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The evolution of crystalline ordering for ligand-ornamented zinc oxide nanoparticles†

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Recent total scattering experiments have opened up the possibility to study nanoparticle formation *in situ* and to observe the structural transformation from precursor clusters to adult particles. Organic ligand molecules interact with precursors of metal oxide nanoparticles, yet their influence onto the evolution of crystallinity during particle formation has not been addressed in detail; nor have *in situ* total scattering experiments ventured into the field of low-concentration, room-temperature syntheses in organic solvents to date. In this report, we follow the crystallization of ZnO nanoparticles in ethanol in the presence of different organic ligands. Low coordinated zinc precursor clusters rapidly polymerize upon base addition to particles of ca. 1 nm in diameter. *In situ* SAXS experiments reveal that the overall particle size increases to 2 to 4 nm with advancing reaction time. Complementary *in situ* PDF experiments show smaller crystalline domain sizes, which are only one third to half as large as the particle diameter. The ZnO particles thus feature a crystalline core surrounded by a disordered shell. Both, the core and the shell diameter are influenced by the different surface-bound organic ligands, which prevent an immediate relaxation to fully crystalline particles. A slow crystallization takes place in solution. We assume a dynamic equilibrium of the ligand and solvent molecules at the particle surface, which enables gradual bond restructuring. With suitably adjusted synthesis conditions, in our case by a continuous base addition, we show how to bypass the disordered intermediates, allowing the spontaneous nucleation of fully crystalline nanoparticles.

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1. Introduction

The focus of research on nanoparticle formation has been on the evolution of particle sizes, but the internal structure is not frequently addressed. Rather, the formation of dense, crystalline particles is implied.^{1–8} For biominerals, such as CaCO₃, amorphous intermediates have long been well known. Just recently it was shown by *in situ* TEM that different pathways – direct nucleation of calcite crystals or their transforma-

tion from amorphous intermediates – are concomitantly possible at moderate to high supersaturations.⁹ The significance that CaCO₃ holds in the field of biominerals is equivalent to that of ZnO as a semiconductor. Many different synthesis strategies to produce ZnO nanoparticles exist including gas phase, hydrothermal and sol-gel processes.^{7,8,10} Sol-gel processes, and in particular reaction pathways in organic solvents have become increasingly attractive in comparison to aqueous routes, as it is easier to tune the nanoparticle size, shape and crystallinity.¹¹ With available knowledge of chemical reaction pathways,^{4,12} *in situ* small angle X-ray scattering (SAXS) and UV-vis spectroscopy have given access to the nucleation and growth behaviour,^{3,4,7,8,13–16} however with somewhat contradictory ripening rates and growth models.¹³ Theoretical attempts to describe ZnO nanoparticle nucleation have involved molecular dynamics (MD) simulations¹⁷ and population balance equation (PBE) modelling.^{1,2} Two independent PBE studies resulted in a three stage model in agreement with *in situ* UV-vis experiments, in which ZnO nanoparticles nucleate, then undergo oriented attachment within minutes and continue to grow *via* Ostwald ripening over several hours. Segets *et al.* base their calculations on Spanhel's magic size cluster model of aggregated tetrahedrons.^{2,18} To our

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knowledge, besides the Spanhel model, all other experimental and theoretical approaches have so far assumed the nucleation of dense particles, which further grow or agglomerate.

The internal structure and crystallinity of the nucleating particles has not been considered in most previous ZnO nucleation and growth models. Just recently, Yttria-stabilized zirconia nanoparticles were shown to nucleate along a multi-step pathway including amorphous intermediates in a solvothermal reaction in supercritical methanol.¹⁹ The total scattering method employed there uses the pair distribution function (PDF) and is a unique tool to study local order and disorder in nanoparticles.^{20,21} Also structural transitions during chemical reactions can be observed in real-time.^{22–26} The PDF is a histogram of interatomic distances weighted by the atomic form factors of the contributing atoms and hence can also probe non-crystalline samples in contrast to approaches by classical powder diffraction analysis. The generally low concentrations of nanoparticles and precursor species in reacting solutions prompted previous PDF studies towards the exploration of hydrothermal or supercritical reactions, where higher concentrations than at ambient conditions are possible.^{19,22,23,26} Supercritical solvents create less background signal due to their lower density since elevated temperatures decrease the intermolecular ordering of the solvent molecules. Here we present the first *in situ* total scattering study, which addresses metal oxide nanoparticle formation at ambient conditions in an organic solvent, namely ethanol. ZnO nanoparticles were nucleated in a sol-gel process from molecular precursors. We observed a rapid polymerization to disordered particles, in which the crystalline domains only extend over roughly 3 to 4 unit cells. Beyond this range, the establishment of crystalline order is a slow restructuring process as a comparison with SAXS directly shows. By using different organic ligand molecules, different crystallization rates were observed. An optimization of the base addition procedure enabled us to bypass the disordered intermediates. Total scattering experiments thus contribute to a mechanistic understanding of crystallization processes and enable us to optimize synthesis conditions by choosing the most favourable nucleation pathway.

