Supplementary Information

Concentration- and Temperature-Dependent Variation of Co_3O_4 Nanoparticle Size and Morphology: Insights into Growth Behaviour and Scalability

Johannes Kießling, *a and Anna S. Schenk*a,b

^a Physical Chemistry IV, University of Bayreuth, Universitaetsstrasse 30, 95447 Bayreuth, Germany

^b Bavarian Polymer Institute (BPI), University of Bayreuth, Universitaetsstrasse 30, 95447 Bayreuth, Germany

*E-mail: johannes.kiessling@uni-bayreuth.de

anna.schenk@uni-bayreuth.de

Contents

- **1. Experimental Details**
- 2. Supplementary Figures and Analyses
- 3. References

1. Experimental Details

1.1 Chemicals and Materials

The educts used for the presented synthetic route are selected to promote a fast and stable reaction procedure. Co_3O_4 nanoparticles (NP) were prepared according to a previously published protocol¹ employing the following reagents: $Co(NO_3)_2 \cdot 6 H_2O$ (Emsure, Sigma Aldrich), oleylamine (OLA; 98% primary amine, Sigma Aldrich), oleic acid (OA; synthesis grade, Sigma Aldrich), EtOH (*p.a.*, VWR), hexane (*p.a.*, VWR), heptane (*p.a.*, VWR), NaOH (*p.a.*, VWR), and deionized water (Merck Milli-Q[®] IQ 7000 water purification system, 18.2 MΩ·cm resistivity). While comparatively inexpensive, the educts may be used as received from the suppliers without further processing. All used chemicals should be as fresh as possible to ensure optimal results. Specifically, upon storage, $Co(NO_3)_2 \cdot 6 H_2O$ releases a slight amount of crystal water which seems to increase the achieved NP size during the growth regime. OLA and OA are slowly oxidized during prolonged contact with air which may interfere with the particle stability. NaOH may incorporate CO_2 from the air which leads to jagged particle shapes. However, since the latter is a slow reaction between the solid and gaseous states, NaOH can be regarded as stable for >1 year. Glassware was cleaned with a diluted mixture of H_2SO_4 and H_2O_2 (piranha solution) and thoroughly rinsed with deionized water afterwards. Before usage, all glassware was washed with distilled water and EtOH *p.a.*.

1.2 General protocol for the synthesis of Co₃O₄ nanoparticles via hydroxide precursor particles

Co(NO₃)₂·6 H₂O (2 mmol, 0.582 g) was dissolved in 20 mL OLA in a three-necked flask with 2 mL of EtOH as phase mediator, and the mixture was subsequently stirred at 80°C for 30 min. For the precipitation of hydroxide-based precursor particles with a green-brown to brown colour, 2 mL NaOH solution (2.0 M in H₂O, 4 mmol) was injected, followed by stirring at 80°C for 1h. Afterwards, the reaction was cooled down to RT with an ice bath, and the low boiling co-solvents (H₂O and EtOH) were removed *in vacuo*. The temperature was step-wise increased to 80°C and held until no further evaporation could be observed. The precursor particles were then decomposed into Co₃O₄ at 180°C for 1h. The resulting nanoparticle dispersion was cooled down to RT, and 2 mL OA was added before stirring the solution for 30 min. Subsequently, the nanoparticles were precipitated with +150 vol% EtOH and separated by centrifugation (7500 rpm, 10 min, Allegra 64R benchtop centrifuge, Beckman Coulter), re-dispersed in hexane, and further stabilized with ca. 0.5 mL OA for at least four hours. Afterwards, the particles were purified by several centrifugation and re-dispersion steps with EtOH and hexane to remove traces of OLA and salts. After drying, the particles were re-dispersed in heptane and filtered through a 0.2 µm PTFE syringe filter.

To study the growth dynamics, variations were implemented with respect to (i) reaction temperatures and (ii) reagent concentrations.

(i) Variation of reaction temperature

For NP synthesis at lower temperatures of 60°C and 70°C, the solution was flash heated to 80°C before setting the target temperature and stirring for 30 min to ensure complete dissolution of $Co(NO_3)_2$ ·6 H₂O. For higher targeted reaction temperatures, the solution was stirred at 80°C for 30 min and subsequently heated to 90°C or 100°C.

(ii) Variation of reagent concentration

Reactions were also performed with systematically increased reagent concentrations. The different masses of the $Co(NO_3)_2 \cdot 6 H_2O$ educt dissolved in OLA and the corresponding concentrations of NaOH in 2 mL H₂O are summarized in **Table S1**.

