Quantitative Evaluation of Size Selective Precipitation of Mn-doped ZnS Quantum Dots by Size Distributions Calculated from UV/Vis Absorbance Spectra

Doris Segets,[+a] So Komada,[+b] Benjamin Butz,[c] Erdmann Spiecker,*[c] Yasushige Mori*[b] and Wolfgang Peukert*[a]

[a] *Institute of Particle Technology, Friedrich-Alexander University of Erlangen-Nuremberg, Cauerstraße 4, 91058 Erlangen, Germany. Fax: +49 (0)9131 8529402; Tel: +49 (0)9131 8529401;*
E-mail: Wolfgang.Peukert@lfg.fau.de

[b] *Department of Chemical Engineering and Materials Science, Doshisha University,1-3 Tatara Miyakodani Kyotanabe, Kyoto 610-0321, Japan. Fax: +81 (0)774 65 6847; Tel: +81 (0)774 65 6626;*
E-mail: ymori@mail.doshisha.ac.jp

[c] *Center for Nanoanalysis and Electron Microscopy, Friedrich-Alexander University of Erlangen-Nuremberg, Cauerstraße 6, 91058 Erlangen, Germany. Fax: +49 (0)9131 8528602; Tel: +49 (0)9131 8528603;*
E-mail: Erdmann.Spiecker@ww.uni-erlangen.de

[+] These authors contributed equally to this work.

CONTENT:

