Analysis of Particle Size Distributions of Quantum Dots: From Theory to Application[†]

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Abstract

Small, quantum-confined semiconductor nanoparticles, known as quantum dots (QDs) are highly important material systems due to their unique optoelectronic properties and their pronounced structure-property relationships. QD applications are seen in the emerging fields of thin films and solar cells. In this review, different characterization techniques for particle size distributions (PSDs) will be summarized with special emphasis on strategies developed and suggested in the past to derive data on the dispersity of a sample from optical absorbance spectra. The latter use the assumption of superimposed individual optical contributions according to the relative abundance of different sizes of a colloidal dispersion. In the second part, the high potential of detailed PSD analysis to get deeper insights of typical QD processes such as classification by size selective precipitation (SSP) will be demonstrated. This is expected to lead to an improved understanding of colloidal surface properties which is of major importance for the development of assumption-free interaction models.

Keywords: particle size distribution, quantum dot, structure-property relationship, classification by size selective precipitation, solubility parameters

1. Introduction

Quantum dots (QDs) are semiconductor nanoparticles which are small enough that quantum confinement occurs in all three dimensions. The first systematic dynamic investigations of interfacial electron and hole processes as well as reports on the size-dependent optical properties of QDs in solution date back to the early 1980s (Duonghong D. et al., 1982; Kuczinski J. and Thomas J.K., 1982; Rossetti R. et al., 1984). Therefrom motivated, Brus was the first who developed a quantum mechanical model based on the effective mass approximation (EMA) of electrons and holes to predict the evolution of the size-dependent band gap energy (Brus L.E., 1983, 1984; Steigerwald M.L. and Brus L.E., 1990).

Afterwards, as recently summarized by Tyrakowski and Snee (Tyrakowski C.M. and Snee P.T., 2014), more than two decades of intense research on QDs passed, covering various aspects from quantum mechanics and optical properties (Alivisatos A.P., 1996), particle synthesis (Park J. et al., 2007), functionalization and ligand exchange (Alvarado S.R. et al., 2014; Lin W. et al., 2015).

Nowadays—although not yet an established mass product—QDs are commercially available via online shops and are highly relevant for the emerging fields of printed solar cells (Debnath R. et al., 2011) and thin-film electronics (Choi J.-H. et al., 2012; Moynihan T., 2015). Moreover, they become increasingly attractive for medical and biological applications (Cottingham K., 2005).

The fine-tuning of a PSD is decisive for any kind of later application. This is due to the aforementioned pronounced size-property relationships of those transient structures situated at the interface between dissolved molecules and solid particles. Thus, QDs are inherently related to interdisciplinary research. Whereas the molecular, rather than the chemical and physical approach is the point where investigations of QDs have originally been started, those nanoparticles provide many aspects that are of equal interest to the field of process engineering and particle technology. Usually, QDs with tailored optical properties in terms of defined absorption onset and emission features in combination with a narrow size distribution are required (Nightingale A.M. and De Mello J.C., 2010; Yen B.K. et al., 2005). This is not only a central issue related to scale-up but equally demanding in terms of characterization—especially when keeping in mind the small particle sizes of a few nanometers in maximum.

To quantitatively compare the narrowness of a PSD throughout different samples, the relative standard deviation (RSD) or coefficient of variation, defined as the stan-

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dard deviation divided by the mean particle size ($RSD = \sigma/x_{\text{mean}}$), is usually applied. Following the convention, “monodispersity” is achieved if $RSD < 0.05$, whereas “narrow” PSDs are found for $RSD < 0.1$. This fundamental requirement of narrow distributions raises the following central questions:

- i) How can QDs that cover particle sizes clearly below 10 nm, often even down to 1 nm, be accurately characterized with justifiable experimental effort?
- ii) To what extent can narrow PSDs with RSDs below 0.1 or even below 0.05 be achieved?
- iii) Can knowledge on i) and ii) be used to access particle-particle interactions of small colloids?

Whereas the second issue has already recently been discussed by Kowalczyk and Mori and the second issue at least partly addressed by Mori (Kowalczyk B. et al., 2011; Mori Y., 2015), the challenge of size characterization remains. Therefore, in the following sections, different strategies based on the deconvolution of absorbance measurements developed by different groups will be discussed and compared to standard and advanced methods of small particle characterization found in the field of QDs and/or particle technology. The latter will be done with respect to accuracy, availability, experimental effort and potential of the method to become a suitable online technique. In the last part of this work, the high potential of size analysis—aiming to make particle interactions accessible—will be demonstrated by a more recent example on QD classification by size selective precipitation (SSP) (Segets D. et al., 2015). The study shows how careful particle characterization on an Å-level is of paramount importance in order to access colloidal surface properties, and how those may be linked in the near future to permit calculation of assumption-free interaction potentials.

2. Size characterization of QDs

In the following sections, methods for QD size characterization will be introduced. First, standard methods such as (high-resolution (HR)) transmission electron microscopy (TEM) and dynamic light scattering (DLS) as well as advanced techniques such as small-angle X-ray scattering (SAXS), field-flow fractionation (FFF) and analytical ultracentrifugation (AUC) will be discussed briefly. Then, special emphasis will be placed on different approaches for the deconvolution of absorption data to derive a PSD beyond a mean particle size and a standard deviation.

(High-resolution) transmission electron microscopy

At first glance, the most obvious way to analyze QDs is (HR)TEM. It not only gives access to the primary particle

size and shape—most of QDs are in good approximation spherical, however, other shapes such as cubes are reported as well (Pietryga J.M. et al., 2004)—but also allows a discrimination of isolated particles from aggregates or superstructures. Moreover, crystallinity and thus the inner structure of the particles can be derived directly from TEM data. Drawbacks are the necessity of an additional drying step and poor statistics that need to be carefully considered when conclusions based on a limited amount of particles (< 1000) are to be drawn for the ensemble ($>> 10^{10}$). Finally, side effects such as ripening on the TEM substrate induced by the electron beam need to be considered as well (Segets D. et al., 2013). Although over the past years, reports on liquid cell TEM (Nielsen M.H. et al., 2014; Zheng H. et al., 2009) and the evaluation of larger datasets due to automatized image analysis (Segets D. et al., 2012; Sun Y. et al., 2012) came more and more into the focus of interest, electron microscopy is demanding and not (yet) suitable for larger sample numbers and online analysis.

