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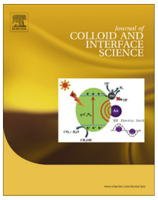

Regular Article

Changes within the stabilizing layer of ZnO nanoparticles upon washing

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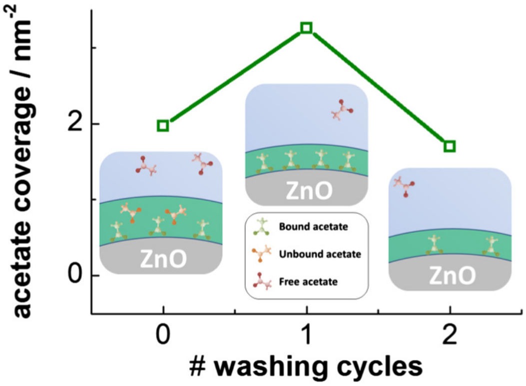
GRAPHICAL ABSTRACT



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ABSTRACT

ZnO nanoparticles (NPs) are highly relevant for various industrial applications, however, after synthesis of the NPs residual chemicals need to be removed from the colloidal raw product by washing, as they may influence the performance of the final device.

In the present study we focus on the effect of washing by antisolvent flocculation with subsequent redispersion of the NPs on the stabilizing acetate shell. Purification of the ZnO nanoparticles is reported to be optimal with respect to zeta potential that has a maximum after one washing cycle. In this work, we will shed light on this observation using small angle X-ray and neutron scattering (SAXS, SANS) by demonstrating that after the first washing cycle the content of acetate in the ligand shell around the ZnO NPs increases.

In detail, it was observed that the diffuse acetate shell shrinks to the size of a monolayer upon washing but the acetate content of this monolayer is higher than within the diffuse shell of the particles of the native dispersion. A second washing cycle reduces the acetate concentration within the stabilizing shell and the stability of the dispersion drops accordingly. After another (third) washing cycle strong agglomeration was observed for all investigated samples.

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1. Introduction

The electro-optical properties of semiconductor nanoparticles (NPs) like ZnO NPs can be adjusted by controlling their size [1–5]. This quantum size effect makes the NPs favorable for many different applications, e.g. for thin film solar cells where they act as an electron transfer system [6–9]. ZnO NPs can easily be synthesized by the sol-gel method [2,10,11] which also allows to change the mean size of the NPs by applying different ripening times and temperatures [12,13]. For the integration into applications, purified dispersions are of high importance as synthesis residuals can influence and possibly decrease the performance of the final device [10,11,14]. However, colloidal stability against agglomeration is mandatory.

Studies on the stabilizing layer of NPs are frequent, many focus on the determination of the amount of stabilizer on dried nanoparticles, i.e. by thermogravimetry [15,16] or fourier-transform infrared spectroscopy FTIR [17,18]. With the detected amount of stabilizer the surface coverage on the NPs is calculated from the mean size of the NPs. However, this does neither account for free stabilizer in solution nor for physisorbed stabilizer molecules nor for dynamic changes of this complex interplay during important processes like washing that is however expected to influence colloidal stability of the NPs.

Along the same lines, a frequently used measure for the colloidal stability of dispersed nanoparticles is provided by zeta potential measurements. This technique allows to conclude from its absolute value the stability changes of the colloidal nanoparticles suspension and has been widely used in research of colloidal nanoparticles [15,19,20]. However, to our knowledge a direct relation between the changes of the zeta potential and the amount of stabilizer on the NP surface could not be shown so far.

During the purification of ZnO NPs an interesting behavior of the colloidal stability was detected by Marczak et al. who revealed an increase of the magnitude of the zeta potential (or electrophoretic mobility which would be the direct measurement value) [21] after one washing step [22]. This effect, ascribed by the authors to a decrease in ionic strength due to ion removal during washing, diminishes after additional washing cycles. This was explained by the continuous removal of acetate species from the surface. However, at that time neither the composition nor the structural details of the stabilizing layer at the NP - dispersion medium interface during the washing process could be analyzed.

