# Droplet-based multistep synthesis of CdSe-QD with narrow particle size distribution

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## Introduction

The synthesis of CdSe quantum dots (QD) using micro- flow reactors has been described in numerous publications.[1,2] Commonly, the premixed precursors were mixed at room temperature and subsequently treated with temperatures up to 320°C for nucleation, but this temperature exceeds the one for continuing crystallization remarkably. To increase efficiency and size-controllability the crystallization process is performed in microfluidic reactors under laminar flow conditions. Due to the broad laminar flow profile inside a capillary a narrow QD particle size distribution cannot be achieved.

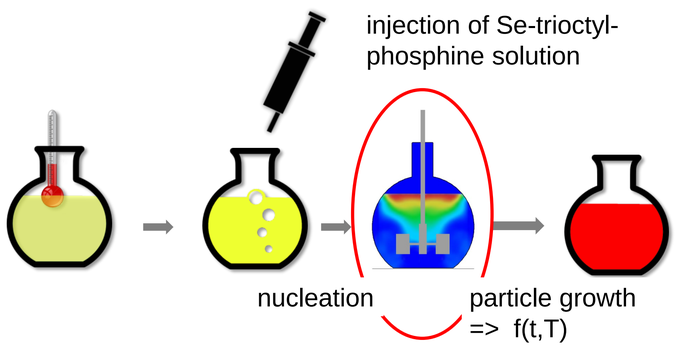
To avoid these drawbacks low concentrated Cd-oleate and Se-trioctylphosphine precursors were preheated up to 320°C and mixed continuously in a flow-through static micro mixer. The nucleation process is subsequently quenched by fast cooling the mixture down to room temperature. With residence times below one second long time-stable seed particle solutions are available (**multi step processing I**). To achieve QDs with a narrow size distribution, this seed crystal solution is injected in continuously flowing droplets of high concentrated Cd/Se precursor solution, and heated on a hotplate up to the crystallization temperature (180°C), which is thermodynamically preferred.. The ratio of seed crystal solution to the precursor solution defines as well as the applied temperature allows a controlled crystal growth (**multi step processing II**).

## Batch synthesis

**Chemicals**

Cd-oleate
Se-trioctylphosphine
Octadecene

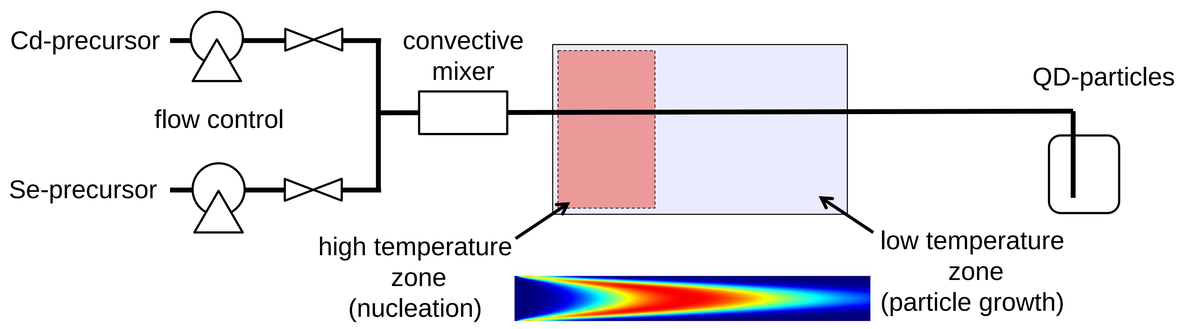
Cd-oleate solution
T > 300°C




**mixing problem !**

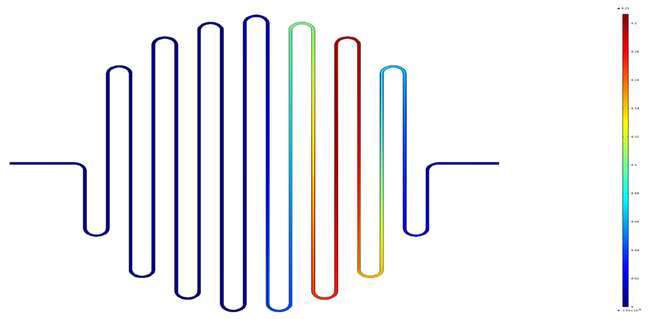
- nucleation faster than mixing
- number of growing particles is constant following the initial nucleation step
- non uniform nuclei leads to larger size distribution of final particles
- non uniform size of resulting nanoparticles
- difficult to reproduce an exact size (particularly smaller nano-crystals)
- purification steps necessary