2. Materials and methods

2.1 Chemicals and synthesis

The synthesis procedure is based upon Spanhel and Anderson²⁷ with changes as suggested by Wood *et al.*,²⁸ Music *et al.*,²⁹ Chory *et al.*³⁰ and Zobel *et al.*³¹ 0.59 g zinc acetate dihydrate (>99%) was dissolved in 100 mL anhydrous ethanol (99.5%, <0.005% H₂O) to yield a 27 mM solution. Along with the zinc acetate, occasionally an additional organic ligand was dissolved at 6.75 mM and magnetically stirred for about an hour at room temperature. The organic ligands employed are known to influence the shape and size of the final nanoparticles due to selective adsorption on certain crystal faces.^{32,33} The ligands were dimethyl-L-tartrate (dmlt, >99%), 1,3,5-diphenyl-1,5-pentanetrione (pent, >98%) and

citric acid (cit, >99.5%). When no additional ligand was used, acetate (ac) itself serves as such. The nanoparticle nucleation is initiated by the addition of the organic base tetramethylammonium hydroxide (TMAH, 25 wt% in methanol) at a ratio $[\text{OH}^-]/[\text{Zn}^{2+}] = 2.6$. With the ligand citric acid, the ratio was increased to $[\text{OH}^-]/[\text{Zn}^{2+}] = 6$. Solvents were obtained from either Roth or Sigma Aldrich. Zinc acetate dihydrate, 1,5-diphenyl-1,3,5-pentanetrione and dimethyl-L-tartrate were purchased from Sigma Aldrich and citric acid bought from Roth.

2.2 Cleaning of glassware

All glassware used for the experiments was cleaned with 1 wt% NaOH and HCl and rinsed three times with tap and Millipore water and afterwards dried at 110 °C in a heating oven prior to usage.

2.3 *In situ* X-ray diffraction (XRD)/total scattering

In situ XRD measurements were carried out at beamlines 11-ID-B at APS, Chicago, and ID-15-B at ESRF, Grenoble, with X-ray energies of 56 and 59 keV, respectively, using a Perkin Elmer amorphous silicon detector. Some experiments have been carried out several times and show good reproducibility. The solution was agitated with a magnetic stirrer for the duration of the experiment to keep the particles suspended at all times. The reacting solution was observed prior to, occasionally during and for several hours after TMAH addition. The solution, respectively dispersion was pumped with a peristaltic pump through a stainless steel flow cell with polyimide windows and an X-ray path length of 3 mm. The volume flow was 190 mL min⁻¹. The TMAH was injected with an externally controlled syringe pump within 2 s, unless specified otherwise. The experiments were carried out at room temperature and multiframe data sets were typically collected for 1 min and averaged, unless indicated otherwise. Distance calibration was done with NIST CeO₂ standards. Background measurements of the pure solvents and solvents with the proper TMAH concentration were done for 10 min while pumping the solvent to guarantee equivalent conditions. The flow cell was cleaned with HCl and Millipore water and dried in a heating oven in between two experiments. The entire tubing was exchanged for each experiment.

2.4 *In situ* small angle X-ray scattering (SAXS)

In situ SAXS experiments were carried out at beamline cSAXS at SLS, Villigen, with an X-ray energy of 15 keV and a time resolution of 5 s, using a Pilatus 2M detector. The experimental setup was comparable to the setup of the *in situ* total scattering experiments, except that the polyimide windows of the flow cell have been exchanged with a thin foil, which was tested in previous experiments to produce negligible scattering signal in the range of SAXS experiments. The detector-sample distance was calibrated using silver-behenate.

2.5 PDF calculation

Radial integration of 2D detector images was done with Fit2D,³⁴ PDF calculation with PDFgetX3.³⁵ Fourier transformation of the diffraction data results in the pair distribution function (PDF), $G(r)$.

$$G(r) = \frac{2}{\pi} \int_{Q_{\min}}^{Q_{\max}} Q [S(Q) - 1] \sin(Qr) dQ.$$

$Q = 4\pi/\lambda \sin \theta$ represents the momentum transfer vector with the wavelength λ and the scattering angle 2θ , and the Fourier transformation runs from the smallest experimentally accessible $Q_{\min}$ to a $Q_{\max}$, suitably chosen to be 15.8 Å⁻¹ (dmlt), 17.9 Å⁻¹ (ac), 14.6 Å⁻¹ (cit), 16.3 Å⁻¹ (4.0 mM TMAH min⁻¹ ramp), 16.3 Å⁻¹ (0.8 mM TMAH min⁻¹ ramp) and 17.7 Å⁻¹ (pent) for reduction of termination ripples and background effects for the *in situ* data and 22.4 Å⁻¹ for the powder data. The total scattering structure function $S(Q)$ corresponds to the usual diffraction data after correction for background, experimental artefacts and proper normalization with the scattering cross-sections of all contributing atoms.