S1 **Sketch of overall particle treatment**

S2 **Calculation of volume density distribution and $x_{1,3}$**

S3 **Classification results of other samples**

S4 **Influence of Mn-doping on absorbance behaviour**

S5 **Reconstructed absorbance spectra of samples *#1…#4***

S6 **Influence of sonication - ripening**

S1. Sketch of overall particle treatment

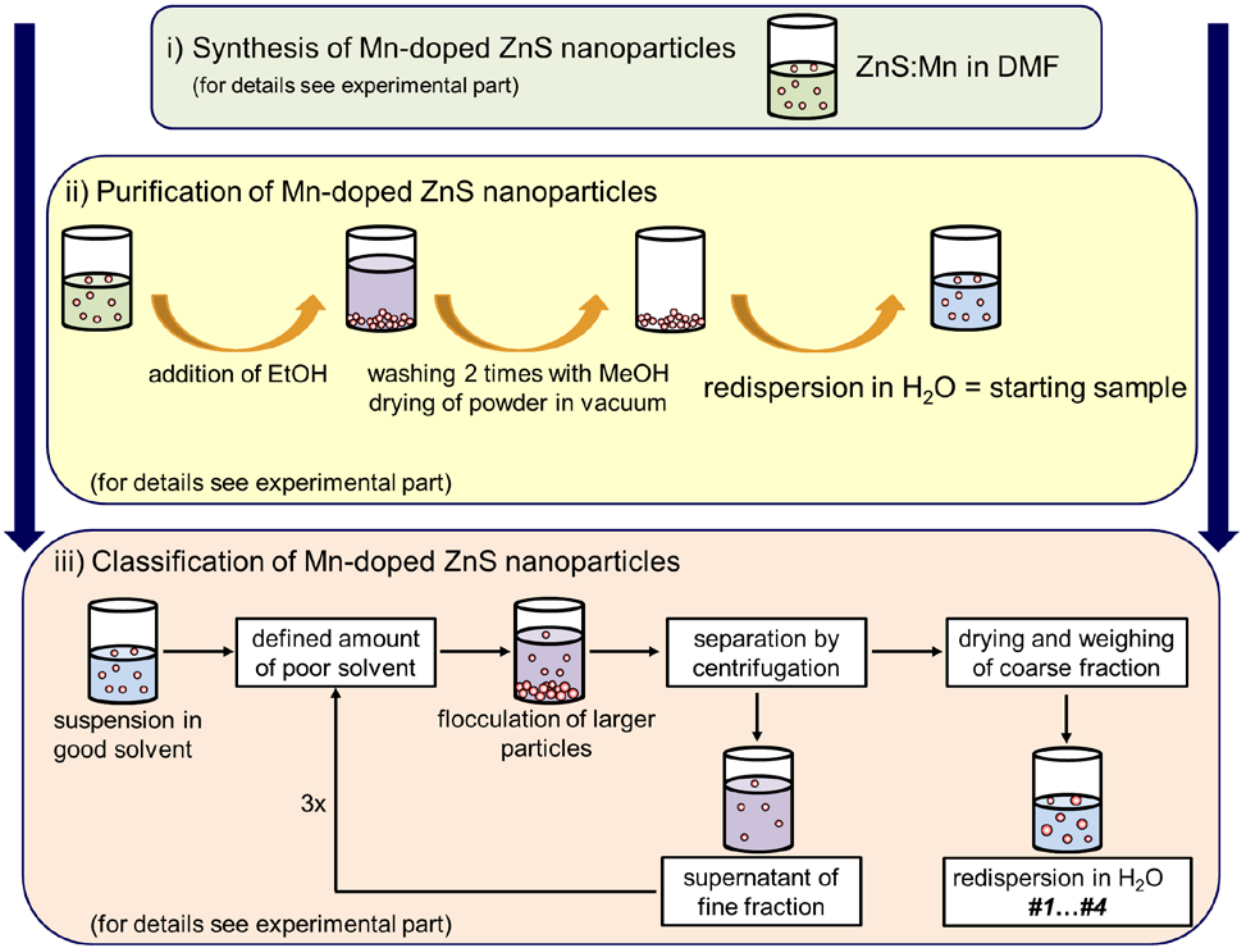

Figure S1_1. Sketch of the overall particle treatment including synthesis, purification and classification.

S2. Calculation of volume density distribution and $x_{1,3}$

According to the literature (Leschonski, K.; Alex, W.; Koglin, B., Teilchengrößenanalyse. *Chem.-Ing.-Tech.* **1974**, 46, 23-26) the volume PSD $q_3(x)$ is calculated from the number size distribution $q_0(x)$ according to:

$$q_3(x_i) = \frac{{x_i}^3 q_0(x_i)}{M_{3,0}} \tag{1}$$

Where $M_{3,0}$ is the third moment of the number density distribution which is defined as follows:

$$M_{3,0} = \sum_i ({x_i}^3 q_0(x_i) \Delta x_i) \tag{2}$$

Finally, the mean volume weighted particle size is defined as:

$$x_{1,3} = \sum_i (x_i \; q_3(x_i) \; \Delta x_i) \tag{3}$$

S3. Classification results of other samples

Table S3_1. Evolution of the particle diameter (calculated by the tight binding model (TBM) of Sapra and Sarma: *Sapra, S.; Sarma, D. D., Evolution of the Electronic Structure with Size in Ii-Iv Semiconductor Nanocrystals. Phys. Rev. B* ***2004,*** *69, 125304*) during classification (samples *#1 … #4*) of other samples of ZnS:Mn quantum dots isolated after different times of reflux evidencing the reproducibility of the applied concept; additionally the values of coarse and fines fractions calculated according to Equations 1 and 2 from the manuscript are provided.

	particle diameter / nm				
reflux time / h	***#0***	***#1***	***#2***	***#3***	***#4***
1	1.78	2.16	1.93	1.83	1.78
5	1.88	1.98	1.88	1.83	1.78
24	2.00	2.15	2.01	1.96	1.88
36	2.15	2.50	2.40	2.30	2.10
48	2.17	2.43	2.38	2.25	2.09
	coarse fraction / -				
1	-	0.07	0.17	0.47	0.29
5	-	0.51	0.15	0.26	0.08
24	-	0.32	0.24	0.27	0.18
36	-	0.09	0.16	0.13	0.61
48	-	0.12	0.18	0.33	0.37
	fines fraction / -				
1	-	0.93	0.76	0.29	0
5	-	0.49	0.34	0.08	0
24	-	0.68	0.45	0.18	0
36	-	0.91	0.75	0.61	0
48	-	0.88	0.70	0.37	0

From Table S3_1 it becomes clear that independently from the starting conditions (*#0*) always the same classification effect which is described in the manuscript is observed: an increase of the mean particle size after the first classification step *#1* followed by a slight decrease with the following classification steps *#2-#4*. Additionally, these findings are supported by the recently published work of Komada *et al.* (*Adv. Powder Technol.* 23 (**2012**), 872-877).