## Continuous micro flow

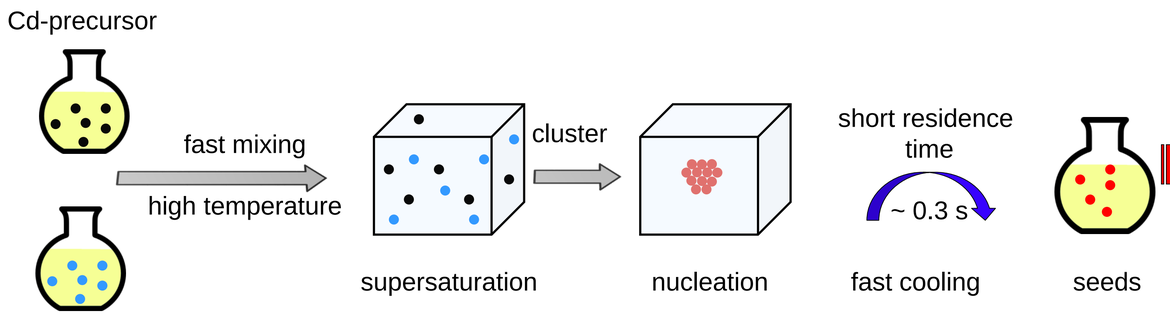


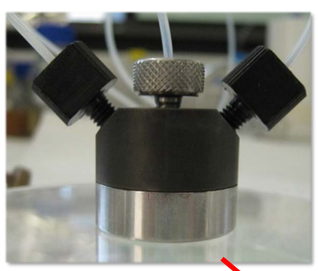

- **Mono-phase flow:**
- mixing problem solved
- large residence time distribution induces broad size distribution

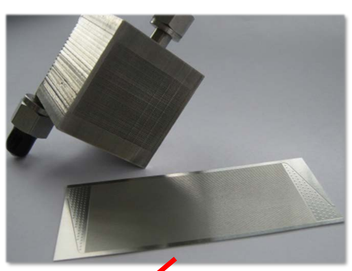
**residence time distribution problem !**