2.6 Modelling of PDF data

Structure simulation was done with the DISCUS software package.³⁶ PDFs of crystalline model particles are calculated as the sum over all interatomic distances r_{ij} between atom pairs ij within the particle:

$$G(r) = \frac{1}{Nr} \sum_i \sum_j \left[\frac{f(Q)_i f(Q)_j}{\langle f(Q) \rangle^2} \delta(r - r_{ij}) \right] - 4\pi\rho_0 r$$

$f(Q)$ is the Q -dependent atomic form factor. By subtracting the average number density ρ_0 , the PDF oscillates around zero. Since the ZnO nanoparticles possess a non-negligible amount of stacking faults in the range of 20% in their dry powder form,³¹ the nanoparticles are simulated as ensemble averages with free parameters for the lattice constants, the thermal parameters as well as the nanoparticle diameter and a fixed stacking fault probability of 20%.^{37,38} The synthesized nanoparticles are not monodisperse, but underlie a size distribution. They are modelled as Gaussian-distributed spheres with an average diameter d_0 and the width σ_{NP} of the distribution according to

$$P(d_0, \sigma_{\text{NP}}) = \frac{1}{\sqrt{2\pi}\sigma_{\text{NP}}} \exp\left(-\frac{(d-d_0)^2}{2\sigma_{\text{NP}}^2}\right)$$

This description is justified because the final particles in the nanoparticle powder were also best modelled with a Gaussian distribution.³¹

The experimental d-PDFs of the sample after subtraction of the ethanol or, ethanol + TMAH background, consist of three contributions: (i) signal from restructured solvent around the nanoparticles,³⁹ (ii) the PDF of the precursor clusters Zn₄OAc₆, and (iii) the PDF of the Gaussian-

distributed nanoparticles. The individual contributions of the nanoparticles, the precursor and the restructured solvent to the overall fit are shown in Fig. S4.† The contribution from the restructured solvent is described by a damped sinusoidal oscillation $w(r)$, see Zobel *et al.* for details on the variables and modelling.³⁹ The clusters and nanoparticles are atom number-weighted contributions and added to the oscillation $w(r)$ according to

$$G(r) = p_{\text{scale}} \sum_{i=1}^2 p_i G_i(r) + w(r),$$

here

$$w(r) = A \sin\left(2\pi\left(\frac{r}{\lambda} - \phi\right)\right) \exp\left(-\frac{(r-r_0)^2}{2\sigma_{\text{eff}}^2}\right).$$

p_{scale} is the overall scale factor, p_i the weighted fraction of phase i and $G_i(r)$ the model PDF for the phase i . The model PDFs of the nanoparticle do not include the ligand chemistry, because the organic ligand molecules do not contribute significantly to the X-ray PDFs. The precursor Zn₄OAc₆ was calculated including the six acetate molecules within an optimized geometry. The accuracy of this strategy was confirmed by molecular dynamics (MD) simulations which showed good agreement of our background-corrected PDFs and the direct assessment of the Zn–O distances (see Fig. S5†). All data sets were successfully modelled using this approach.

2.7 Modelling of the SAXS data

The SAXS data acquired with a Pilatus 2 M detector was radially integrated using the Nika extension for Igor (Wavemetrics)⁴⁰ and the data was modelled with the Irena extension.⁴¹ The background before the TMAH addition was used in the data reduction. In separate experiments it was verified, that the SAXS signal of the ethanol is not altered by the TMAH addition. The data was modelled in the Q -range from 0.01 to 0.6 Å⁻¹. Depending on the organic ligand, up to three polydisperse lognormally distributed spherical populations were needed to fit the data. An example for such a fit showing the individual contributions from the different populations, is displayed in Fig. S6.† The total particle volume and the mean radius were refined, while the standard deviation of the radii distribution, *i.e.* the polydispersity, was fixed at 50% of the mean radius. The fit results for the three ligands are shown in Fig. S7 to S9.†

2.8 Molecular modelling

The Zn₄OAc₆ cluster was initially prepared in vacuum and subjected to geometry optimization from quantum calculations using the 6.311G** basis set at the MP2 level (Gaussian03). Using empirical force fields, we then embedded the precursor cluster in ethanolic solution (including 4% water content).¹⁷ For this system and the pure ethanol/water solvent model we sampled PDF data from 10 ns MD simulations

imposing ambient temperature and pressure. The MD simulations were performed for cubic simulation cells of 4 nm dimensions using a time step of 1 fs and particle mesh Ewald summation.