Co(NO ₃) ₂ ·6 H ₂ O					
Amount of substance [mmol}	2	4	6	8	10
Mass [g]	0.582	1.164	1.746	2.328	2.910
Concentration [mol/L]	0.1	0.2	0.3	0.4	0.5
NaOH					
Concentration [mol/L]	2	4	6	8	10

Table S1: Overview of experimental parameters for the synthesis of Co_3O_4 nanoparticles in 20 mL oleylamine.

1.3 Growth series of Co_3O_4 nanoparticles prepared *via* hydroxide precursor particles with a growth time of four hours

With the aim to study the kinetics of NP formation, particle growth was monitored in different concentration regimes over a period of 4 h. These growth experiments were carried out solely at 100°C, since the narrowest particle size distributions (PSD) were obtained under these conditions. Otherwise, synthesis was performed as stated in chapter 1.2 with a growth time of 4h after the injection of NaOH. To achieve a higher overall particle count, all employed masses and volumina were tripled compared to the general protocol. The altered masses of $Co(NO_3)_2 \cdot 6 H_2O$ and the corresponding amounts of NaOH in 6 mL H₂O are summarized in **Table S2**.

$Co(NO_3)_2 \cdot 6 H_2O$				
Amount of substance [mmol}	6	12	18	24
Mass [g]	1.746	3.492	5.238	6.984
Concentration [mol/L]	0.1	0.2	0.3	0.4
NaOH				
Concentration [mol/L]	2	4	6	8

Table S2: Experimental parameters for the synthesis of Co_3O_4 nanoparticles in 60 mL oleylamine.

Aliquot extraction during a four-hour growth experiment

To gain mechanistic insights, aliquots were extracted from the reaction mixture after 1, 2, 3, 4, 5, 10, 15, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220, and 240 min reaction time. Per aliquot, 200 μ L of dispersion was withdrawn with a sterile 1 mL syringe and quenched in 2 mL of hexane. One droplet of the diluted dispersion was drop-casted onto a carbon-coated copper grid. After drying, the grid was washed with EtOH to remove the excess OLA. Subsequently, the dried specimen was subjected to transmission electron microscopy (TEM) analysis.

1.4 Instrumental Analysis

Transmission electron microscopy

Transmission electron microscopy (TEM) and selected area diffraction (SAED) images were acquired on a Zeiss EM922 Omega instrument equipped with a thermal LaB₆ cathode, an in-column omega filter, omega-type spectrometer and a Koehler illumination system at 200 kV. Image acquisition was performed with a Gatan CCD Camera (Ultrascan 1000) controlled by Gatan Microscopy Suite (GMS) 1.9 software. Prior to the measurements, nanoparticles were immobilized by drop-casting onto Cu TEM grids covered with a thin amorphous carbon layer (Plano GmbH, Germany). High-resolution (HR) TEM micrographs were obtained with a JEOL JEM-2200FS microscope (JEOL GmbH, Germany) equipped with a Schottky field emission gun (FEG Zr/W(100)) and an in-column omega energy filter at 200 kV. Images were recorded with a Gatan CMOS (One View) camera with GMS 3.11.

Image analysis was performed using *Gatan Digital Micrograph* and *Fiji* software.^{2,3} The particle dimensions were obtained as Feret diameters. Average particle diameters were determined by fitting a log-normal or Gaussian distribution depending on profile shape. Particle size distributions were calculated from the full width at half maximum (FWHM) of the fit functions. Wherever possible, an automated particle size determination was performed on binary images with image analysis tools implemented in *Fiji*. For specimens where images with insufficient contrast were obtained or the particles showed pronounced aggregation (mostly lower particle sizes and the entire time series for sample 100_{2mmol}^{4h}) at least 300 NPs were measured manually per data point/aliquot. SAED images were evaluated using the CrystBox software.⁴ Lattice spacings were measured with *Fiji*.

Powder X-ray diffraction

Powder X-ray diffraction (PXRD) data were measured in Bragg-Brentano geometry with an Empyrean diffractometer (PANalytical B.V.; Netherlands) using Cu-K_{α} radiation (λ =1.54187 Å). Diffractograms were analyzed with the *X'pert Highscore Plus* software. Nanoparticles were purified, dried and ground to powder prior to characterization by XRD.

