

Stabilization Mechanism of ZnO Quantum Dots

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ABSTRACT

The current work addresses the understanding of the stabilization of small ZnO quantum dots in ethanolic suspension. Thereby different degrees of purification were investigated. The results revealed that not only the well-known ζ -potential as a representative for the surface charge determines the colloidal stability but also the surface coverage of acetate groups bound to the particle surface. Those acetate groups act as molecular spacers between the nanoparticles and prevent agglomeration. Regarding DLVO-calculations using a core-shell model, not only the height of the maximum but also the depth of the primary minimum has to be considered to see if a colloidal suspension is stable or not.

Keywords: ZnO, quantum dot, purification, stability, core-shell model

1 INTRODUCTION

ZnO semiconductor quantum dots have attracted considerable attention during the past ten years due to their promising electro-optical properties. Besides fundamental research on the particle synthesis itself,¹ especially the nanoparticles optimization regarding electronic devices or solar cells is increasingly in the focus of interest. However, for the successful incorporation of nanoparticles into electronic devices, stable suspensions and high solid concentrations are required. At first glance, the stabilization of small nanoparticles seems to be rather challenging as the collision events between the particles are supposed to be very frequent due to the strong influence of Brownian motion in this size regime. In contrast, experiments have revealed that ZnO particles around 5 nm in diameter can be stored over months at room temperature without noticeable aggregation. This is recently explained in the literature using an extended core-shell model of the well-known DLVO-theory which considers not only the surface charge of the nanoparticles but also a protecting shell around them.^{2,6} Thus, the current work shows that for a successful stabilization of nanoparticles not only the height of the maximum but also the depth of the primary minimum has to be considered.

2 EXPERIMENTAL

2.1 Synthesis of ZnO nanoparticles

All chemicals were analytical grade reagents used without further purification. ZnO nanoparticles were obtained using a preparation procedure adapted from Spanhel et al.³ and Meulenkamp.⁴ In the first step 1.1 g of zinc acetate dihydrate (ACS Grade, 98.0%, VWR, Germany) was dissolved in 50 mL of boiling ethanol (99.98%, VWR, Germany) at atmospheric pressure. The obtained zinc acetate solution was cooled down to 25 °C. A white powder of anhydrous zinc acetate precipitated close to room temperature. In the second step lithium hydroxide (98%, VWR, Germany) was dissolved in 50 mL of boiling ethanol and also cooled down to the synthesis temperature. Then, the lithium hydroxide solution was added dropwise to the cold zinc acetate solution under vigorous stirring. The reaction mixture became transparent as the zinc acetate reactant was consumed during the ZnO particle formation. The particles were grown in their mother liquors to achieve different particle sizes before the purification was started by adding an excess of n-heptane.

2.2 Purification of ZnO nanoparticles

To purify the so-prepared ZnO nanoparticles in order to remove the reaction byproduct lithium acetate, the precipitation-redispersion procedure introduced by Meulenkamp⁴ was performed. Thereby, the unwanted byproduct was removed by reversible flocculation of the ZnO nanoparticles with the addition of n-heptane with a fivefold excess of the antisolvent to the ZnO colloid. White ZnO flocculates precipitated immediately after the addition of heptane. Afterwards, the supernatant containing the lithium acetate was separated from the white ZnO precipitate by centrifugation and decantation. The suspension was investigated after one, two and three times of washing.

For the optical characterization by using UV-Vis absorption spectroscopy and DLS, the ZnO flocculates were easily redispersed in ethanol using sonication. For the compositional characterization by using TGA, the ZnO flocculates were dried under nitrogen for about 5 min at room temperature in order to obtain a solid powder. The detailed specification of the measuring devices can be found in the literature.^{2d}

3 RESULTS AND DISCUSSION

3.1 Particle size distributions from absorption spectra

A model for the calculation of particle size distributions (PSD's) of colloidal ZnO nanoparticles using their absorption spectra is presented. Using literature values for the optical properties of bulk ZnO which are correlated with the measurement wavelengths by a tight binding model (TBM) from the literature,⁵ an algorithm deconvolutes the absorption spectra into contributions from the distinct size fractions. Thereby an excellent agreement between the size distribution determined from TEM-images and the calculated PSD's is found.¹

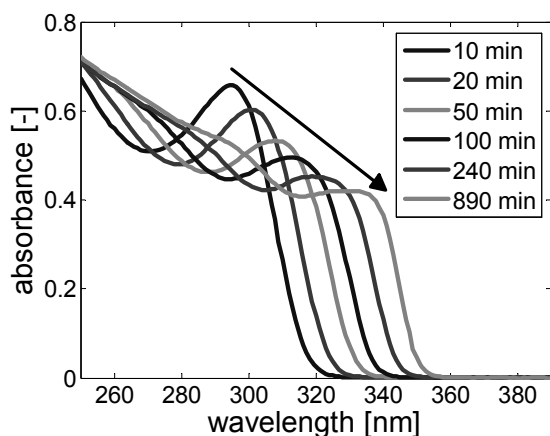


Figure 1: Absorption spectra of ZnO during ripening used for the validation of the algorithm.¹