3. Results and discussion

3.1 *In situ* scattering experiments

From the time-resolved XRD data, the experimental differential PDFs (d-PDFs) of the reacting sample are calculated by subtracting the solvent background, with or without TMAH, from the sample signal. All d-PDFs were modelled as described in Materials and methods. Exemplarily, Fig. 1 shows two fits of the ZnO ac system, together with the resulting Gaussian size distributions in the insets, for a very early (20 min, panel a) and intermediate (250 min, panel b) reaction time. All interatomic distances within the nanoparticles are described well by the model of a wurtzitic ZnO particle and thus the fitted diameters d_0 refer to the dimensions of crystalline domains. The original data consisted to >99% of background. Hence, the d-PDFs are subject to comparatively high noise (termination ripples), which causes the high frequency oscillations in the difference curves (in offset) in particular in the low r regime. Fig. 1c shows the experimental, background-corrected SAXS curves and fits for the ZnO ac system at comparable points in time. SAXS, in contrast to PDF, sees particle sizes independent of the internal structure and thus the fitted, lognormal size distributions display the overall particle sizes. It is known, that the PDF technique is not well suited to derive exact particle size distributions.^{42–44} A refinement with a single particle size, however, does not describe our data well. Significant differences remain, particularly in the high r region. The fit improves considerably by invoking a Gaussian distributed particle size.³¹ We chose a Gaussian distribution, because it was the only particle size distribution implemented in the PDF modelling software which was calculated with reasonable calculation time. We are aware that other polydisperse distribution types might

give a comparable PDF fit quality. Due to this awareness and since the PDF describes the size distribution of the crystalline cores in contrast to the morphological size distribution of the overall particle diameters determined from SAXS, we see no conflicting situation.

3.2 Change of zinc coordination during base addition

In contrast to ionic reactants in aqueous media, Zn^{2+} does not exist as free ions in alcoholic solvents, because zinc acetate or zinc ethoxy complexes are more stable as shown by partial charge calculations.¹⁸ In general, metal ions are readily chelated by organic ions. The stability of the metal–ligand complexes depends on the ligand and its functional groups.⁴⁵ The formation of primary precursors Zn_4OAc_6 of tetrahedral shape in the ZnO sol–gel synthesis was first postulated in 1998.⁴⁵ These precursors have then been implemented as the simplest building blocks into nucleation models.¹⁸ The general procedure for ZnO nanoparticle syntheses in ethanol involves a 3 hour long refluxing step at elevated temperatures, after which an enrichment of Zn_4OAc_6 clusters was evidenced by EXAFS.¹⁴ These clusters were shown to exist throughout the entire synthesis.³

Within our approach, referring to room temperature without refluxing, the Zn^{2+} concentration is about one third compared to the reflux strategy due to the room temperature solubility limit of the zinc acetate dihydrate salt used as reactant. Our zinc acetate solutions, stirred for 1 h prior to base addition, see Fig. 2a (purple curve), do not contain Zn_4OAc_6 clusters. The displayed theoretical Zn_4OAc_6 PDF (green curve) was derived from *ab initio* quantum dynamical simulations, in which we calculated the most stable configuration of this cluster. Extended stirring up to 19 h (blue curve) also did not result in Zn_4OAc_6 clusters, however the zinc coordination increased compared to the 1 h solution as evidenced by the higher 3.1 Å peak. The broad peaks at ca. 2.1 Å and 3.1 Å stem from zinc-ethoxy or zinc-acetate complexes, in which zinc is not yet covalently bonded to oxygen

Fig. 1 Experimental d-PDFs (a, b) and background-corrected SAXS curves (c) together with their fits for ZnO ac nanoparticles for early and intermediate reaction times, i.e. 20 and 250 min (20 and 235 min for the SAXS data) after TMAH addition. The experimental d-PDFs (black) were modelled with Gaussian particle size distributions of mean diameter d_0 and width σ_0 , shown in the insets, whereas the SAXS fits are based on lognormal distributions with a polydispersity set to 0.5. The difference curves of the PDF fits are in offset. The SAXS data are plotted with double-logarithmic axes. The different sizes from PDF and SAXS are discussed in section 3.3.

Fig. 2 Evolution of local zinc coordination in zinc acetate solutions. (a) Experimental d-PDFs of zinc acetate solutions after 1 (purple) and 19 h (blue) of ageing and at different TMAH concentrations, 7.9 (orange) and 71 mM (red, $t = 1.5$ min), as well as calculated PDFs of a Zn_4OAc_6 cluster (green) and a 1 nm ZnO particle (black). Without the addition of a critical amount of base, the peak at 3.2 Å does not appear. Only sufficient TMAH concentration can induce tetrahedral coordination, which is then immediately followed by the formation of larger agglomerates with local wurtzitic structure up to 1 nm in diameter. This can be seen from the similarity of the red and the black curve, which compares the solution after addition of 71 mM TMAH with a 1 nm crystalline particle. The d-PDFs are scaled to identical amplitude of the 2.0 Å peak to ease comparison of the 2.0 Å/3.2 Å intensity ratios. (b) Evolution of d-PDFs of the zinc acetate solution directly after TMAH addition. Distinct peak shifts are observable below 5 Å for ca. 0.5 min after base addition and new peaks occur beyond 5 Å thereafter.

