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Automated synthesis of quantum dot nanocrystals by hot injection: Mixing induced self-focusing

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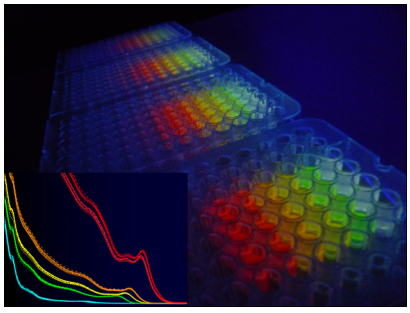
HIGHLIGHTS

- Successful automation of the hot injection synthesis of cadmium selenide as challenging model system.
- Implementation of high-throughput experimentation for nanocrystal synthesis.
- High reproducibility of produced samples with some having nearly identical numbers of building blocks.
- Observation of mixing-induced focusing/defocusing.
- Unique insight to process-structure relationships during quantum dot synthesis.

GRAPHICAL ABSTRACT



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ABSTRACT

The hot injection technique for the synthesis of quantum dots (QDs) is a well-established and widely used method in the lab. However, scale-up rules do not exist. One reason is that in particular the role of process parameters like mixing on particle formation is largely unknown, as systematic examination of the latter is impossible for the laborious and complex manual synthesis. Herein we studied the mixing induced self-focusing of particle size distributions (PSDs) of CdSe QDs using automation in combination with a defined stirrer geometry. Basis for our study is a platform that allows parallelization with inline temperature monitoring, defined injection rate, accurate sampling times as well as controlled stirring. Reproducibility in terms of optical product properties was analyzed by absorption and emission whereas reproducibility in terms of the PSD was verified by deconvolution of UV/Vis absorbance spectra and especially by analytical ultracentrifugation (AUC) complemented by transmission electron microscopy (TEM). In line with previous results, AUC confirmed that even QDs made by hot injection in an automated setup are polydisperse with multimodal size distributions. Finally, reproducibility in combination with early stage sampling and controlled mixing allowed us for the first time to analyze the influence of stirring on focusing and defocusing of PSDs, that has been expressed in terms of the evolution of the relative standard deviation (RSD). Our work paves the way to gain in-depth understanding of often forgotten process-structure relationships of colloidal nanoparticles which eventually is a first step in the direction of the development of scalable synthesis and reliable application of high-quality QDs in technical applications.

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1. Introduction

Although hot injection is a widely used technique for the preparation of quantum confined semiconductor nanoparticles (usually referred to as quantum dots (QDs)), [1] with manifold applications in the fields of energy, [2–4] biology, [5–7] telecommunication, [8,9] and display technology, [10–13] design rules for scalable processes for this complex kind of synthesis do not exist. This originates from an insufficient understanding of the underlying particle formation dynamics in combination with even less knowledge on the role of process parameters that finally prevents the design of appropriate equipment, unit operations and processes. Several aspects can be identified why this is so: (i) ill-defined mixing due to the nearly exclusive use of small-volume standard glassware in combination with magnetic stirrer bars in case of batch reactions, (ii) time consuming synthesis and characterization procedures that hamper the derivation of larger datasets and (iii) the human factor that severely affects reproducibility. Especially if the latter is questionable or cannot be sufficiently assured, it is impossible to discriminate real physico-chemical effects from experimental noise. Finally, (iv) "dispersity" imposes that not only the correct material but the correct material with the required particle size distribution (PSD), shape (distribution), composition and, at least for nanoparticles, surface properties [14,15] needs to be produced. This is leading to an increased degree of complexity as multiple dimensions in terms of feed composition and process parameters have to be addressed [16]. An answer to this multidimensional challenge is the use of automation in a setup that allows a systematic variation of process parameters to clarify e.g. the impact of mixing on the dynamic evolution of dispersity. This is expected to be important for developing future scale up rules.

Automation was successfully implemented in several fields including catalyst development, [17] optimization of paints [18] and polymers [19] as well as biotechnology [20]. However, very few platforms for liquid phase batch synthesis of nanomaterials are available [21]. Most notably, Chan et al. reported a pioneering study where they implemented an automated platform (*Workstation for Automated Nanomaterial Discovery and Analysis*, WANDA) that was used for deriving an optimum chemistry and synthesis temperature for CdSe QDs by hot injection, however still very close to the usually used laboratory approach (synthesis in small glass vials with magnetic stirrer bars).