Dynamic light scattering

A frequently used technique for particle size analysis is DLS. It is commercially available, applicable in the liquid phase, and comparatively fast ($\sim$ min). It is based on the dynamic change in the scattering of coherent, monochromatic laser light due to the diffusion of small particles in a fluid. An autocorrelation function for the analysis of those fluctuations gives access to the diffusion coefficient D . With known temperature T and viscosity of the fluid η , the hydrodynamic particle diameter x_h (particle core + adsorbate/ligand shell) is available via the Stokes-Einstein equation:

$$D = \frac{k_B T}{3\pi\eta x_h} \quad (1)$$

If the extinction-weighted distribution of hydrodynamic particle sizes is to be transferred to a volume or number PSD, a Mie correction is necessary to consider the size-dependent extinction coefficient.

Regarding smallest nanoparticles such as QDs, it becomes obvious that a core size distribution is hardly accessible via DLS due to the fact that the ligand shell is no longer negligible (Marczak R. et al., 2010; Oshima H., 2009; Reindl A. and Peukert W., 2008). Additionally, the scattering intensity of particles below 10 nm is small, causing a low resolution of commercial devices in the size range of interest between 1 and 10 nm.

Small-Angle X-ray Scattering

In addition to the already mentioned standard techniques, other methods also exist to characterize PSDs with good or even outstanding accuracy. For instance, SAXS can be applied in situ to characterize colloids with

respect to primary particle size and, if required, gives access to agglomerates and even hierarchical structures such as mesocrystals (Seto J. et al., 2012; Sun Y. and Ren Y., 2013). The scattering signal correlates with the electron density distribution within the sample and is thus sensitive to concentration, size and shape (Keshari A.K. and Pandey A.C., 2008; Pauw B.R., 2013). As only one superimposed scattering curve is recorded, data interpretation is challenging and cross-validation against other, independent techniques is required. However, once established for a certain system, SAXS is a powerful technique for particle analysis (Abécassis B. et al., 2015; Caetano B.L. et al., 2010; Polte J. et al., 2010).

Field-Flow Fractionation

A versatile method for the size characterization of not only QDs but also of proteins, polymers, macromolecules, cells and colloids in general is field-flow fractionation (FFF) (Baalousha M. et al., 2011). It is a chromatographic technique, which means that it includes classification of the solute during the measurement. This is seen as a clear advantage with respect to resolution and also with respect to detection (Kowalczyk B. et al., 2011; Mori Y., 1994, 2015). Regarding the measurement principle, no column is needed but separation rather occurs in a laminar flow channel which is superimposed with an orthogonal second field. This second field is often a flow field, but also thermal, electric, magnetic and gravitational fields are possible (Baalousha M. et al., 2011; Williams S.K.R. et al., 2011). For nanoparticles, asymmetric flow FFF (AsFIFFF or A4F) is usually applied. A further advantage of FFF is the flexible detection that can be realized online (e.g. UV/Vis, organic carbon, fluorescence) or offline (e.g. TEM, atomic force microscopy, AUC). Thus, although the investment costs are comparatively high and solute concentrations are an issue, FFF is a promising technique, especially in combination with multiple detectors and with other, complementary analytical methods for size characterization (Dieckmann Y. et al., 2009; Hagendorfer H. et al., 2012).

Analytical Ultracentrifugation

Another outstanding characterization technique is AUC. Due to rotor speeds of up to 60 krpm, it has unrivaled resolution on an Å-level and can detect smallest particles even below 1 nm. The sedimentation of the particles in a centrifugal field is recorded and—usually based on extinction analysis over time—the sedimentation velocity is derived. From this, the particle size, shape and surface properties in terms of the ligand shell are accessible, which makes AUC an excellent technique for the characterization of smallest colloids (Lees E.E. et al., 2008). In parallel, special emphasis has been devoted to the development of advanced evaluation routines and al-

gorithms (Brookes E.H. and Demeler B., 2008; Walter J. et al., 2015b). More recently, AUC has been developed further to allow not only for the detection of a single wavelength but to extend for multiwavelength (MWL) data analysis (Balbo A. et al., 2005; Bhattacharyya S.K. et al., 2006; Strauss H.M. et al., 2008; Walter J. et al., 2014). As a result, the optical properties of individual species in a mixture, such as the absorbance of discrete-sized QDs, will become accessible.

Although the availability of AUC is still limited and online analysis is not possible, it is expected to become the gold standard for particle characterization due to its unmatched resolution of multimodal size distributions and the possibility to extend towards multidimensional characterization. For instance, size and spectral properties, size and shape or size and density (Carney R.P. et al., 2011; Walter J. et al., 2014; Walter J. et al., 2015a; Walter J. et al., 2015b).

At this point it should be briefly mentioned that the same holds true for analytical centrifugation (AC) which works with lower gravitational fields but extends the measurement range to larger particle sizes (Detloff T. and Lerche D., 2008; Jafarzadeh S. et al., 2011; Krause B. et al., 2010; Walter J. et al., 2015c). Noteworthy, offline information from AUC, like for instance the optical properties of discrete QD fractions, could be implemented in evaluation routines based on UV/Vis spectroscopy. The latter is widely available and well-suited for fast online investigations which are needed for kinetic studies at high-time resolution (~ ms). Hence, the technique will be discussed in more detail in the following text with special emphasis on different approaches of data evaluation.