in tetrahedral motifs. Distances of $\text{Zn}^{2+}\text{-OH}^-$ bonds are known to range from 2.0 to 2.2 Å, well in accord with the peaks observed in the stirred zinc acetate solutions.¹⁷ $\text{Zn}^{2+}\text{-O}^{2-}$ covalent bond distances, on contrary, are found between 1.8 and 2.1 Å.¹⁷ The addition of a small amount of base (7.9 mM TMAH, yellow curve) results in such $\text{Zn}^{2+}\text{-O}^{2-}$ bonds with a peak at slightly below 2 Å. The tetrahedral coordination is however not yet obtained as evidenced through the offset of the 3.1 Å peak compared to the peak of the theoretical tetrahedral cluster expected at 3.2 Å (green curve). A larger

amount of base is necessary to form tetrahedral motifs in the precursor clusters. In order to observe continuously the changes in the zinc coordination induced by the base, we injected the base at high supersaturation (71 mM) automatically and observed the solution directly after base addition with a time resolution of 10 s (base addition only takes 2 s). Fig. 2b shows a colour plot of the d-PDFs over time, wherein we refer to the logarithmic colour scheme of Fig. 3. Upon the base addition at high supersaturation, the coordination of zinc changes abruptly. After 0.5 min, local rearrangement has taken place and tetrahedral coordination is achieved. Almost simultaneously, smeared-out peaks beyond 5 Å appear. The d-PDF for $t = 1.5$ min including these peaks is displayed in Fig. 2a (red curve) as well, in order to ease comparison to the theoretical PDFs of a precursor cluster (green curve) and a 1 nm ZnO nanoparticle (black curve). The intensity ratios of the 2.0 and 3.2 Å peaks differs strongly between these three PDFs, with the nanoparticle PDF being closer to that of the 1.5 min solution. The red curve also features a peak at 5.4 Å. This peak is already similar to the 5.6 Å peak in the PDF of the 1 nm ZnO particle. This shows that in this 1.5 min solution networks of tetrahedral motifs are present, which are larger than an individual Zn_4OAc_6 cluster. From this discussion it can be concluded that both long stirring and slight base addition do not induce tetrahedral zinc coordination for 30 mM Zn^{2+} solutions. High hydrolysis ratios, however, immediately transform zinc acetate and ethoxy clusters into extended agglomerates, which feature crystalline domains of ca. 1 nm in diameter. Spanhel proposed a growth model for ZnO based on a series of regular Koch pyramids, also called 3D Sierpinski triangles.^{18,45} Within our experiments, there is no hint for the prolonged existence of hierarchical structures with fixed formulas such as $\text{Zn}_{10}\text{O}_4\text{Ac}_{12}$, which are entirely overrun by the fast polymerization kinetics induced by the base addition. Moreover, we can rule out the existence of any octahedral phases, because those would feature inter-atomic distances of 2.8 Å, where no peak occurs at any time after base addition.

3.3 Evolution of crystallinity influenced by ligands

The observation of the zinc acetate solution from Fig. 2b was carried on for more than 8 hours with a 1 min time resolution. Similar PDF experiments were done for the ligands dmlt, cit and pent. Fig. 3 compares the colour plots for ac (panel a) and dmlt (panel b) in order to contrast different crystallization rates. ZnO ac nanoparticles relax faster to the crystalline wurtzitic structure and are bigger than the dmlt particles, which show gradual peak shifts in particular during the first 150 min. Upon base injection, the tetrahedral coordination builds up instantaneously for all ligands as the 2.0 and 3.2 Å peaks appear and do not shift much. Broad peaks at offset positions compared to wurtzitic ZnO are detectable up to 25 Å for ac and 20 Å for dmlt. The PDF refinements result in crystalline domain sizes of 1 nm at early reaction times, which then grow over time, see Fig. 4 (the fit results of

Fig. 3 Temporal evolution of nanoparticle crystallinity in the d-PDFs for the ligands ac (a) and dmlt (b). The yellow horizontal line indicates the injection of 71 mM TMAH, the colour bar to the right represents the colour scheme. The first 150 min are enlarged for better visibility of peak shifts. The PDFs of the final crystalline particles are overlaid in red for comparison. The ZnO ac particles feature sharp peaks at rather constant positions over all times. ZnO dmlt particles show smeared-out peaks at $r > 5$ Å for $0 < t < 150$ min. The peaks shift and grow in intensity, which mirrors the gradual crystallization.

cit are compared to ac and dmlt in Fig. S1a,[†] and the corresponding widths of the Gaussian distributions are plotted in Fig. S1b,[†] the solution composition in Fig. S2[†]). The scatter of the data points is due to the accuracy with which size can be determined from PDF refinements and the trend lines are included as a guide to the eye. As the crystalline domain sizes

increase in the fits in Fig. 4, several peaks in the d-PDFs in Fig. 3 shift from their original positions to interatomic distances, where peaks in wurtzitic ZnO structures are expected. For ZnO ac this peak shift is most pronounced for the 5.6 Å peak, for dmlt many peaks and regions are clearly affected (5.6, 8.6, 12–15 Å). This prolonged shift and even delayed occurrence of some peaks is demonstrated further in Fig. S3.[†]

