Experimental report

09/03/2016

Proposal: **9-12-424** **Council:** 4/2015

Title: Functionalization of ZnO Nanorods via Ligand Exchange

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: ZnO + 3,6,9 trioxodecanoic acid
ZnO + catechol

Instrument	Requested days	Allocated days	From	To
D33	0	0		
D22	0	0		
D11	3	2	04/12/2015	06/12/2015

Abstract:

In order to preserve the unique properties of nanoparticles (NPs), it is crucial to overcome their strong tendency to form agglomerates in solution. Finding adequate stabilizers, which introduce steric and/or electrostatic repulsion forces to the particle surface, enables the formation of colloidal stable suspensions. We use charged organic molecules, equipped with catechol anchor groups for attaching them covalently to the NPs to stabilize them due to electrostatic repulsion. We focus on TODA (3,6,9-Trioxadecanoic acid)-stabilized ZnO nanorods which are further functionalized with charged catechol. Single stabilized, positively charged ZnO nanorods are obtained by mono-functionalization. However, to directly investigate the functionalization in situ, the combination of different small angle techniques is necessary. By the combination of SAXS and SANS we were able to identify the acetate layer around ZnO NPs and want to determine now the stabilizing TODA shell before ligand exchange and the catechol shell after ligand exchange. By matching the contrast of the solvent to the catechol shell, the influence of residual TODA will be studied. Thus, we apply for 3 days of beamtime at D11.

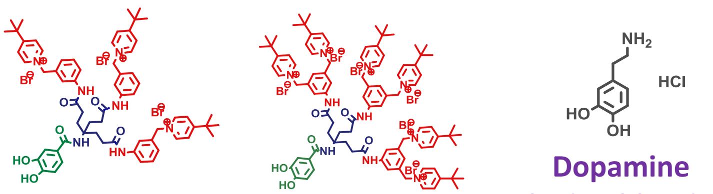
Experimental Report for proposal 9-12-424: Functionalization of ZnO Nanorods via Ligand Exchange

In order to preserve the unique properties of nanoparticles, it is crucial to overcome their strong tendency to form agglomerates in solution. Finding adequate stabilizers, which introduce steric and/or electrostatic repulsion forces to the particle surface, enables the formation of colloidal stable suspensions. We focus on the synthesis of charged organic molecules, equipped with catechol anchor groups for attaching them covalently to inorganic nanoparticles. This leads to nanoparticles which are stabilized in solution due to steric hindrance and electrostatic repulsion.[1,2] In the current work we focus on TODA (3,6,9-Trioxadecanoic acid)-stabilized ZnO nanorods which are further functionalized with catechols to introduce permanent positive charges to the nanorod surface.[3] Single stabilized, positively charged ZnO nanorods are obtained by either mono-functionalization or mixed-functionalization approaches. However, to directly investigate the functionalization in situ, the combination of different small angle techniques is necessary.[4]

The ZnO nanorods are prepared by a standard routine, in which $ZnAc_2$ x $2H_2O$ is solved in methanol and potassium hydroxide is added and the solution is refluxing for 49 h to form the ZnO nanorods. Afterwards the ZnO nanorods are precipitated, washed and redissolved in ethanol to which TODA is added to suppress the high tendency for aggregation of the nanorods.[3] However, after several hours the nanorods also show slight agglomeration, which can be cracked by ultrasonic treatment. In order to obtain stable, single stabilized ZnO nanorods solutions, we use charged catechol molecules, which exchange with the TODA molecules due to the stronger bond of the catechols compared to carboxylic acids. Different concentrations of the catechol will be used in order to detect the efficiency of ligand exchange.

Table 1: Sample number and stabilizer used.

Sample	Stabilizer
1	AB034
2	AB062
1A	AB034+Dopamine
2A	AB062+Dopamine



AB 034 AB 062 Dopamine hydrochloride

Figure 1: Structure of the stabilizer molecules in this study and abbreviations as used in Table 1.

We studied the effect of the functionalization with two slightly different molecules called AB 034 and AB 062 (shown in Figure 1). In addition we also tested mixed-functionalization in which the charged catechol molecules were mixed with dopamine chloride (see also Figure 1). For all samples SANS measurements in deuterated ethanol and in a mixture of protonated and deuterated ethanol, whose scattering length density matched that of the ZnO core, were performed. In addition, these samples were also measured using X-rays. The obtained scattering curves are exemplarily depicted for sample 2 in Figure 2. All curves were fitted simultaneously on an absolute scale and a very good fit was obtained (see solid lines in Figure 2).

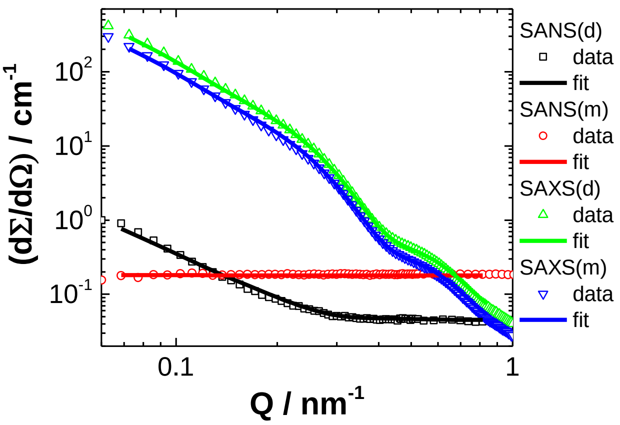


Figure 2: SAXS and SANS pattern (open symbols) and corresponding curves of the simultaneous SAXS-SANS fit (solid lines) of sample 2.

The fit parameters of the scattering contrast of the shell and its thickness can further be used to get insight into the stabilization of the ZnO nanorods. It became clear that the thickness of the shell is about 1.5 nm for all samples. However, the contrast of the shell differs slightly between the studied samples. This difference is used to calculate the number of stabilizing molecules on the ZnO nanorods. The numbers can be seen in Table 2.

Table 2: Comparison of number of stabilizer molecules as deduced from simultaneous fit. For mixed functionalized samples (1A & 2A) the amount of dopamine was calculated by the excess volume of stabilizer in comparison to the mono-functionalized samples. Additional work will give further insight into the amount of dopamine on the ZnO surface.

sample	Volume of stabilizer / nm³	Number of stabilizer molecules per ZnO nanorod
1	5600	4000 AB 034
2	3000	1500 AB 062
1A	5700	4000 AB 034 + 500 dopamine
2A	3200	1500 AB 062 + 500 dopamine

For the mono-functionalized samples the number of stabilizers depends on the volume needed by the stabilizer molecule. While the less bulky AB034 has a number of about 4000 molecules per nanorod it is clearly reduced for

AB062, which has only 1500 molecules per nanorod. In case of mixed-functionalization the volume of the stabilizer in the shell is increased. However, from the given data it is not possible to distinguish between dopamine and the larger catechol molecules. Further titration experiments are intended to determine the ratio of dopamine to the large catechol to determine the overall number of both molecules in the shell of the mixed functionalized ZnO nanorods.

Literature:

[1] J.-F. Gnichwitz, *J. Am. Chem. Soc.* **2010**, *132*, 17910

[2] A. Burger, *Chem. Eur. J.*, **2015**, 21, 5041

[3] S. Schäfer, *Thin Solid Films*, **2014**, *562*, 659

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