

The synthesis and metrology of colloidal semiconductor nanocrystals

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Abstract

Due to their unique electronic and optical properties, as well as their promising application in many modern technologies, the demand for semiconductor nanocrystals has rapidly increased over the past few years. While the synthesis of monodisperse nanoparticles is possible via various methods, each sample still has to be characterized and validated for its use. To assess all features like size, concentration, polydispersity and morphology, most commonly UV/VIS-spectroscopy and transmission electron microscopy (TEM) are combined. TEM is known to be a less accessible and strongly time consuming method. As a possible faster but, in terms of accuracy, equal alternative we explored small angle x-ray scattering (SAXS) as a metrological precision tool. SAXS measures the sample as an ensemble and furthermore provides information towards particle interaction while enabling a direct measurement of dispersions, not requiring an elaborate sample preparation prior to the measurement, and not being restricted to a local focus.

In the beginning the main focus of this study was laid on the development of correlating models between these methods and the complete metrology of any given sample. First measurements were done on the well-known cadmium selenide (CdSe) system. The synthesis of monodisperse semiconductor nanoparticles, including an investigation of different synthesis approaches, utilising various ligands/shells or solvents, constituted the base of the routine within this work. Therefore, the synthesis parameters have been analysed towards their influence on the system via each analysis method. The correlation of the collected data to the most accessible features (size and absorption) is in great accordance with the literature. The processing of further experimental data will yield a comprehensive model function fully characterizing a monomorph sample. Until methods have been developed to distinguish between individual characteristics within the absorbance spectra of a polymorphic sample, SAXS is able to support the identification of each fraction and allow a thorough metrological analysis.

Keywords: Semiconductor nanocrystals, metrology, SAXS, TEM, absorption, correlation models

1. Introduction

Over the past three decades semiconductor nanocrystals have been a great enrichment in the field of nanotechnology due to their special optoelectronic behaviour and are used in a variety of applications such as bioimaging [1], LEDs [2], solar cells [3] and computing [4]. Each field requires monodisperse and monomorph particles, wherefore a thorough characterization is inevitable. To support a quick initial analysis previous works correlated the fast and broadly accessible absorption spectroscopy with the actual size of the sample, visualized by the lesser available and more time consuming TEM. This relation was evaluated by Yu *et al.* [5] assuming a size independent as well as by Jasieniak *et al.* [6] with a size dependent extinction coefficient. Both approaches serve as the main reference in this work.

Nonetheless, the dimensional characterization of semiconductor nanocrystals based on absorption spectroscopy alone is currently lacking in precision since it relies on the mean average of one specific system (synthesis, morphology, solvent, ligands), the polydispersity can only approximately be assumed and fractions of different morphologies may only partially be assigned (i.e. rod structure [7]). Therefore absorption spectroscopy on its own is not sufficient from a metrological point of view until more detailed models are established and traceability is guaranteed to a reference method.

This work suggests SAXS as a high precision reference method and more time efficient TEM alternative, giving information about the size, polydispersity and polymorphology. Absorption spectroscopy could then be used to verify the correlating optical properties and to determine the concentration of the sample. For the better comparison of the obtained data with the references, the used particles were synthesized following the same standardized procedure as given in the literature.

2. Synthesis

The semiconductor nanocrystal synthesis was adapted from the original literature [8] which was cited in both references. Briefly, cadmium diacetate dihydrate, oleic acid and octadecene were mixed and heated to 100 °C for 30 minutes to remove water. Afterwards the solution was heated to 300 °C under nitrogen atmosphere. At this temperature a solution of trioctylphosphine selenide was swiftly injected. The growth temperature was set to 250 °C and any desired particle size was subsequently taken as a function of reaction time.



Figure 1. Colloidal CdSe samples taken from left to right with increasing reaction time.

3. Methods

To obtain data comparable to the literature and equivalent correlating models each sample has been analysed by UV/VIS spectroscopy, TEM, and SAXS.