2. Supplementary Figures and Analyses

2.1 Powder X-ray diffraction analysis of Co₃O₄ nanoparticles

The diffraction pattern of Co_3O_4 NPs produced in a 80_{2mmol}^{1h} reaction is displayed in **Figure S1**. The characteristic Bragg reflections can be assigned to the peak pattern of a Co_3O_4 reference diffractogram (Crystallography Open Database: 9005896). A pronounced sample-related background originating from X-ray fluorescence of Co-containing specimens illuminated with Cu-K_a radiation was subtracted from the data. For this reason, the inherently weak (222) reflex cannot be readily distinguished from noise.



Figure S1: X-ray diffractogram of a representative product of a 80_{2mmol}^{1h} reaction in 20 mL OLA. The red droplines indicate the peak positions of a Co₃O₄ reference pattern (Crystallography Open Database: 9005896). The detected peak signature is in agreement with previously reported data on NPs with spinel structure synthesized under similar conditions.¹

2.2 Selected area electron diffraction analysis of Co₃O₄ nanoparticles

Enlarged versions of the SAED images presented as insets in in **Figure 1**, corresponding to experiments performed at $T = 90^{\circ}$ C with $Co(NO_3)_2 \cdot 6 H_2O$ amounts of 2-8 mmol are displayed in **Figure S2**. In agreement with volume-averaging XRD data (Figure S1), all patterns in this series show the characteristic intensity signature of spinel-type Co_3O_4 even though the inherently weak (111) and (224) reflection give rise to only faint rings in some of the images.



Figure S2: SAED patterns corresponding to sample types (a) $90_{2\text{mmol}}^{1\text{h}}$, (b) $90_{4\text{mmol}}^{1\text{h}}$, (c) $90_{6\text{mmol}}^{1\text{h}}$, (d) $90_{8\text{mmol}}^{1\text{h}}$. Visible diffraction signals attributable to spinel-type Co₃O₄ are exemplarily indicated in (c), where the most pronounced and continuous ring pattern was observed. Peak assignment was performed according to Crystallography Open Database: 9005896.

Figure S3 exemplarily displays the characteristic background-corrected peak profile processed from the SAED image of a sample prepared with 6 mmol at T = 90°C. The observed peak pattern is in good agreement with the XRD signature presented in **Figure S1**. For better comparability, the scattering angle scale provided in the reference diffractogram used for peak assignment (Crystallography Open

Database: 9005896) was transformed to scattering vectors to match the data obtained from the TEM measurements. The peak positions of the nanoparticle sample appear slightly shifted compared to the reference diffractogram of bulk Co_3O_4 , which does, however, not prevent the identification of the spinel structure based on SAED. Peak shifts may occur due to internal strain or increased surface tension and are frequently observed for NPs.^{5,6} Changes to the lattice parameters of Co_3O_4 NPs have also been reported before.⁷ Higher order peaks seem to be shifted more noticeably compared to lower order ones, where such non-uniform peak shifts may for example be caused by stacking faults within the structure or by anisotropic strain along different lattice directions.⁸



Figure S3: Background-corrected diffraction profile obtained from sample type $90_{6\text{mmol}}^{1\text{h}}$ (**Figure S2 c**) compared to a calculated diffractogram of bulk Co₃O₄ with spinel structure (Crystallography Open Database: 9005896).

2.3 Concentration- and temperature-dependent synthesis of Co₃O₄ nanoparticles

 Co_3O_4 NPs were synthesized with concentrations of 2, 4, 6, and 8 mmol of $Co(NO_3)_2 \cdot 6 H_2O$ in 20 mL OLA at temperatures between 60 and 100°C. TEM micrographs of the reaction products are displayed in **Figure S4**. The resulting sizes and PSDs are summarized in **Table 1** in the main text.



Figure S4: TEM micrographs of Co_3O_4 NPs synthesized with $Co(NO_3)_2$ ·6 H₂O concentrations of 2, 4, 6, and 8 mmol in 20 mL OLA. The reaction temperature was varied between 60-100°C in steps of 10°C.