For all ligands, the tetrahedral Zn–Zn peak position (3.2 Å) changes the least. However, at early times its intensity compared to the Zn–O peak is distinctly lower compared to this ratio in the bulk. Thus from the PDF data it can be interpreted that the local tetrahedral zinc coordination is readily established, but the tetrahedrons are tilted against each other. The order over intermediate distances is lost, which results in disordered particles. This disorder is most pronounced for dmlt. In addition to the diameters of the crystalline domain sizes as determined from the d-PDF refinements, Fig. 4 also contains the nanoparticle diameters from the SAXS data modelling. No SAXS data can be shown for ac for $t > 230$ min, as the SAXS measurements had been aborted and the missing data points for the ZnO ac curve for $90 < t < 115$ min are due to a beam loss of the synchrotron beam. The SAXS particle sizes of ac and dmlt are larger at all times than the PDF crystalline domain sizes, providing evidence for internally disordered particles. The degree of disorder is larger for ac than for dmlt since the ratio of the particle diameter to the crystalline diameter is larger. In a separate study, we characterized the dry nanoparticle powders with the four different ligands by means of HR-TEM, XRD and PDF.³¹ The particle sizes determined from *in situ* SAXS for late reaction times here, are very well in accord with particles sizes observed in the dry ZnO nanoparticle powders (Table S1[†]).

The comparison of the SAXS and PDF data clearly shows, that the particle size and the particle crystallinity increase over time. The ratio of the crystalline core to the overall

Fig. 4 Evolution of particle (open symbols) and crystalline domain sizes (filled symbols) over time for ZnO nanoparticles with ligands ac (red dots) and dmlt (blue rhombs). Particle sizes were determined from SAXS, crystalline domain sizes from PDF experiments and lines through the PDF diameters are guides to the eye. At all times the overall particle size is larger than the crystalline domain sizes, which implies the existence of a disordered shell within the particle. This disordered shell is larger for ac than for dmlt. (Due to computational effort, only every 20th data set of the experiment was fitted and the results of three of these averaged for clarity of display. For SAXS only every 10th dataset is displayed. The small jumps in particle diameters are due to changed fitting models and are explained in the ESI,[†] Fig. S6–S9. The missing data points from 90 to 115 min for ZnO ac are due to a beam dump at the beamline. The measurement was followed up to 230 min.)

particle size agrees well with MD simulations on ZnO nanoparticle formation by Kawska *et al.*, which predict a 1 nm size core for 1.8 nm large particles.¹⁷ The gradual crystallization to the energetically more favourable wurtzitic crystal structure is directly observable for all ligands in the d-PDFs as peak shifts at $r > 5$ Å. Moreover, the existence of the disordered regions around the crystalline core is visible as broad, smeared-out peaks at offset positions for $r > 10$ Å, in particular for dmlt. In view of the influence of the organic ligands on the crystallinity of the initially formed particles and their subsequent crystallization rates, we propose a crystallization pathway for sol-gel reactions at high supersaturation, which is illustrated in Fig. 5. The initial high hydrolysis ratio very rapidly forms primary precursors of tetrahedral coordination (Zn_4OAc_6 clusters and similar building blocks), which instantly polymerize to nanoparticles of a certain size distribution. These particles possess crystalline domains of *ca.* 1 nm in diameter and disordered regions, which add up to a total diameter of *ca.* 1.5–2.5 nm. The particles are sketched as cuts through the hexagonal *ab*-planes of wurtzite with blue regular hexagons for crystalline and purple distorted hexagons for disordered regions. They are stabilized against strong agglomeration, aggregation and further rapid growth by organic ligand molecules, illustrated as red zig-zag lines representative of the carbon backbones of these ligands. Organic ligands and organic ions in general are known to adsorb on the particle surface and prevent growth.⁴⁵ Slow crystallization leads to the final, ligand-capped ZnO particles. During the modelling of the SAXS curves, we introduced an additional particle population to model aggregates, whenever the shape of the SAXS curves required such. For dmlt the onset of noticeable aggregation was after 170 min and the introduction of this additional population creates the tiny offsets of the particle diameters in Fig. 4 and Fig. S8.† The agglomerates were however not bigger than 8 nm in diameter. Only for the ligand pent, strong aggregation to 80 nm large aggregates occurred spontaneously, but in accordance with macroscopic cloudiness of the suspension, shown in Fig. S9.†