2.1 Deconvolution of absorbance spectra

A rather simple and straightforward strategy for the inline PSD analysis of QDs is the use of optical properties such as absorption and emission. This is possible due to the pronounced structure-property relationships of these materials such as—one of the most prominent examples—the size-dependent band gap energy $E_g(x)$. As exemplarily depicted in **Fig. 1** for Cd-based materials, both absorbance and emission can be tuned over a wide wavelength range by adjusting the particle size (Yu W.W. et al., 2003).

Knowledge of $E_g(x)$ allows correlation of different features of an absorbance spectrum such as i) wavelength of the absorption onset, ii) wavelength of the absorption maximum of the first peak or iii) point of inflexion with discrete particle diameters. This leads to a rough estimation of the particle sizes present in a sample. However, although QD size distributions are narrow, often with RSDs below 0.1 or even below 0.05, Mićić et al. pointed out more than 20 years ago that already small polydispersity

Fig. 1 UV/Vis and PL spectra of CdTe, CdSe and CdS nanocrystal samples. A typical TEM image of CdTe is shown in the upper right corner. Reprinted with permission from Yu et al., “Experimental Determination of the Extinction Coefficient of CdTe, CdSe, and CdS Nanocrystals” *Chem. Mater.* 2003 15(14), p. 2854–2860. Copyright 2003 American Chemical Society.

values of 0.1 noticeably affect the emission properties (Mićić O.I. et al., 1997). For instance, emission line width strongly depends on which particle sizes in a sample are excited. As can be seen from **Fig. 2**, if the excitation energy at 10 K is small, only electrons in large particles are excited and a small band width is monitored. If the excitation energy is gradually increased by using smaller wavelengths (spectra a–e), the emission blue shifts to larger photon energies and becomes broader. If a larger excitation energy (spectrum f) is used that is shifted to the blue end of the first absorption peak of the QD ensemble, a large fraction of all QDs in the sample is excited. Therefore, the global emission is substantially broader due to polydispersity.

With respect to applications such as displays, it is obvious that a narrow emission is required and that the development of synthesis protocols and theoretical models to decrease polydispersity has been strongly in the focus of interest (Embden J.V. et al., 2009; Rogach A.L. et al., 2002). However, on the one hand standard techniques for the derivation of PSDs such as DLS and TEM are not convincing with respect to size resolution and measurement time, whereas on the other hand, advanced techniques such as SAXS or AUC are either not directly available or are only suitable for offline analysis. Therefore, several approaches were developed to deconvolute the absorbance data of quantum-confined semiconductor nanoparticles with a direct band gap to PSDs. Although

Fig. 2 PL spectra at 10 K for an ensemble of InP quantum dots with a mean diameter of 3.2 nm for different excitation energies. The first absorption peak of the QD ensemble is at 2.17 eV, so that the PL curves a–e result from excitation (1.895–2.070 eV) in the red tail of the onset region of the absorption spectrum and are fluorescence-line-narrowing (FLN) spectra; curve f is a global PL spectrum since its excitation was at 2.14 eV and is well into the blue end of the first absorption peak. Reprinted with permission from Mićić et al., “Size-Dependent Spectroscopy of InP Quantum Dots” *J. Phys. Chem. B* 1997 101(25), p. 4904–4912. Copyright 1997 American Chemical Society.

possibly not as accurate as SAXS, FFF and/or AUC, UV/Vis absorbance spectroscopy is a standard technology that is widely available and suitable for fast inline analysis (~ ms).

At this point it needs to be mentioned that photoluminescence (PL) spectroscopy is sometimes applied as well to get an impression of the dispersity of a sample (Peng X. et al., 1998). However, as already mentioned by the authors of this work, the assumptions of (i) a δ -function emission and (ii) a size-independent emission intensity lead to an overestimation of the width of the reported PSDs. Moreover, as later pointed out by Viswanatha and Sarma, the PL approach is restricted to fully passivated samples and thus would, e.g. fail in the case of ZnO QDs that do not show a band edge tuning (Viswanatha R. and Sarma D.D., 2006).

Therefore in the following text, only approaches based on absorbance analysis will be discussed (Mićić O.I. et al., 1994; Pesika N.S. et al., 2003a; Pesika N.S. et al., 2003b; Segets D. et al., 2009; Segets D. et al., 2012; Viswanatha R. and Sarma D.D., 2006). Despite differences in the exact deconvolution procedure, they all use the same basic assumptions and restrictions, namely

- semiconductor nanoparticles with a direct band gap which are small enough that the scattering contribution to the total extinction is negligible and quantum confinement occurs,
- a monotone dependency between particle size and

Fig. 3 Sketch of the correlation between polydispersity in particle size and absorbance that is finally accessible by UV/Vis/NIR analysis (Segets D. and Peukert W., 2014).

band gap energy,

- iii) a linear superposition of the individual contributions of the different particle size fractions as illustrated in **Fig. 3**.

Within a polydisperse sample of quantum-confined particles, every size fraction has its specific absorption spectrum. According to the relative abundance of the differently sized QDs in the macroscopic sample, the global absorption is created. The challenge is to deduce from an absorbance measurement the size of the underlying species together with their relative abundance and therefrom to create a PSD.

Approach 1: Least squares fit and pre-assumption of PSD shape

Mićić et al. were the first who derived PSDs from absorbance data. In doing so, they already followed a highly innovative two-step approach (Mićić O.I. et al., 1994). First, they synthesized rather polydisperse InP QDs and determined the underlying PSD by HRTEM. Then, they derived by a fit to experimental data (Palik E.D., 1985) an analytical equation for the absorption coefficient α as a function of energy $h\nu$ (or wavelength, respectively) and band gap E_g . The latter included the particle size x (or strictly the particle radius $r = x/2$) and two fitting parameters n and p :

$$\alpha = f[h\nu, E_g(r, n, p)] \quad (2)$$

Now assuming a PSD following the frequently observed shape of a lognormal distribution, a least squares fit was performed to find a PSD that gives a best match with the measured absorbance data (**Fig. 4**, dataset a). Noteworthy is that after having calibrated parameters n and p , they were kept constant throughout all further PSD calculations that matched the expectations well (**Fig. 4**, datasets b and c) (Mićić O.I. et al., 1994).