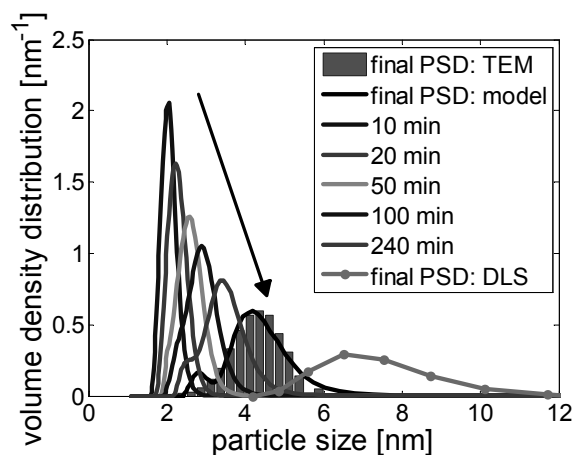


Figure 2: Comparison between PSD's calculated using the algorithm, optical image analysis of TEM-micrographs and dynamic light scattering (DLS).¹

3.2 Temperature influence on ripening

To investigate the temperature influence on the ripening behavior of the particles the suspensions were put into a thermostated cuvette and the change of the optical properties was monitored with time. The final particle size distributions for $T = 25\text{ }^\circ\text{C}$ and $T = 35\text{ }^\circ\text{C}$ obtained from the absorption spectra are shown in Figure 3.⁶

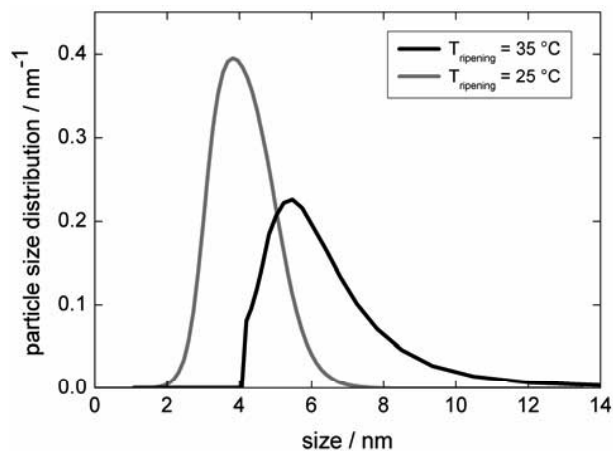


Figure 3: Particle size distributions after ripening at $25\text{ }^\circ\text{C}$ and $35\text{ }^\circ\text{C}$, respectively, obtained from absorption spectroscopy.⁶

3.3 Washing

For the washing the procedure of precipitation and redispersion was performed one, two and three times. After each washing step the ζ -potential was determined and the amount of acetate molecules bound to the particle surface was measured using thermogravimetric analysis (TGA). The results are shown in Figure 4.

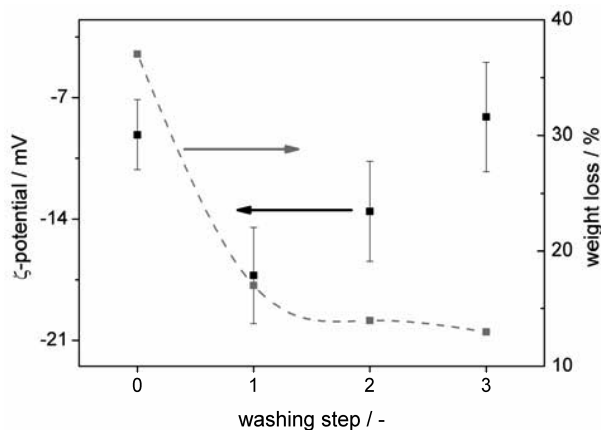


Figure 4: ζ -potential and conductivity obtained by DLS and corresponding weight losses obtained by TGA after zero, one, two and three washing steps.⁶

Thereby it becomes clear that the amount of the ζ -potential increases after the first washing as ions are removed from the solvent which are leading to a compression of the double layer. However, with subsequent washing, the amount of the ζ -potential decreases again as then the acetate ions directly bound to the particle surface are washed away. This removal of acetate can be monitored using TGA where the weight loss significantly decreases from nearly 40% for the unwashed sample down to 13% for the samples after three times of washing. However, after washing the powders could be easily redispersed without changing the original particle size distribution.⁶

Regarding the three-times washed sample it is highly unstable. This is leading to a white precipitate of agglomerates obtained without the addition of heptane immediately after the washing procedure has finished (see Figure 6).