Although the qualitative reproducibility of size selective precipitation is sufficiently supported by this data, for quantitative control of the obtained PSDs an understanding of the classification process is necessary. Only by this control of the isolated coarse fractions throughout the course of classification is possible. However, this would require extensive studies on process parameters like (just to mention a few of them) energy input by stirring, energy input by sonication during redispersion, mixing time of good solvent and poor solvent or temperature. Due to the fact that the focus of the present work is not process design but the development of an evaluation technique, future studies are needed for an in-depth control of the classification result.

S4. Influence of Mn-doping on absorbance behaviour

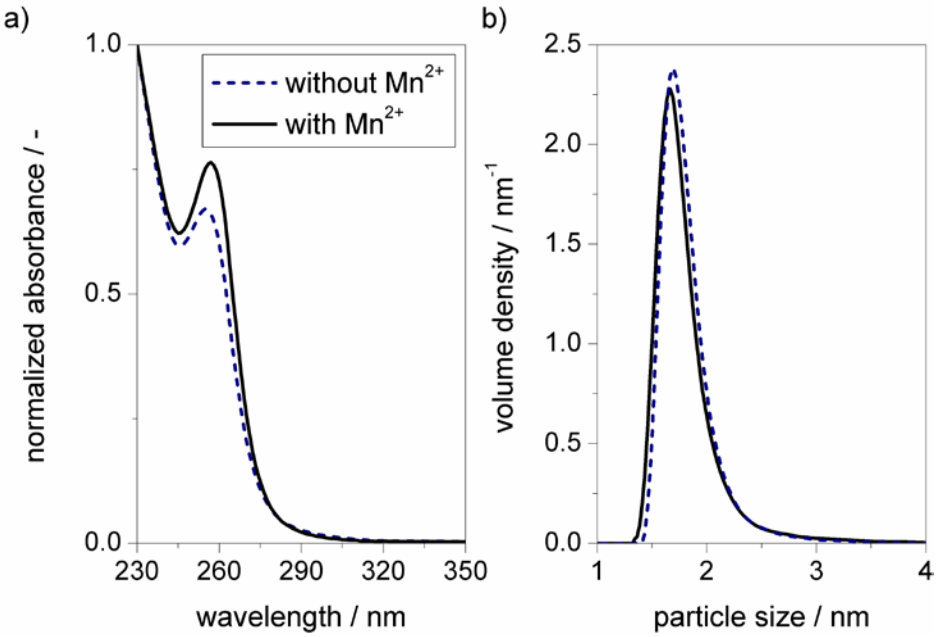

Figure S4_1. a) Normalized absorbance of ZnS quantum dots synthesized at the same conditions (reflux temperature: 100 °C, reflux time: 2 h) without (black solid line) and with (blue dashed line) the presence of Mn^{2+} ions; except of the absolute heights of the spectra that can be ascribed to slightly different particle concentrations, the peak position is identical; b) volume PSDs that were calculated by the algorithm from the absorbance measurements shown in a) evidencing the independence of the PSD from the presence of Mn-doping.