Disadvantages are the limited number of particles that were evaluated for the calibration PSD, the missing validation of $E_g(x)$ against literature data and the predefined shape of the PSD. However, the first two points can be clearly attributed to the time when the study was performed. In the early 90s, TEM capabilities were much lower than nowadays and reference data did not yet exist

Fig. 4 Experimental absorption spectra (circles) for InP QD colloids with fit to model shown as a solid line: (a) fit made to yield the dependence of QD band gap on QD size; (b and c) fit made to yield the size distribution from the results of (a). Reprinted with permission from Mićić et al., “Synthesis and Characterization of InP Quantum Dots” *J. Phys. Chem.* 1994 98(19), p. 4966–4969. Copyright 1994 American Chemical Society.

as QDs and related research had just started to come into being. Thus, the work is pioneering in a way that it not only allows the calculation of non-symmetric lognormal PSDs, but even offers the possibility to derive $E_g(x)$ as a material property.

More than a decade later, Viswanatha and Sarma confirmed the applicability of this concept to other material systems by generalizing it to experimental data of ZnO, ZnS and CdSe QDs (Viswanatha R. and Sarma D.D., 2006). In contrast to the earlier work of Mićić, they used Gaussian instead of lognormal distributions and did not calibrate $E_g(x)$ but used fundamental literature data. For instance, in the case of ZnO, a carefully validated tight-binding model (TBM) was applied (Viswanatha R. et al., 2004). Moreover, they proved the assumption of the parallel-shifted bulk absorption spectrum to higher energies for decreasing particle sizes. Therefore they compared the results of the original approach to the outcome when a simple 0-1 step function was used for the shape of the absorption coefficient α . It was found that the difference in the calculated PSDs was negligible. Finally, the apparent width of the experimental and simulated absorbance data of various material systems (ZnO, ZnS(e), CdS(e), GaAs, InAs, InP) on a particle size scale (Δd_{app}) was compared to the true widths of the underlying PSDs (ΔD_{actual}). A material-independent, empiric relationship was thereby identified that allows a quick estimate of a sample's polydispersity from Δd_{app} . In addition to the absorption data, only knowledge of $E_g(x)$ is required:

$$\Delta D_{actual} = -0.0025 \times \frac{\Delta d_{app}^2}{nm} + 0.524 \times \Delta d_{app} - 1.41 nm \quad (3)$$

However, for both approaches, the aforementioned is-

sue of a predefined shape of the underlying PSD remains. Therefore, in the following sections, two alternatives that are able to access multimodal distributions without any assumptions on the PSD shape(s) will be discussed.

Approach 2: Wavelength-based deconvolution for arbitrary shaped PSDs

In 2003, the first concept of deriving arbitrary shaped PSDs from absorbance data was developed by Pesika et al. (Pesika N.S. et al., 2003a; Pesika N.S. et al., 2003b). Although the first report of their method was rather restricted to ZnO QDs, they summarized the procedure in the same year again with a more general point of view.

Based on absorbance data of a (0001) ZnO single crystal (**Fig. 5**), they came up with a comparatively simple but useful assumption, namely that in the case of a direct band gap semiconductor, the absorption coefficient α in the vicinity of the onset is given by (Pesika N.S. et al., 2003a; Pesika N.S. et al., 2003b):

$$\alpha = \frac{C(h\nu - E_g^{\text{bulk}})^{1/2}}{h\nu} \quad (4)$$

C is a constant, $h\nu$ is the photon energy and E_g^{bulk} is the bulk band gap.

Using an effective mass model according to Brus (Brus L., 1986) for the correlation between band gap energy and particle size and further assuming spherical particles and a size-independent absorption coefficient, the following connection between absorbance A , particle size x and relative abundance n was derived (Pesika N.S. et al.,

2003a; Pesika N.S. et al., 2003b):

$$A(x) \propto \int_x^\infty \frac{\pi}{6} x^3 n(x) dx \quad (5)$$

From **Eq. 5** it becomes clear that (i) the absorbance of QDs is a volume signal that (ii) can be used to calculate the relative abundance of distinct sizes from the local slope of the absorbance spectrum (boundary condition: $n(x) = 0$ for $x \rightarrow \infty$):

$$n(x) \propto -\frac{\frac{dA}{dx}}{\frac{\pi}{6} x^3} \quad (6)$$

As becomes clear from **Fig. 6**, validation of the calculation results revealed an excellent agreement with the size distributions determined by TEM. However, in contrast to the formerly discussed approaches, even bimodal distributions of arbitrary shape could be derived without any input parameters. This was proven by the evaluation of absorbance data of mixed suspensions containing controlled amounts of small and large particles. A nearly perfect match was found when the results from the bimodal absorbance spectrum were compared to the expected distributions obtained from the individually evaluated absorbance data of small and large particles. Another advantage of the technique is its comparatively simple implementation as only a correlation for the size-dependent band gap energy $E_g(x)$ and the local slope of the absorbance spectrum are required. The only drawback, how-

Fig. 5 (a) Absorbance spectrum for a (0001) ZnO single crystal and (b) absorbance spectrum for a suspension of ZnO quantum particles after 2 h of growth at 65 °C. The inset shows the spectrum for the ZnO single crystal plotted as $(Ah\nu)^2$ versus $h\nu$. Reprinted with permission from Pesika et al., “Relationship between Absorbance Spectra and Particle Size Distributions for Quantum-Sized Nanocrystals” *J. Phys. Chem. B* 2003 107(38), p. 10412–10415. Copyright 2003 American Chemical Society.