3.1. UV/VIS spectroscopy

The absorption of each sample reveals all energetic states within the scanned range. The first peak on the lower energy side describes the characteristic semiconductor band gap energy. Assuming different degrees of quantum confinement for different particle sizes, this value will continuously shift between the initial core nucleation and its bulk behaviour. The *half width at half maximum* of this peak hints at the polydispersity of the sample while the optical density can yield an empirical approach to the concentration [5, 6].

3.2. Transmission electron microscopy (TEM)

TEM gives precise information about the actual particle size, polydispersity and morphology.

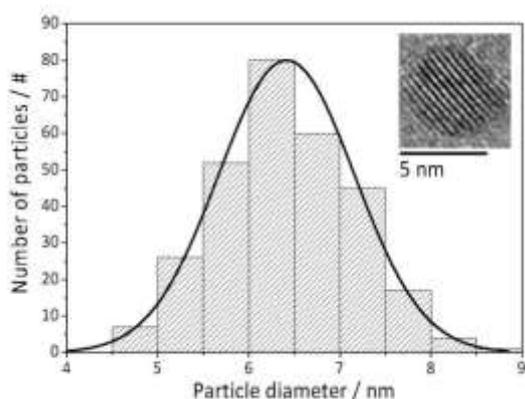


Figure 2. Size distribution of a CdSe sample determined by TEM image analysis. Inlet: TEM picture of a spherical CdSe particle.

3.3. Small angle x-ray scattering (SAXS)

SAXS detects the radiation at very small angles which has been scattered by particles and gives clear indications about their size, polydispersity and morphology. Unlike TEM, SAXS is not limited to a local focus and analyses the ensemble. By indirect Fourier transformation of the scattering curve one obtains the pair distance distribution function (PDDF), which is more accessible to interpret.

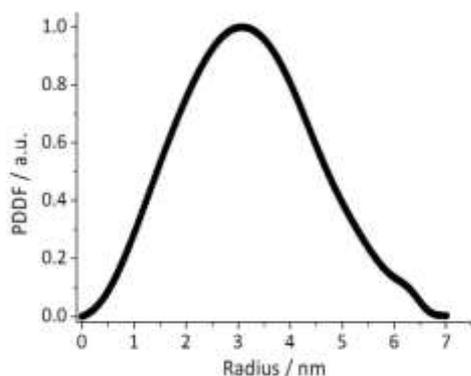


Figure 3. Pair distance distribution function of a CdSe sample.

4. Method correlation

The correlation of all three methods and their comparison to the literature are shown in figure 4.

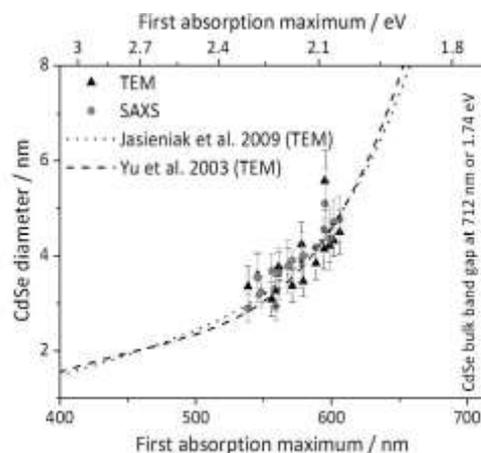


Figure 4. The TEM and SAXS data of this work are plotted against the measured first absorption maxima. As a comparison, both references curves from literature [5, 6], both based on TEM measurements, are shown.

5. Conclusion and outlook

Multiple CdSe particles with varying sizes have been analysed using absorption spectroscopy, TEM and SAXS. The collected data is in great accordance with the literature. Furthermore SAXS has been successfully implemented in the analytical process and provides particles dimensions nearly identical to the TEM analysis. Thus, SAXS can be used as a more time efficient TEM alternative.

Further data will be collected to derive a customized model function and to minimize standard deviations.

Future work will focus on the extension and validation of the correlating model as well as the in depth characterization of the absorption spectra to support the metrology of a sample solely by spectroscopic methods.

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