Here, we studied the change of the shell with increasing amounts of catechol. Seven different catechol concentrations which refer to monolayer coverages between 0.01 and 3 ML were chosen and in addition two further samples were measured, which were once and twice washed after the addition of the highest catechol concentration. A sample without any catechol was also measured as a reference.

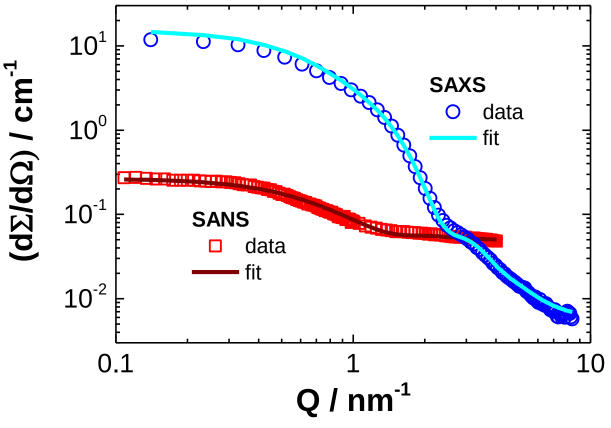

Figure 2: SAXS and SANS pattern of ZnO NPs after the addition of 3 ML of catechol. The corresponding fits are shown as solid lines.

In addition to the SANS measurements the SAXS pattern were also recorded and both data sets calibrated to the absolute scale. With this the shell characteristics could be studied, which has also been shown before.[4] The SAXS and SANS data for the sample with the highest catechol concentration and the according fits can be seen in figure 2. The shell thickness is plotted against the amount of added catechol in figure 3 (bottom). The shell thickness is for the sample without catechol similar to that of a monolayer of acetate. With more added catechol the value rises and comes closer to the value expected for a monolayer of catechol. For very high amounts of catechol (3ML) a further increase in shell thickness is observed, which is referred to as physisorbed catechol, which has already be determined in this region. Accordingly after washing of the samples the shell thickness is decreased again.

In addition to the shell thickness, the contrast of the shell can also be found (see figure 3, top). In combination with the shell thickness, three regimes can be seen. First the catechol replaces the acetate (up to 1 ML), in the intermediate regime the amount of catechol within the shell increases, while at very high catechol concentrations further catechol adds to the shell but is only physisorbed. As a differentiation between the acetate and catechol within the shell is not possible, further titration experiments are planned and will help to fully understand the changes within the shell during the addition of catechol.

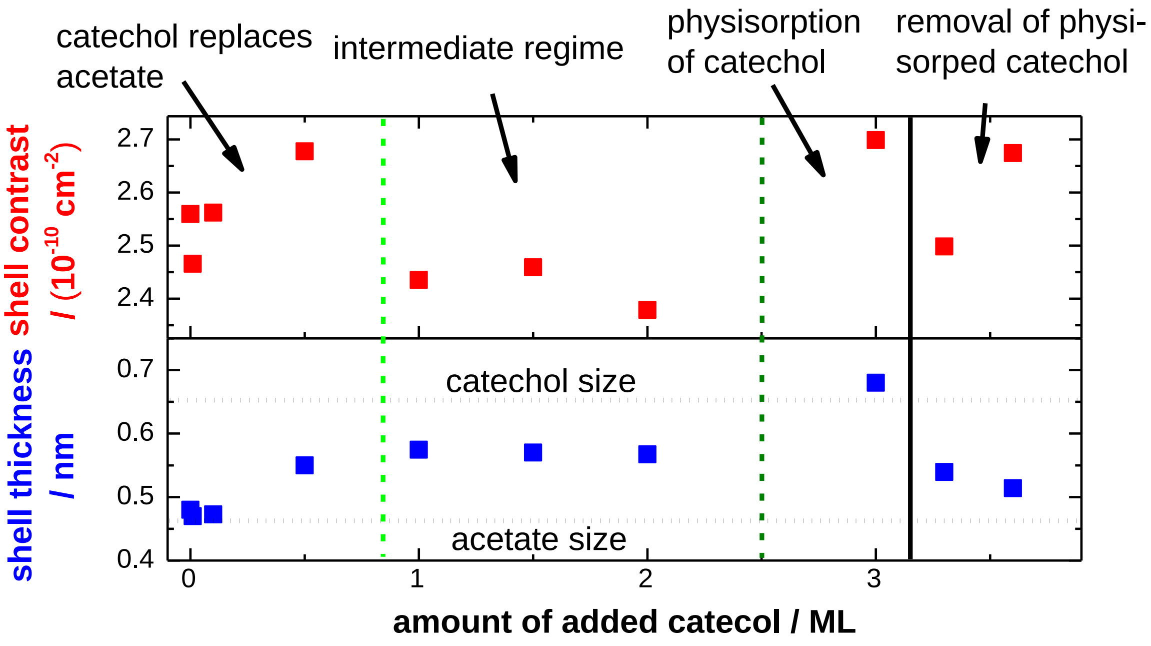

Figure 3: Analysis of the parameters as obtained from the simultaneous fits shown exemplarily in figure 2. The shell thickness increases with increasing catechol concentration, while the contrast also increases, after the loss of acetate, the contrast shrinks due to the lower contrast of catechol compared to acetate. After washing the physisorbed catechol is removed.

[1] L. Spanhel, *J. Sol-Gel Sci. Techn.,* **2006**, 39, 7

[2] B. Cossairt *et al.*, *J. Phys. Chem. Lett.,* **2011**, 2, 3075

[3] L. Spanhel *et al.*, *J. Am. Chem. Soc.*, **1991**, 113, 2826

[4] T. Schindler *et al.*, *Langmuir*, **2015**, 31, 10130