Fig. 6 Distribution results of ZnO QDs after 2 h of growth at 65 °C. The histogram was obtained from analysis of high-resolution transmission electron microscope images of 125 particles. The solid line was obtained from the absorbance spectrum. Reprinted with permission from Pesika et al., “Relationship between Absorbance Spectra and Particle Size Distributions for Quantum-Sized Nanocrystals” *J. Phys. Chem. B* 2003 107(38), p. 10412–10415. Copyright 2003 American Chemical Society.

ever, is the strong assumption of a step function for the absorbance of monodisperse particles. Simply trying to make a reconstruction of the original absorbance spectrum by using a known $n(x)$ and applying Eq. 5, the minimum observed after the first absorbance peak is never obtained—especially in the case of smaller nanoparticles.

To address this issue, Segets et al. developed a more flexible approach with respect to the shape evolution of the shifted absorption coefficient (Segets D. et al., 2009; Segets D. et al., 2012). Instead of using a step function, the bulk absorption coefficient was used as an assumption for the shape of the monodisperse QD absorption evolution. The size dependency was simply addressed by a parallel shift of the bulk absorption to smaller wavelengths according to $E_g(x)$. Regarding the deconvolution of a measured absorbance spectrum $A(\lambda)$ into partial spectra $A_i'(\lambda)$, each of these assumed to have the form of the bulk absorption $\alpha(\lambda)$, the algorithm is realized as follows (Segets D. et al., 2009; Segets D. et al., 2012):

(i) First, the bulk absorption α is parallel-shifted in a way that its peak position matches the largest wavelength under consideration (λ_i). The particle diameter that is related to this specific wavelength needs to be derived either from quantum mechanics or from a separate calibration by matching calculated PSDs^{calc} against PSDs^{TEM}, as suggested by Mićić et al. In the following text, this shifted absorption coefficient will be denoted as $\alpha_{\text{shift},i}(\lambda)$.

(ii) Then, $\alpha_{\text{shift},i}(\lambda)$ is scaled in a way that it coincides with the measurement value $A(\lambda_i)$:

$$A_i'(\lambda) = \frac{\alpha_{\text{shift},i}(\lambda)}{\alpha_{\text{shift},i}(\lambda_i)} \times A_i(\lambda_i) \quad (7)$$

This leads to the first partial absorbance spectrum that exactly matches the measurement value at position λ_i .

(iii) Dividing $A_i'(\lambda_i)$ by the value of the shifted absorption coefficient at this wavelength ($\alpha_{\text{shift},i}(\lambda_i)$), the particle size interval $\Delta x = x_{i+1} - x_i$ under consideration and the optical path length d_c , the first value of a size distribution that is still related to the total mass of solid QD material is obtained (Segets D. et al., 2009). Worthy of note is that x_{i+1} is the particle size which is linked with the next smaller wavelength analyzed. Thus, Δx_i depends on the measurement settings.

(iv) Then, the absorbance contribution of this known, largest particle size fraction is subtracted from the measurement spectrum according to:

$$A(\lambda) = A(\lambda) - A_i'(\lambda) \quad (8)$$

Thus, a new spectrum is created and steps (i–iv) are repeated until all relevant wavelengths are analyzed.

(v) Finally, the concentration-related distribution is converted to a PSD that fulfills the requirement of a nor-

Fig. 7 Comparison between the calculated PSDs, DLS and optical image analysis of two different samples of b) small and d) large ZnO QDs and the related measured (black solid line) and reconstructed (blue and red solid lines) absorbance spectra for a) smaller and c) larger-sized samples. Reprinted with permission from Segets et al., “Analysis of Optical Absorbance Spectra for the Determination of ZnO Nanoparticle Size Distribution, Solubility, and Surface Energy” ACS Nano 2009 3(7), p. 1703–1710. Copyright 2009 American Chemical Society.

malized density distribution:

$$\sum_{x_{\min}}^{x_{\max}} [q_3(x) \cdot \Delta x] = 1 \quad (9)$$

As already expected from the analysis of Viswanatha and Sarma (Viswanatha R. and Sarma D.D., 2006) using Gaussian distributions, the final results are not strongly affected by the assumed shape of the parallel-shifted bulk absorption (Segets D. et al., 2012) also in the case of arbitrary PSDs. To illustrate this, **Fig. 7** shows the deconvolution results of absorbance data derived for small (a, b) and large (c, d) ZnO QDs using two different datasets for the bulk absorption coefficient (Bergström L. et al., 1996; Yoshikawa H. and Adachi S., 1997). For validation, TEM and DLS results are presented as well.

It becomes clear that while the calculated PSDs are not affected by the dataset used for the absorption coefficient, the reconstructed absorbance measurements do depend on the optical properties chosen. Noteworthy is that the shifted bulk absorption is not yet expected to be the correct absorption evolution of monodisperse QDs. However, as soon as discrete optical properties are accessible, for instance via AUC analysis, they are easily implemented to the existing code. A proof of the correct optical properties would be obtained as soon as not only the forward calculation of a PSD^{calc} is done correctly, but when also

Fig. 8 a) Absorbance spectrum of the bimodal PSD after mixing the two suspensions in the same volume ratio (black line) and its corresponding reconstructions (blue and red lines); b) bimodal PSD calculated from the bimodal absorbance spectrum with the bulk properties from Bergström and Yoshikawa (blue and red lines), expected bimodal PSD calculated from the PSDs of the pure unmixed suspensions (green dotted line), and bimodal PSD measured with DLS (black line). Reprinted with permission from Segets et al., “Analysis of Optical Absorbance Spectra for the Determination of ZnO Nanoparticle Size Distribution, Solubility, and Surface Energy” ACS Nano 2009 3(7), p. 1703–1710. Copyright 2009 American Chemical Society.

the reconstructed absorbance spectrum based on PSD^{calc} matches the measurement data. As already discussed, the analysis of bimodal distributions without any input parameters is possible as well using this approach. This is summarized in **Fig. 8**.

