

## Reaction Intermediates Determine the Nucleation of Semiconductor Nanocrystals

Klaus Boldt<sup>1</sup>, Nicholas Kirkwood<sup>2</sup>, Daniel Wurmbbrand<sup>1</sup>, Michael Seybold<sup>1</sup>, Florian Enders<sup>1</sup>, Danja Fischli<sup>1</sup>, and Rose Rosenberg<sup>1</sup>

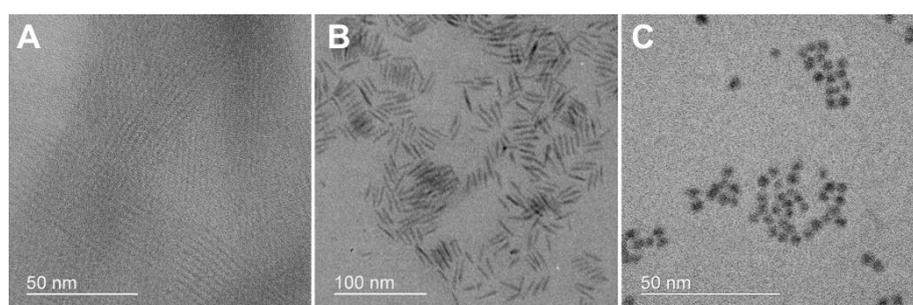
<sup>1</sup> University of Konstanz, Department of Chemistry, Konstanz, Germany

<sup>2</sup> The University of Melbourne, School of Chemistry, Parkville, Australia

The synthesis of colloidal nanocrystals is generally described by LaMer's model of nucleation and growth in which nuclei form from a supersaturated solution of monomeric species of the target material, followed by growth of those nuclei once the monomer concentration falls below a critical value. Mounting evidence suggests that this model may be too simplistic: instead of a homogeneous nucleation a number of intermediates form, which fundamentally impact the reaction pathway and outcome. The most prominent example are magic size clusters (MSC), small nanocrystals of defined size and stoichiometry that grow in a quantised rather than continuous manner [1].

Here we present two intermediates of cadmium chalcogenide synthesis, MSCs and large coordination polymers (CP) of the semiconductor materials, which can be selectively formed by the addition or removal of protic additives [2,3]. The intermediates bind free monomer, which strongly impacts the course of the reaction. Depending on the reaction conditions this leads to either a local, high monomer concentration or a depletion of free monomer. In kinetic terms this allows either reaction or diffusion control of the growth mechanism and forms the basis for rational synthesis control.

In addition to binding monomers CP form a mesostructure that acts as a template for its own conversion into semiconductor nanocrystals: When present at high concentrations such as in a dried film pyrolysis leads to the formation of nanorods, while spherical particles form under dilute conditions (see Figure 1). This provides a rich chemistry to elucidate the emergence of anisotropy in colloidal nanocrystals.



**Figure 1.** TEM micrographs of (A) polymeric CdSe intermediate and its reaction products after pyrolysis at (B) high and (C) low concentration of the intermediate.

[1] S M Harrell, J R McBride, S J Rosenthal, *Chem. Mater.* **25** (2013), 1199.

[2] N Kirkwood, K Boldt, *Nanoscale* **10** (2018), 18238.

[3] D Wurmbbrand, J W A Fischer, R Rosenberg, K Boldt, *Chem. Comm.* **54** (2018), 7358.

**Acknowledgement:** The authors acknowledge funding from the German Research Foundation (grant no. BO4516/4-1) and the Australian Synchrotron (grant no AS191/XAS/14479).