S5 Reconstructed absorbance spectra of samples *#1…#4*

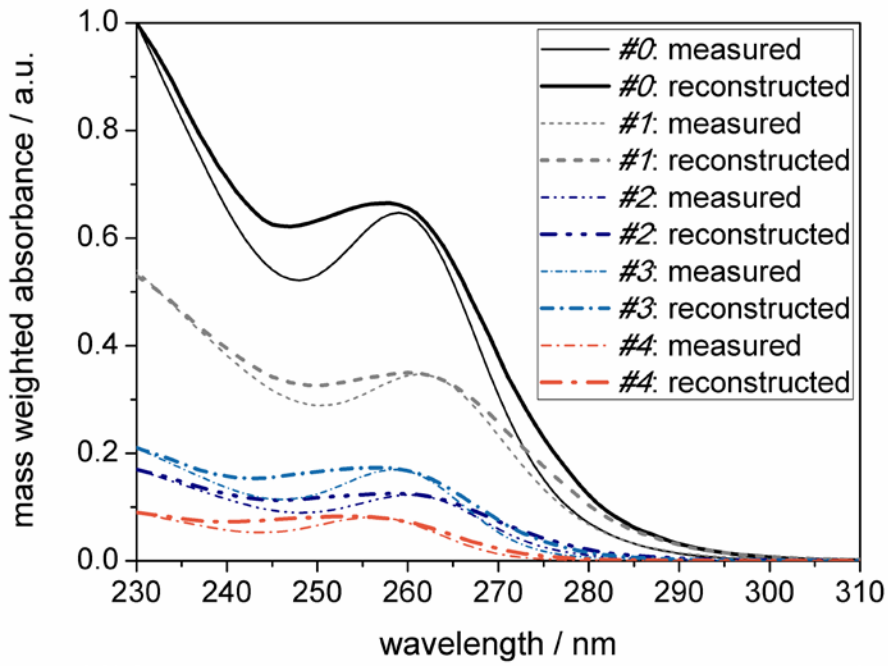

Figure S5_1. Reconstructed absorbance (thick lines) of classified samples *#1* (gray), *#2* (dark blue), *#3* (light blue) and *#4* (orange) together with the measurement data (thin lines) and the reconstructed and measured absorbance of the starting sample *#0* (black).

S6 Influence of sonication - ripening

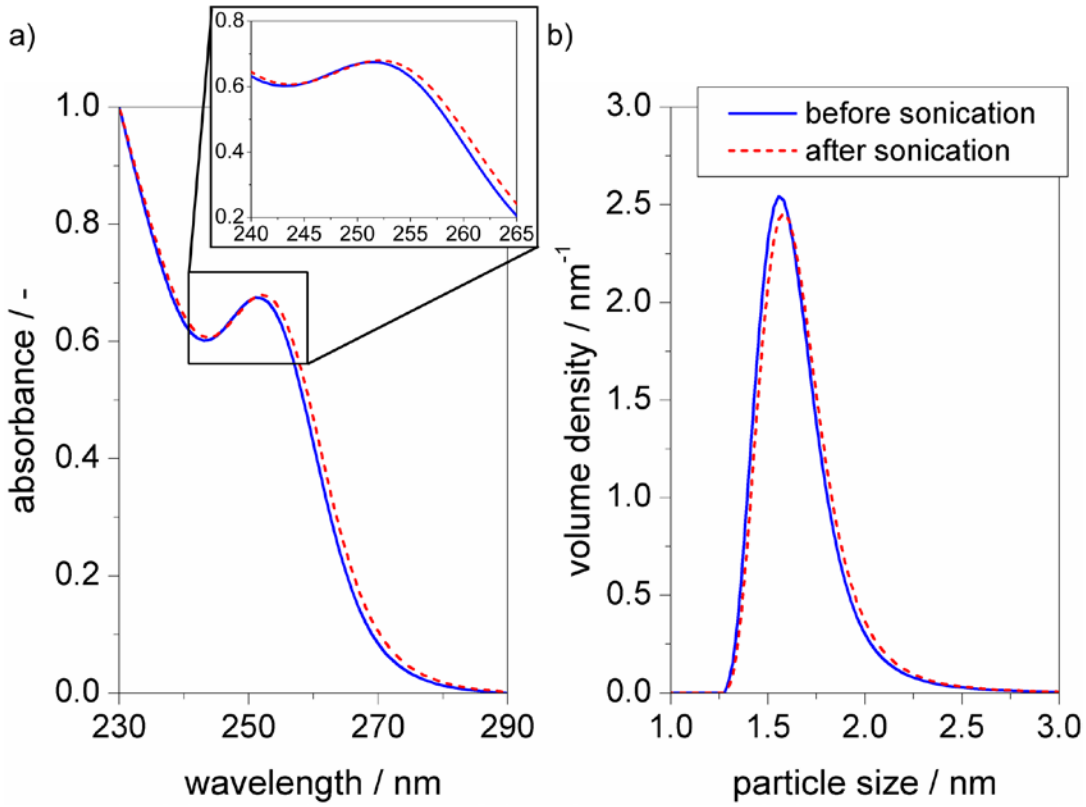

Figure S6_1. a) Absorbance spectra and b) PSDs of ZnS:Mn quantum dots before and after 1 h of sonication confirming the presence of slight ripening effects due to the energy input.