Additionally, in a subsequent work, the original idea of Mićić to derive $E_g(x)$ by careful calibration was picked up again (Segets D. et al., 2012). A study on PbS(e) was performed to demonstrate the general applicability of the method originally developed for ZnO by means of a completely different QD system. In addition, in the case of PbS(e) QDs that were chosen for this study, well-established and properly validated literature data on $E_g(x)$ is available. Small and large particles were synthesized and aberration-corrected TEM micrographs were analyzed by semi-automatized image analysis. In parallel, a power law with three empiric parameters a [nm], b [–] and c [nm] was used for description of the size-dependent band gap energy $\Delta E_i(x_i)$:

$$x_i = a \left(\frac{\Delta E_i}{eV} \right)^b + c \quad (10)$$

Finally, a , b and c were modified until a best match was obtained between $PSDs^{calc}$ derived by the algorithm and $PSDs^{TEM}$ derived by image analysis. It was found to be preferable to analyze two samples covering two different particle size regimes in order to arrive at compromise values for a , b and c . This leads to a function of $E_g(x)$ which is valid over a wide size range. The results are shown in **Fig. 9**.

Fig. 9 Relationship between fundamental band gap energy and particle size as derived in this work along with comparison to literature data for a) PbS (Borrelli N.F. and Smith D.W., 1994; Cademartiri L. et al., 2006; Kane R.S. et al., 1996; Moreels I. et al., 2009) and b) PbSe (Dai Q. et al., 2009; Koole R. et al., 2008; Lipovskii A. et al., 1997; Liu Y. et al., 2010; Ma W. et al., 2011; Moreels I. et al., 2007; Pietryga J.M. et al., 2004; Sashchiuk A. et al., 2001; Steckel J.S. et al., 2003) as indicated. Reprinted with permission from Segets et al., “Determination of the Quantum Dot Band Gap Dependence on Particle Size from Optical Absorbance and Transmission Electron Microscopy Measurements” ACS Nano 2012 6(10), p. 9021–9032. Copyright 2012 American Chemical Society.

It becomes clear that an excellent agreement exists with literature data collected over the past decades. This confirms the large potential of QD absorbance data analysis. Thus, the usefulness of PSD calculation from absorbance measurements by various approaches with all of them having their specific advantages and disadvantages is sufficiently proven. Future directions are seen in the combination of different characterization methods (e.g. SAXS, FFF, AUC and UV/Vis analysis) to increase accuracy and resolution even further.

Especially the latter is somewhat limited by the absorbance approach as i) information on small particles might be hidden in the tail of absorbance spectra of larger sizes and as ii) the resolution is somewhat limited by the requirement of a noticeable change of $E_g(x)$ for two different particle diameters. Therefore, AUC that provides a maximum knowledge gain with respect to a PSD with sub-nm resolution, composition and surface chemistry becomes one of the most important techniques for QD characterization (Carney R.P. et al., 2011; Lees E.E. et al., 2008). In combination with in-situ techniques such as UV/Vis or SAXS, it is expected to provide new, mechanistic insights of QD formation with unrivaled accuracy.

3. Application to classification

At this stage, some fundamental conclusions with respect to colloidal interactions are possible. This is demonstrated by applying the method to classification on a sub-10 nm scale. Worthy of note is that various approaches

Fig. 10 Illustration of the experimental procedure of SSP. With kind permission from Springer Science+Business Media: Segets et al., “Quantitative evaluation of size selective precipitation of Mn-doped ZnS quantum dots by size distributions calculated from UV/Vis absorbance spectra” J. Nanopart. Res. 2013 15:1486, Scheme 1.

for nanoparticle classification and purification exist that are already described in excellent review papers (Kowalczyk B. et al., 2011; Mori Y., 2015; Sapsford K.E. et al., 2011). However, for QDs, size selective precipitation (SSP)—which is the preferred flocculation of larger particles in a non-solvent—is still the most important post-processing strategy.

In the following sections, first the working principle of SSP will be introduced. It will be discussed how SSP can be described theoretically based on results obtained from careful PSD and mass balance analysis. Finally, things are set into perspective by an outlook that shows how classification by SSP is linked to Hansen solubility parameters (HSP) which in turn give access to the Flory-Huggins interaction parameter χ . Knowledge of χ is decisive for derivation of the osmotic interactions between the ligand shells around QDs and thus represents an important parameter in the context of steric stabilization.

3.1 Size selective precipitation

The working principle of SSP first reported by the groups of Murray and Weller is as rational as it is simple (Murray C.B. et al., 1993; Vossmeier T. et al., 1994). Starting from QDs dispersed in a good solvent, a non-solvent is added that induces the preferred, reversible flocculation of larger particles.

In the case of nanoparticles with polar surface termination, a non-solvent would be something non-polar such as toluene or heptane, in the case of nanoparticles with hydrophobic surface properties, a non-solvent would be hydrophilic, e.g. ethanol or acetone. Due to the fact that the flocculates are in the size range of μm to mm , a solid-liquid separation by centrifugation in a typical lab centrifuge with up to $\sim 10\,000\text{ g}$ is sufficient to separate the flocculated larger particles from small QDs in the supernatant. As illustrated in **Fig. 10**, the process can be repeated in several cycles and even redispersion of the QDs on a primary particle level after centrifugation is possible. In the

past it was demonstrated in various works that SSP is a highly efficient procedure that is able to substantially narrow PSDs and improve the emission properties of a sample (Komada S. et al., 2012; Nag A. et al., 2007). For instance, Mastronardi et al. subdivided a starting suspension of Si nanoparticles into the impressive amount of 14 differently sized samples with all of them revealing substantial differences in their optical properties (Mastronardi M.L. et al., 2011).

However, in addition to the final outcome of SSP in terms of samples with small RSD as well as varying absorbance and emission properties, the classification process itself can be analyzed by means of well-known concepts from the field of process engineering and particle technology (Segets D. et al., 2013; Segets D. et al., 2015). This will be briefly summarized in the following section.