In fact, such structural details are only accessible by advanced characterization techniques like the combination of small angle neutron and X-ray scattering (SANS and SAXS) that was found to be well-suited for the study of NPs and their stabilizing shell in dispersion [23–28], which we could also demonstrate for ZnO recently [29]. We found a stabilizing layer of acetate surrounding the ZnO NPs which changed in size and acetate content during ripening. For all investigated samples the shell was thicker than the length of an acetate molecule (0.47 nm) with values up to 1.3 nm after ripening at elevated temperatures. The acetate content within the shell was observed to be below 50% in all cases. Thus, the stabilizing shell surrounding the NPs is a diffuse shell with a mixture of acetate and ethanol and a closed monolayer of pure ligand surrounding the ZnO NPs does obviously not exist in the native dispersion.

Herein, we studied for the first time the structural changes within the stabilizing layer around ZnO NPs upon purification by in situ SAXS/SANS experiments to unambiguously clarify the reason for the change in zeta potential (or electrophoretic mobility). Differently sized NPs were systematically investigated to reveal the influence of the washing step on the shell thickness as well as on the acetate content within the shell. It is shown that the amount of bound acetate is increased after the first washing cycle and reduced again after the second, which coincides with zeta potential measurements detecting a maximum in terms of its order of magnitude after the first washing. Thus, our method allows for the first time unraveling the dynamic evolution of ligand shells around ZnO NPs in situ.

2. Materials and methods

2.1. Particle synthesis

The particle synthesis was conducted similar as described before [29], in short, the ZnO NPs were prepared according to a modified route based on the routine developed by Spanhel and Meulenkamp [10,11,30]. 97.75 mg zinc acetate ($ZnAc_2$, 0.5 mmol) was dissolved in 5 ml of deuterated ethanol (EtOD) and additional 18 µl of D_2O (1 mmol), which was added to include the same amount of water as in the normal synthesis in which zinc acetate dihydrate is used. The dispersion was refluxed at 80 °C for 3 h and rapidly mixed with an equimolar solution of lithium hydroxide (LiOH, 0.012 g, 0.5 mmol) in EtOD to form the ZnO NPs.

The homogenous nanosuspension was divided in two parts and stored at 20 °C and 50 °C, respectively. Small samples were taken from the suspension after mixing (sample A), after storage at 20 °C and storing times of 3 h (sample B) and 24 h (sample C), while the samples from the suspensions stored at 50 °C were taken after 1 h (sample D) and 3 h (sample E). All samples were purified three times using the routine described in the following and after each purification cycle a part of the sample was used for the SAXS and SANS measurements. The samples were stored at 10 °C and also kept at this temperature during the measurements.

2.2. Washing routine

For purification, the antisolvent heptane was added in six-fold excess to the ZnO NP solution inducing flocculation. After 5 min of centrifugation at 6000 rpm, the supernatant was removed and the particles were dried using N_2 flow. The dried nanoparticles were redispersed in deuterated ethanol. All samples were measured by SAXS and SANS at a temperature of 10 °C to prevent further ripening during the measurements.

2.3. SANS instrument

The SANS measurements were performed at the KWS-1 instrument at the Jülich Center for Neutron Science (JCNS) at the Heinz Maier-Leibnitz Zentrum (MLZ) in Garching, Germany [31]. The beam dimensions were set to $8 \times 8\ \mathrm{mm}^2$ at the sample position and the detector was placed at a sample detector distance (SDD) of 1.77 m with a collimation length of 8 m. The velocity selector provided a wavelength of $\lambda = 4.967$ Å with a spread of $\Delta\lambda/\lambda = 10\%$. By this setting a Q-range between $0.1\ \mathrm{nm}^{-1}$ and $2\ \mathrm{nm}^{-1}$ could be accessed which was chosen to overlap with the Q-range of the SAXS measurements. The samples were filled into Hellma QX 404 quartz cuvettes (Hellma GmbH, Müllheim, Germany) with a sample thickness of 1 mm and placed in a multi-position copper sample holder provided at the instrument. The temperature was controlled by an external water bath and set to 10 °C for all measurements. To prevent condensation of water droplets on the cuvettes a constant flow of dried air was directed toward the cells. Each sample was measured for 1 h to achieve reasonable statistics.

For data reduction the QTIKWS program was used [32]. The recorded data were corrected for background in the neutron guide hall with a boron carbide sample, for transmission using a measurement at a detector distance and a collimation length of 8 m