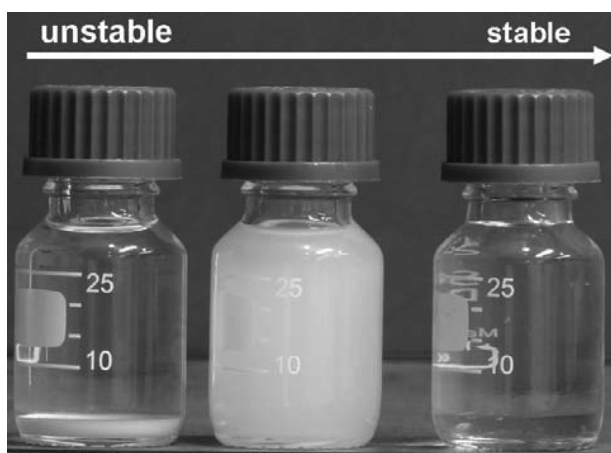


Figure 6: Evaluation of stability.

For a deeper understanding of the mechanisms which are leading to stable or unstable suspensions, calculations based on the DLVO-theory using a Core-Shell model were performed.

3.4 Core-Shell model

As shown in the previous section the stability of the nanoparticles can not be explained solely by electrostatics. Therefore Figure 7 shows the devolution of the interaction potential of a ZnO suspension calculated with a core-shell model with and without the consideration of acetate molecules bound to the particle surface. It becomes clear that for a proper interpretation of the stability not only the height of the maximum has to be evaluated but also the depth of the primary minimum. Thereby, the interaction potentials for the unwashed suspension as well as for the samples after one and two cycles of washing, were calculated under consideration of a protecting shell of acetate ions around the particle surface. They show neither a maximum nor a noticeable minimum.

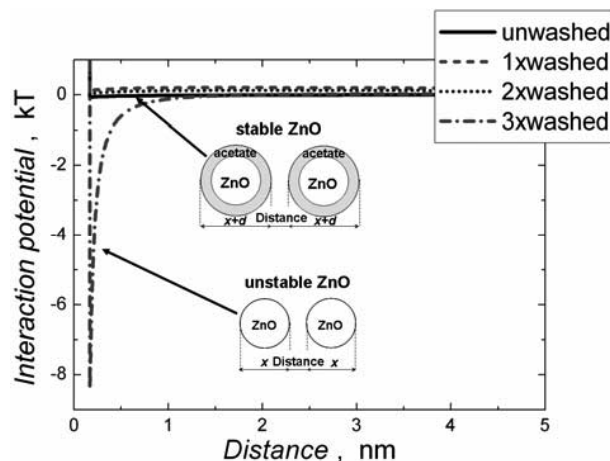


Figure 7: Comparison of the interaction energy of 5 nm ZnO nanoparticles before washing (solid line), after one (dashed line), two (dotted line) and three (dash-dotted line) washing cycles.⁶

In contrast, the suspension after three times of washing which was calculated with a hard-sphere model shows a comparatively deep primary minimum.⁶ Thus, when two particles approach down to the minimum contact distance at 0.165 nm they “feel” a remarkable force sticking them together and agglomeration of the suspension is observed.

However, this holds for the assumption of a complete removal of acetate ions bound to the particle surface. For a detailed understanding of all influencing factors on particle stabilization being present at the particle surface, a more general approach has to be found which independently compares the influence of electrostatics, surface coverage and attractive forces.⁶

4 CONCLUSION

In the present work the stabilization of ZnO quantum dots was investigated. Thereby the particle size distributions were calculated from the absorption spectra, the ζ -potentials were determined for different washing cycles and the weight loss of acetate molecules bound to the particle surface was measured with TGA. For a clear identification of stable conditions under consideration of electrostatics as well as the protecting acetate coverage around the particles DLVO calculations using a Core-Shell model were performed. They revealed that for understanding colloidal stability not only the height of the maximum but also the depth of the primary minimum has to be considered.

However, for the future a more general approach has to be found. Thereby the different influencing factors on nanoparticle stabilization, namely electrostatics, surface coverage and attractive forces have to be considered independently.

5 ACKNOWLEDGMENTS

The authors would like to thank the German Research Council (DFG) for their financial support (Projects PE427/18-2) which supports within the framework of its Excellence Initiative the Cluster of Excellence 'Engineering of Advanced Materials' (www.eam.uni-erlangen.de) at the University of Erlangen-Nuremberg.

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