Knowing the relative masses of the coarse fraction g ($= m_{\text{recovered}}/m_{\text{in}}$) and the fine fraction f ($= m_{\text{supernatant}}/m_{\text{in}}$) after drying as well as the PSDs of the feed $q_F(x)$, the coarse $q_g(x)$ and the fines $q_f(x)$ from UV/Vis data, the following parameters are accessible (Segets D. et al., 2015):

- (i) The cut size x_i at the intersection between the mass weighted density distribution of the coarse $g \cdot q_g(x)$ and the fines $f \cdot q_f(x)$.
- (ii) The separation efficiency:

$$T(x) = \frac{g q_g(x)}{q_F(x)} \quad (11)$$

- (iii) The separation sharpness κ to characterize the steepness of the cut with $x_{25,t}$ and $x_{75,t}$ being the particle sizes at which $T(x)$ is 0.25 or 0.75, respectively:

$$\kappa = \frac{x_{25,t}}{x_{75,t}} \quad (12)$$

- (iv) The yields for coarse η_g and fines η_f to evaluate the efficiency of the process:

$$\eta_g = \frac{\int_{x_t}^{x_{\max}} [g q_g(x) dx]}{\int_{x_t}^{x_{\max}} [q_F(x) dx]} \quad (13)$$

$$\eta_f = \frac{\int_{x_{\min}}^{x_t} [f q_f(x) dx]}{\int_{x_{\min}}^{x_t} [q_F(x) dx]} \quad (14)$$

For more details the reader is referred to the literature (Leschonski K., 1977; Leschonski K. et al., 1974; Rhodes M.J., 1999; Rumpf H., 1990), however, two important aspects shall be stressed here: the intrinsic inclusion of the mass balance in $T(x)$ (note that $f + g = 1$ and $f q_f(x) + g q_g(x) = 1$) and its independency of the quantity (number, area, volume/mass) based on which the PSD is derived. Thus, $T(x)$ is a perfect measure for the classification process whereas RSD is a perfect measure for the classification result in terms of the derived product PSD.

Using **Eqs. 11–14** and performing classification studies on ZnS QDs with different feed distributions and various good solvent/poor solvent combinations, Segets et al. found the following analytical description of SSP that can be understood as a law of mass action (Segets D. et al., 2015) with dissociation constant K_{diss} :

$$K_{\text{diss},i}(x_i) = \frac{f q_f(x_i)}{g q_g(x_i)} = \frac{q_F(x_i) - g q_g(x_i)}{g q_g(x_i)} = \frac{1 - T(x_i)}{T(x_i)} \quad (15)$$

Thus, the cut of an SSP experiment neither depends on the feed PSD nor on process parameters such as stirring, time of poor solvent exposure or dosing. Even the solids concentration of the feed does not have any influence as long as it does not clearly exceed a comparatively high, critical upper limit (e.g. $\gg 10 \text{ g L}^{-1}$ in the case of ZnS). SSP is determined in terms of the steepness and position of the cut by the chemical structure of the good and the poor solvent as well as their volume ratio. Comparing the effect of different solvents, the relative permittivity of the final mixture—which is of major importance for the van der Waals interaction—is not the sole influencing factor on SSP. In fact, the specific chemistry of the applied solvents and their interaction with the stabilizing ligands adsorbed at the QD surface are significant as well. This represents the connection between classification results, solubility parameters and steric stabilization and will be described in the following section.

3.2 Link to Flory-Huggins interaction parameter

It was found that the best way of data representation is to plot the QD dispersibility of a specific size fraction in a 3-dimensional Hansen space normalized to the Hamaker constant of the core material in the solvent mixture

(Segets D. et al., 2015). Further, it turned out that the HSP of decorated nanoparticles which are understood as the ensemble of QD core plus ligand shell need to be clearly distinguished from the HSP of the unbound, free ligands on a molecular level. The balance of van der Waals attraction and HSP is in agreement with works of the groups of Korgel and Roberts. They reported that in the case of SSP, a steric repulsive force comprised of an elastic and an osmotic interaction due to solvation of the ligand tail by the solvent—the latter being related to solubility parameters—needs to be balanced vs. van der Waals adhesion (Kitchens C.L. et al., 2003; Saunders S.R. and Roberts C.B., 2009; Shah P.S. et al., 2002a; Shah P.S. et al., 2002b; Vincent B. et al., 1986). As recently pointed out by Mori (Mori Y., 2015), this can be extended by electrostatic and Born repulsion, possibly entropic effects such as depletion might need to be considered as well (Mao Y. et al., 1995). However, in line with the findings of Segets et al. (Segets D. et al., 2015), especially the study of Mori revealed that van der Waals adhesion and osmotic interaction are the main contributors to the total interaction.

Analyzing the osmotic term in more detail, two quantities are decisive: the volume fraction of the ligand ϕ and the Flory-Huggins interaction parameter χ_{12} (with index 1 referring to the solvent and index 2 referring to the ligand). Whereas the former can be estimated by the surface coverage or is directly accessible via AUC or small-angle neutron scattering (SANS) (Whitell G.V. and Kitchens C.L., 2010), the latter is even more challenging. It relates to the Hildebrand solubility parameter δ_i (or the cohesive energy density $c_i = \delta_i^2$):

$$\chi_{12} = \frac{V_m}{RT} (\delta_1 - \delta_2)^2 \quad (16)$$

With V_m being the molar volume, R being the ideal gas constant and T being the temperature.

Hansen subdivided the energy of cohesion into a polar contribution δ_p , a disperse contribution δ_d and the ability to exchange electrons δ_h according to the concept of Lewis acids and bases (Hansen C.M., Hansen C.M. and Skaarup K.J., 1967). **Eq. 16** can be rewritten as (Hansen C.M., 2007):

$$\chi_{12} = \frac{V_m}{RT} \left[(\delta_{d2} - \delta_{d1})^2 + 0.25(\delta_{p2} - \delta_{p1})^2 + 0.25(\delta_{h2} - \delta_{h1})^2 \right] \quad (17)$$

Thus, once having access to the HSP of small nanoparticles, χ_{12} can be derived. Together with additional knowledge of the surface coverage, the osmotic interaction potential is accessible and steric effects can be balanced vs. van der Waals adhesion.