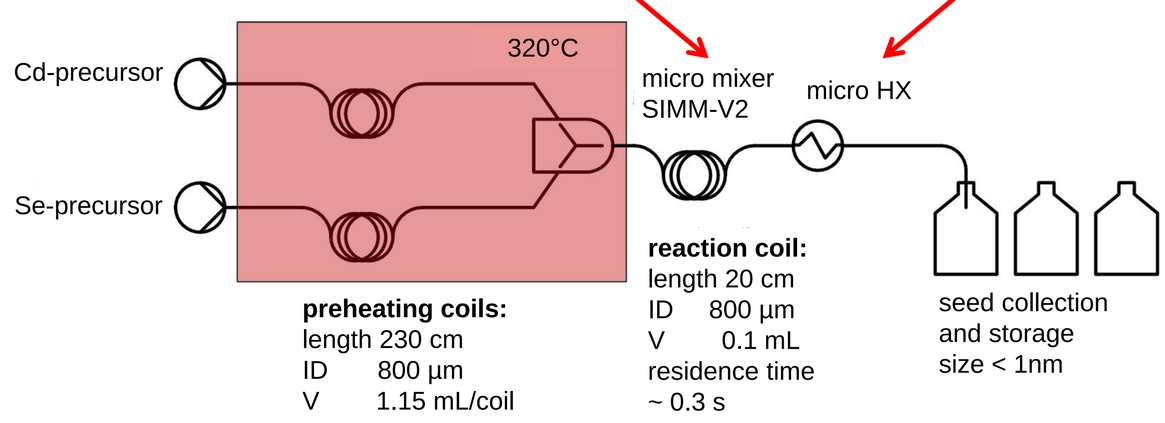


## Multi step processing I: seeds synthesis

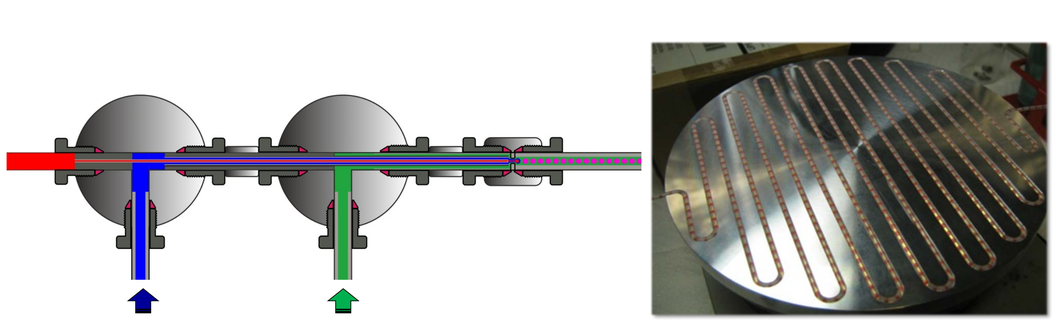


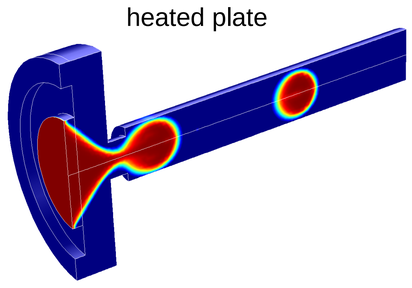







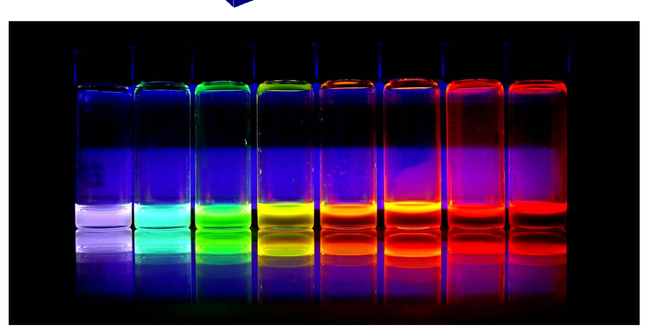

## Multi step processing II: controlled QD-particle synthesis



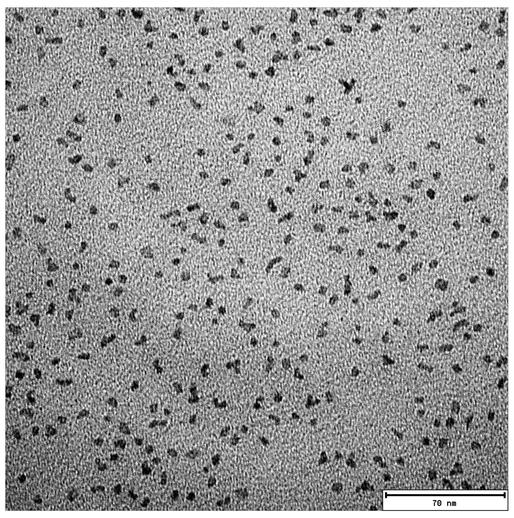
- **Two-phase (droplet) flow** [3,4]
- droplets as isolated rectors
- controlled seed crystal injection
- residence time distribution is determined by drop expansion
- particle size can be adjusted by :

**temperature and residence time**
(It is obvious that the concentration of seeds will have an impact on particle size and size distribution also, but this could not be validated)

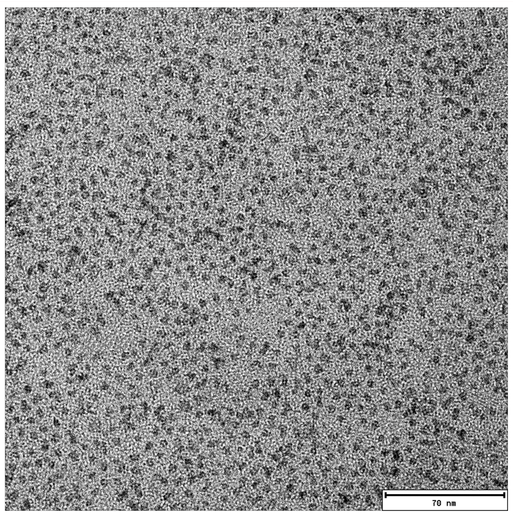


**CdSe-QD's with different sizes synthesized by changing the residence time**

## Preliminary results: TEM-images (without purification)




**Batch process: T ~ 195°C**
**C = 0.01 molL$^{-1}$ (each)**
**t = 30 min**




**Multistep process: T ~ 195°C**
**C = 0.01 molL$^{-1}$ (each)**
**t = 30 min**

## Summary

The separation of seed generation and crystal growth is an advantageous process towards a controlled QD synthesis with narrow mono-modal size distribution. Seeds of CdSe QDs can be prepared in advance and stored without undesired aging in a solid oleate matrix. Adding the seeds to the mixed precursor Cd and Se solution starts the crystal growth at lower temperatures (approx. 195°C) as required for prior seed generation in conventional processes (>300°C) LIT. Also, the performing of QD growth in continuous flowing droplets allows easily to generate different nanoparticle sizes without changing the protocol except the seed concentration or residence time.

## References

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