Mechanistically, the crystallization follows the reaction principles of sol-gel chemistry: metal oxide salts, $\text{M}(\text{OR})_n$ exposed to high supersaturation in solutions of a coordinating solvent, rapidly undergo fast hydrolyzation and condensation reactions. The result is a fast polymerization of primary building blocks. As an amorphous network forms, bonds which are once formed, cannot disintegrate immediately, but exist over certain time scales before they restructure to the energetically more favourable crystalline state.^{46–49} The chosen solvent, ligand and degree of supersaturation influence the ratio of dense particles and branched chains.⁴⁸ Strong complexing ligands (SCL) such as carboxylic acids (ac, cit), beta-diketones (pent, dmlt) and allied derivatives result in the formation of new precursors $\text{M}(\text{OR})_{n-x}(\text{SCL})_x$, which are less hydrolysable and thus alter the nucleation and crystallization.⁴⁹ For zirconia in propanol, polydisperse disordered particles were shown to form at high hydrolysis ratios in presence of acetylacetone as ligand.⁴⁴ The crystallization of such disordered intermediates can be promoted at elevated temperatures, *e.g.* under hydrothermal conditions, where reorganization and reprecipitation to equilibrium conditions is favoured.^{47,49} This applies to the fast crystallization observed recently *in situ* for yttria-stabilized zirconia in supercritical methanol.¹⁹ In contrast to these experiments, the ambient conditions chosen within this study, slow down the crystallization and are thus very suitable to distinguish changes to the crystallization kinetics induced by the different ligands.

The disordered ZnO particles of this study most likely feature internal hydroxyl groups. Two of these hydroxyl groups have to overcome the energetic barrier to split off a water molecule, which then releases enough energy to propagate this process throughout the entire particle to enable the formation of internally hydroxyl-free ZnO particles.¹⁷ The water molecules have to diffuse out of the dense agglomerates, which needs time and further explains the very gradual peak shifts in the PDFs. The surfaces of the disordered nanoparticles are intrinsically capped with ethoxy and in

Fig. 5 ZnO nanoparticle crystallization *via* disordered intermediates. From left to right: upon base addition precursor clusters form in solution. At high supersaturation these instantly polymerize to nanoparticles of the final diameter, but with internal disordered structure (purple) and only partially crystalline domains (blue). Cuts through the *ab*-plane with hexagonal motifs illustrate the wurtzitic structure. Organic ligand molecules stabilize the particles against agglomeration and are sketched by the red zig-zag lines indicating the carbon backbone. Relaxation processes in solution finally result in entirely crystalline particles.

particular with hydroxyl groups. The additional ligands partially replace some surface hydroxyls.^{32,46} In solution all these surface bonds are dynamic. The lifetime of ligand bonds is of a few hours. Thus bonded ligand molecules prevent immediate further condensation reactions of internal hydroxyl groups to a pure oxide network.⁴⁷ The disorder is trapped within the particles due to the ligands. This has hardly been addressed up to now.^{50–52} The crystallization of initially disordered 2 nm triphenylphosphine-capped CdSe particles was observed in a 200 °C hot solution and the process was attributed to the gradual healing of surface defects enabling relaxation reactions and surface reconstruction.⁵¹ For disordered dodecanethiol-stabilized CdSe nanoparticles dynamic surface-exchange phenomena of coordinating solvent and ligand molecules were used to explain the observed post-synthesis crystallization kinetics in heated pyridine solutions.⁵⁰ Within this study, we observed different crystallization rates induced by different organic ligands. To our knowledge, this is the first time that the influence of organic ligands onto the internal crystallinity of nucleating particles has been monitored directly. The organic ligands not only influence the initial degree of crystallinity of the disordered intermediates, but also the subsequent crystallization. The acetate ligand binds very weakly and produces the largest particles in the dry powders and the sol and shows a fast crystallization rate. The Zn-ac complexes in the solution prior to the TMAH addition are also weak and very variable in composition⁵³ compared to dmlt, cit or pent complexes.³³ Cit, dmlt and pent are multifunctional ligands. Pent preferentially binds with its ketonic groups in the bidentate configuration and chelates metal ions strongly.^{54,55} Cit and dmlt were shown to form strong metal complexes in solution, too.^{33,47} The more stable pent-, cit- and dmlt-Zn complexes are hydrolysed slower upon TMAH addition and thus form more strongly disordered intermediates than ac. Also the particle growth rate and overall size is smaller in the presence of these ligands, which bind stronger to the surface Zn ions.³²

3.4 Comparison to existing nucleation models

Previous studies on the nucleation and growth of ZnO nanoparticles, focussed on either the primary precursors¹⁴ or the particle size after the nucleation event and during subsequent growth. Various *in situ* SAXS studies for refluxed systems share the observation of initial particle sizes of *ca.* 2 nm in diameter.^{3,14,56} This is roughly in accordance with average particle sizes observed by us. In general, our particles are smaller due to the lower zinc concentration at room temperature as well as the use of additional ligands as compared to the particle sizes of the purely acetate-capped ZnO particles of the studies under reflux. Different growth models including oriented attachment, formation of fractal aggregates and Ostwald ripening have been suggested for ZnO. We also observe continued particle growth, particularly for ZnO ac particles, because acetate stabilizes the least, whereas ZnO dmlt