By the careful analysis of PSDs established from absorbance spectra, the principal applicability of HSP to QDs

could already be demonstrated (Segets D. et al., 2015). Now suitable measurement techniques for HSP, for instance by using analytical centrifugation in the liquid phase (Lerche D. and Sobisch T., 2014), need to be established and validated against numeric data like it was already done in the case of polymers (Díaz I. et al., 2013) or gas-phase results, e.g. obtained by inverse gas chromatography (Liu Y. and Shi B., 2008). Thus, the careful evaluation of QD dispersity not only gives important insights into the classification process itself but can even make an important contribution to a better understanding of the steric stabilization of small colloids.

4. Conclusion and perspectives

Different methods for analyzing the particle size distribution (PSD) of quantum dots (QD) were discussed. In addition to standard techniques such as high-resolution (HR) transmission electron microscopy (TEM) and dynamic light scattering (DLS) as well as advanced techniques such as small-angle X-ray scattering (SAXS), Field-Flow Fractionation (FFF) and analytical ultracentrifugation (AUC), the focus was put on the conversion of absorbance spectra to PSDs. In this context four approaches were presented, with two of them (according to Mičić et al. and Viswanatha et al.) using predefined PSD shapes (lognormal and Gaussian) and two of them (according to Pesika et al. and Segets et al.) using a step-wise deconvolution approach. The two latter are seen to be preferred whenever the shape of the target PSD is not known. The technique of Pesika et al. uses the local slope of the absorbance spectrum. The approach of Segets et al. uses a shifted bulk absorption coefficient that brings the possibility to include the optical properties of discrete QD size fractions as soon as they are available. Worthy of note is that data of such monodisperse fractions is becoming more and more available, e.g. by using AUC equipped with multiwavelength (MWL) detection.

In the last part of this work, a clear perspective of exactly why precise PSD characterization on an Ångström level matters was presented. A colloidal classification technique that is widely applied in the field of QDs, the so-called size selective precipitation (SSP) was introduced. It is based on the precise tailoring of steric interactions vs. van der Waals adhesion and can be evaluated with established routines from the field of process engineering and particle technology. SSP is not only described well by the separation efficiency $T(x)$ following a law of mass action, but classification results can be illustrated in a 3D Hansen space normalized to van der Waals attraction.

Based on this finding, knowledge on PSDs potentially allows the determination of Hansen solubility parameters (HSP). The latter give access to the osmotic interaction

potential originating from the ligand shells adsorbed at the QD surface and thus lead to a better description of steric stabilization. This is of major importance not only with respect to tailored classification processes but also with respect to formulation issues.

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Nomenclature

Abbreviations

AC	analytical centrifugation
AsFIFFF	asymmetric flow field-flow fractionation
AUC	analytical ultracentrifugation
A4F	asymmetric flow field-flow fractionation
DLS	dynamic light scattering
EMA	effective mass approximation
FFF	field-flow fractionation
FLN	fluorescence line narrowing
HR	high resolution
HSP	Hansen solubility parameters

MWL	multiwavelength
PL	photoluminescence
PSD	particle size distribution
QD	quantum dot
RSD	relative standard deviation
SANS	small angle neutron scattering
SAXS	small angle X-ray scattering
SSP	size selective precipitation
TEM	transmission electron microscopy

Greek Symbols

α	absorption coefficient ($\text{M}^{-1} \text{m}^{-1}$)
$\alpha_{\text{shift},i}(\lambda)$	shifted absorption coefficient ($\text{M}^{-1} \text{m}^{-1}$)
χ	Flory Huggins parameter (–)
ΔD_{actual}	true width of PSD (m)
Δd_{app}	apparent width of absorbance data on a particle size scale (m)
δ_d	disperse contribution to HSP ($(\text{J m}^{-3})^{0.5}$)
δ_h	HSP for ability to exchange electrons ($(\text{J m}^{-3})^{0.5}$)
δ_i	Hildebrand solubility parameter ($(\text{J m}^{-3})^{0.5}$)
δ_p	polar contribution to HSP ($(\text{J m}^{-3})^{0.5}$)
ϕ	volume fraction of ligand (–)
σ	standard deviation (m)
η	dynamic viscosity (Pa s)
η_f	yield of fines (–)
η_g	yield of coarse (–)
κ	separation sharpness (–)
λ	wavelength (m)

Latin Symbols

A	absorbance (–)
$A(\lambda)$	measured absorbance (–)
$A_i'(\lambda)$	partial absorbance (–)
a	empiric parameter (m)
b	empiric parameter (–)
c	empiric parameter (m)
C	constant ($\text{eV}^{0.5} \text{m}^{-1}$)
c_i	cohesive energy density (J m^{-3})
D	diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
d_c	optical path length (m)
E_g	band gap energy (eV)
f	relative mass of fine fraction (–)
g	relative mass of coarse fraction (–)
$h\nu$	energy (J)
K_{diss}	dissociation constant (–)
m	mass (kg)
n	fitting parameter (–)
$n(x)$	relative abundance (–)
p	fitting parameter (–)
q_3	volume density (m^{-1})
R	ideal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
r	particle radius (m)
T	temperature (K)
$T(x)$	separation efficiency (–)
V_m	molar volume ($\text{m}^3 \text{mol}^{-1}$)
x	particle diameter (m)
x_h	hydrodynamic particle diameter (m)
x_t	cut size (m)

Author's short biography

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Dr. Segets is currently affiliated at the Institute of Particle Technology of the Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU). She received her PhD in 2013 and her research interests include the characterization and tailoring of technically relevant colloidal interfaces, the development of new concepts for process engineering and the scale-up of colloidal nanoparticles, micro reaction technology and high-throughput experimentation (HTE) as well as the application of well-defined nanoparticles for ultra-filtration and chromatography.