Although some QD synthesis routes at room temperature in aqueous solution do exist, [22–24] *hot injection* which is focused in here involves the fast addition of a cold precursor (at ~25 °C) to a hot metal-organic precursor (typically at temperatures >225 °C), enabling the separation of nucleation and growth processes [25,26]. Thus, so-called nearly *monodisperse* products with high crystallinity are obtained [27]. However, especially within the first minute, particle growth is fast and optical properties change rapidly. This is challenging with respect to sampling time as well as sampling frequency, especially if several different particle sizes with varied band gaps are required. It is also obvious that the production of such a high-quality product by hot injection requires highly skilled experimentalists due to (i) high temperatures and pronounced temperature gradients, (ii) sensitivity of QD syntheses against smallest changes in feed quality and reactant concentrations, (iii) fast kinetics, (iv) demanding requirements in terms of cleanliness and the (v) additional need to exclude oxygen and humidity.

Herein, we systematically investigate the role of mixing on the self-focusing of the PSD of CdSe QDs. To get rid of any issues with the underlying chemistry, we apply a recipe with optimized temperature that was already found by Chan et al. [21]. To assure reproducibility, we use an automated platform that comprises a liquid handling tool, rack holders for various vials and plates, six feed vessels as well as six stainless steel reactors that can be operated in parallel. In contrast to the usually used comparatively simple magnetic stirrer bars, our setup is operated with triple blade stirrers that allow the adjustment of controlled mixing conditions. First, we confirm reproducible disperse properties of all our samples by deriving PSDs from optical absorbance spectra, [28,29] transmission electron microscopy (TEM) and analytical ultracentrifugation (AUC) [30]. Especially the latter is seen as gold standard for nanoparticle analysis and evidences that PSDs of particles produced in different reactors throughout various synthesis runs are on the one hand multimodal which is in agreement with previous studies, [31–33] but on the other hand also nearly or quasi-identical from one batch to another. Based on the remarkable reproducibility of our system, we could then observe to the best of our knowledge for the first time focusing and defocusing of QD PSDs in dependence of the mixing. In fact, only when a critical stirrer speed (expressed by the impeller Reynolds number) was introduced to the system, the effect of focusing which is a self-narrowing of the PSD due to size-dependent growth, was observed and relative standard deviations (RSDs) below 10 % could be obtained.

Thus, our work sets the frame for future studies where this effect will be investigated in more detail in combination with fundamental mixing studies. It paves the way to an in-depth understanding of the aforementioned process-structure relationships which are indispensable for any kind of scale-up and process design.

2. Material and methods

2.1. Chemicals

Cadmium oxide (CdO) powder 99.999 %, selenium powder ≥99.5 %, tri-octylphosphene (TOP) 97 %, 1-octadecene 90 % for synthesis solvent (ODE) and oleic acid solvent (OA) were purchased from VWR and Sigma Aldrich. All chemicals were only opened and used in inert environment (H_2O below 5 ppm, O_2 below 20 ppm, N_2 atmosphere) without further purification.

2.2. Absorbance spectroscopy

High-Throughput (HT) characterization of all synthesized particles was done by a BioTek© Synergy MX micro titer plate (MTP) reader. It uses a Xenon flash light source for each well of the plate and analyzes absorbance and emission spectra for wavelengths ranging from 200 to 999 nm for absorbance, 300 to 900 nm for emission and 250 to 900 nm for excitation, with a maximum resolution of 1 nm. For all measurements, we used 96 well MTPs made from polystyrene (Rotilabo ®).

2.3. Transmission electron microscopy (TEM)

TEM has been carried out using a Philips CM300 UltraTWIN microscope (FEI Company, Netherlands), having a nominal point resolution of 0.17 nm at Scherzer defocus. The device is equipped with a LaB_6 filament and was operated at an accelerating voltage of 300 kV. Samples have been prepared by drop casting on standard copper TEM grids coated with a continuous amorphous carbon film. Bright-field TEM (BFTEM) images as well as high resolution TEM (HRTEM) images were recorded with a F214 charge coupled device (CCD) camera from TVIPS (Tietz Video and Image Processing Systems, Germany), having an image size of 2048 × 2048 pixels. Images were analyzed and processed using the open-source software ImageJ (version 1.49o).