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Controlling the Nano-particle Size by Manipulating the Diffusion Coefficient of the Solute

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INTRODUCTION

Colloidal semiconductor nanocrystals or quantum dots (QDs) are typically produced via a hot injection synthesis (HIS). For QDs to be implemented in a broad range of applications, a precise control over their size is essential. We show that efficient size tuning at high reaction yield is possible by changing the chain length of the carboxylic acid. By combining an extended experimental

reaction screening with reaction simulations, we demonstrate that this size tuning is due to a change in the diffusion coefficient and the solubility of the solute. The relation between size tuning by the ligand chain length and the coordination of the solute by the ligands is further explored by expanding the study to amines and phosphine oxides.

CARBOXYLIC ACIDS: LONGER CHAIN ACIDS = SMALLER NANOCRYSTALS - NUCLEATION AND GROWTH



- DIFFUSION COEFFICIENT D



→ D of carboxylic acids and CdOA₂ were measured with NMR

- → Correlation between D and #C of the carboxylic acids
- → Size(CdOA₂) ≈ 2. size(OA) and 2. $D_{CdOA2} \approx D_{OA}$



Amount of oleic acid (OAc) \uparrow in an OAc synthesis: \rightarrow Monomer solubility $[M]_0 \uparrow^{(1)}$ $\rightarrow d_{NC}$ and $\sigma_d \uparrow$ Amount of oleic acid (OAc) \uparrow in a DAc synthesis: $\rightarrow d_{NC}$ and $\sigma_d \downarrow$

Changing the ligand chain length affects other parameters, next to the solute solubility, that have an influence on the balance between the nucleation and growth rate.

- AMINE CHAIN LENGTH



- \rightarrow No influence of chain length on QDs
- \rightarrow No influence of amines on diffusion
- coefficient of CdOA₂
- \rightarrow Weak coordination of CdSe QDs by



 \rightarrow Minor effect on d_{_{NC}} and $\sigma_{_{d}}$ for low concentrations.

 λ / nm

 \rightarrow Resembles amines

diffusion coefficient.

 \rightarrow Effect rather due to a change of the

solubility of the monomer and not its





With two different CdSe nanocrystal syntheses, we find that longer chain carboxylic acids result in smaller nanocrystals with improved size dispersions.

3.2

- This size tuning is due to a change in the diffusion coefficient and the solubility of the solute.
- In line with the weak coordination of CdSe nanocrystals by amines, no influence of the chain length on the nanocrystals is found.
- The size tuning brought about by phosphine oxides can be attributed to a solubility change.
- The ligand chain length provides a practical handle to optimize the outcome of a hot injection synthesis in terms of size and size dispersion and can be used to probe the interaction between ligands and the actual solute.

References (1) Abe, S.; Capek, R. K.; De Geyter, B.; <u>Hens, Z. ACS Nano 2013, 7, 943–949</u>.





This research has been funded by FWO-Vlaanderen (G.0760.12)



Fonds Wetenschappelijk Onderzoe Research Foundation – Flanders