and pent particles seem to be more stable and stay smaller in solution. The PBE simulations with the most comparable sets of parameters (25 °C, 40 mM Zn²⁺, 90 mM KOH (ref. 1); 20 °C, 50 mM Zn²⁺, 100 mM LiOH (ref. 2)) modelled particle diameters of about 2 nm after few minutes of reaction time and further subsequent growth.^{1,2} One of these PBE studies is based on Spanhel's nucleation concept of self-similar building blocks, which we regard as not applicable for high hydrolysis ratios as used in all previous studies and modelling attempts. High hydrolysis ratios result in rapid polymerization reactions which oppose the occurrence of magic size clusters up to 2 nm in diameter. In general, the composition of particles in this size range of 2 nm is no longer purely determined by electronic stability due to closed electronic shells, but by geometric factors. Larger variability in the composition prevails against the magic-number concept.⁵⁷ The formation of disordered particles as presented here is more sensible from a mechanistic point of view. Moreover, it has to be stressed that our SAXS data is comparable in its overall trend to the data published by Caetano *et al.*,³ who also report particle growth and simultaneous agglomeration for later reaction times. However, our study provides further mechanistic insight into the crystallinity of the nanoparticles and shows the need for complementary measurements like *in situ* total scattering in order to fully understand nanoparticle crystallization processes.

3.5 Bypassing disordered intermediates

Supersaturation is one of the key factors determining the ratio of dense to branched particles in sol-gel reactions. Supersaturation can be achieved by a change of external conditions such as temperature or pressure, or by an increase of the concentration of the reactants, *i.e.* the base as initiator of the reaction. In our standard experiments, discussed above, the entire base volume (71 mM TMAH) is injected at once. In two ramp experiments, we added the TMAH continuously with a constant dosing speed of 0.8, respectively 4.0 mM TMAH min⁻¹ up to the final TMAH concentration of 71 mM. Then the experiments were aborted. Fig. 6a shows the colour plot for a ramp experiment with 4.0 mM min⁻¹ for the ligand pent, where $c[\text{TMAH}, t = 0 \text{ min}] = 0 \text{ mM}$ and $c[\text{TMAH}, t = 40 \text{ min}] = 71 \text{ mM}$. There are no interatomic distances beyond 5 Å for base concentrations below a critical limit. Once a certain TMAH concentration is reached, a spontaneous polymerization occurs and entirely crystalline particles form straight away. All peaks in the PDF instantly appear at wurtzitic positions out to the particle diameter. The critical TMAH concentration was found to be 43 mM for both ramp speeds. Further experiments will be needed to substantiate a pure concentration dependence within a certain range of ramp speeds.

Fig. 6b compares the evolution of nanoparticle crystallinity in the two ramp experiment with the standard experiment by comparing three selected PDF peak positions for each experiment. The three most prominent peaks of the ZnO nanoparticles at 3.2, 5.6 and 8.6 Å describe the short-range order

Fig. 6 Hydrolysis ratio changes initial crystallinity of ZnO nanoparticles. Continuous TMAH addition with 4 mM min^{-1} leads to a gradually increasing supersaturation and spontaneous nucleation of crystalline particles at 43 mM (a). Gaussian fits of the peak positions at 3.2 , 5.6 and 8.6 Å are shown in panel (b) for continuous ramps with 0.8 (blue triangles) or 4 mM min^{-1} (red circles) and complete injection of 71 mM at $t = 0 \text{ min}$ (green rhombs). The ramp experiments were aborted once the 71 mM were reached, whereas the standard experiment was run for 3 hours. Vertical lines indicate the appearance of peaks and coincide for all three peaks for the spontaneous nucleation of the ramp experiments. A delayed appearance and peak shifts are observed for the injection experiment.

between neighbouring shells of tetrahedrons within the particles and were fitted for each data set with Gaussian profiles. The resulting peak positions are compared. Both ramp experiments feature a spontaneous burst nucleation and all three peaks appear almost simultaneously. The 3.2 Å peak appears slightly earlier in both cases due to precursor formation. Vertical dotted lines highlight the onset of the peaks. The standard experiments with manifold initial supersaturation results in disordered particles, as discussed above for ZnO ac,

cit and dmlt. Already the 5.6 Å peak needs *ca.* 45 min to appear and the 8.6 Å distance takes even 60 min. Moreover, their peak positions shift over time, which reflects the slow crystallization process within the initially disordered particles. Comparing these experiments, we can directly conclude that well-chosen synthesis parameters can bypass the disordered intermediates.

4. Conclusion

In summary, we followed the evolution of crystallinity in ligand-capped ZnO nanoparticles during their formation in a sol-gel process in ethanol by combining *in situ* total scattering with SAXS. We provide real-time mechanistic insight into the large impact that organic ligand molecules possess onto the nanoparticle formation. The high supersaturation and the strongly binding organic ligands prevent full, immediate crystallization of nucleating particles and result in disordered intermediates. Gradual relaxation processes enable a slow crystallization to wurtzitic, crystalline particles. The extent of the initial disorder and the rate of rearrangement were shown to depend on the organic ligands. Most importantly, suitably adjusted synthesis conditions enable to bypass the disordered intermediates, allowing the spontaneous nucleation of fully crystalline nanoparticles.

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