Poster Presentation

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Magic Sized Clusters in ZnO Nanoparticle Formation – an in-situ PDF study

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Semiconductor nanoparticles (NP) such as zinc oxide (ZnO) are commonly produced in sol-gel processes. The final NP powders are well characterized with respect to their crystallinity, which fundamentally governs their physical and chemical properties. Nevertheless, the nucleation process and the evolution of crystallinity of the nucleating NPs is not yet understood [1]. With the advent of the Rapid Acquisition Pair Distribution Function (PDF) method, time-resolved PDF studies have become possible, and the distinction between molecular clusters and nanoparticles in 1 M aqueous solutions of metal oxide NPs [2] has been demonstrated. However, nucleation in dilute sol-gel processes in more complex organic solutions remains untackled [1]. Our experiments are, to our knowledge, the first in-situ PDF studies in organic solvents. We used a 30 mM ethanolic solution of zinc acetate dihydrate. Several hours after the addition of the organic base tetramethylammonium hydroxide, monodisperse ZnO powders can be obtained. However, directly upon the base addition primary tetrahedral precursors Zn4OAc6 form. Approx. 1 hour later, they evolve into stable magic sized clusters (MSC) of 1.3 nm diameter and wurtzitic structure. Though known to exist for II-VI semiconductor NP such as CdSe [3], MSCs have not been demonstrated for ZnO before. With ongoing reaction time, the final spherical NPs of 2.5 nm diameter evolve at the expense of the MSCs and exist for several hours without undergoing further growth. SAXS studies confirm the PDF data. Fig. 1 shows the experimental PDFs and their fits. The fits are multiphase models of the precursor, the MSC and NP. The solvent shows intermolecular ordering effects whose contribution to the PDF was modelled by a low-frequency wave function. The MSC and NP sketches show a view along the crystallographic c-axis. Based upon these state-of-the art in-situ PDF studies, we suggest a nucleation model based on the existence of magic-sized clusters.

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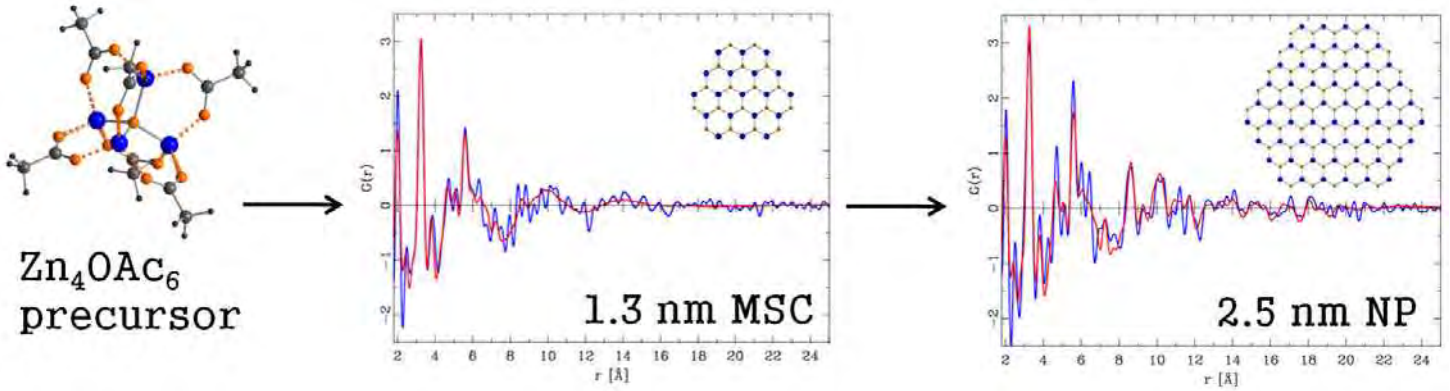

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