2.4 Co₃O₄ nanoparticle synthesis at an elevated salt concentration

A control experiment with a very high salt concentration of 10 mmol $Co(NO_3)_2 \cdot 6 H_2O$ in 20 mL OLA and a reaction temperature of 100°C yielded particles with a size of 9.10 nm ±2.75 nm and a broad size distribution (30.2% PSD) as readily apparent in **Figure S5**. As compared to sample 100_{8mmol}^{1h} (13.49 nm ± 1.63 nm), the average particle size is also reduced. Based on these results, we conclude that a concentration of 10 mmol $Co(NO_3)_2 \cdot 6 H_2O$ in 20 mL OLA exceeds the solubility limit. Thus, we estimate the maximum of $Co(NO_3)_2 \cdot 6 H_2O$ loading (in 20 mL OLA) to be in the range between 8 mmol and 10 mmol. For this reason, experiments with 10 mmol $Co(NO_3)_2 \cdot 6 H_2O$ were not performed at temperatures below 100°C temperatures due to the even lower salt solubility to be expected. Since a similar result was observed with 8 mmol of $Co(NO_3)_2 \cdot 6 H_2O$ at T = 70°C, a reaction with this high amount of salt was also omitted at the lowest considered reaction temperature of T = 60°C.



Figure S5: TEM micrograph of Co_3O_4 nanoparticles synthesized with $[Co(NO_3)_2 \cdot 6 H_2O] = 10 \text{ mmol}/20 \text{ mL OLA of}$ at T $= 100^{\circ}C$ exhibiting irregular shapes and a high PSD of 30.2%.

2.5 Co₃O₄ nanoparticle synthesis at temperatures above 100°C

The decomposition temperature of solid $Co(NO_3)_2 \cdot 6 H_2O$ is stated as $100^{\circ}C.^{9}$ However, this does not appear to hold true when dissolved in OLA since the reaction works unhindered at $100^{\circ}C$. Therefore, control experiments were performed at elevated temperatures of $110^{\circ}C$ ($^{110}_{6mmol}$), $120^{\circ}C$ ($^{120}_{6mmol}$), and $130^{\circ}C$ ($^{130}_{6mmol}$). The results are displayed in **Figure S6** and the corresponding average NP sizes show a systematic decrease with increasing temperature as documented in **Table S3**.



Figure S6: TEM micrographs of Co_3O_4 NPs obtained from sample types 110_{6mmol}^{1h} , 120_{6mmol}^{1h} , 130_{6mmol}^{1h} .

While sample type 110_{6mmol}^{1h} , in particular, appears to be a good candidate if reaction conditions for narrow size distributions are desired, it should be noted that the yield is significantly reduced compared to an experiment performed at $100^{\circ}C$ (100_{6mmol}^{1h}) . This trend continues when the temperature is raised even further. Finally, $Co(NO_3)_2 \cdot 6 H_2O$ decomposes at temperatures >125°C accompanied by smoke emission. The low number of remaining NPs exhibits a broad PSD. At 120°C, impurities become apparent in TEM analysis, which may be attributable to the effects of boiling water or the onset of $Co(NO_3)_2 \cdot 6 H_2O$ decomposition.

Table S3: Particle sizes and size distributions of 1	$110_{6 \text{mm}}^{-1 \text{h}}$	$_{\rm ol}$ 120 $_{\rm 6mmol}^{\rm lh}$, and $130_{6\mathrm{mmo}}^{1\mathrm{h}}$	J.
--	-----------------------------------	---	---	----

Temperature [°C]	Particle size [nm]	PSD [%]
110	11.29 ± 1.34	11.9
120	10.83 ± 1.47	13.6
130	9.50 ± 2.55	26.8

2.6 The synthesis of Co_3O_4 nanoparticles in the absence of NaOH at T = 100°C

At T = 100°C, Co₃O₄ NPs may also be synthesized without utilizing NaOH for the intermediate formation of the hydroxide-based precursor. While the yield of this reaction is comparable to sample type 100_{2mmol}^{1h} , the particle size histogram shows a bimodal distribution with maxima around 7.5 nm and 12 nm (**Figure S7 b**). A NaOH-free experiment at T = 80°C did not yield any NPs, though. Based on these results, it appears that NaOH indeed facilitates the precipitation of Co(OH)₂ precursor particles and leads to a narrower PSD.



Figure S7: a) TEM micrograph of Co_3O_4 NPs synthesized without the addition of NaOH ($^{100_{2}}$ mmol) and b) the corresponding count-size histogram.

2.7 Co₃O₄ growth series over four hours

Time-resolved nanoparticle growth experiments were performed at $T = 100^{\circ}C$ at different reagent concentrations to assemble the growth curves presented in **Figure 2**. The formation and development of the Co₃O₄ particles were monitored over a time period of four hours (after NaOH injection) by aliquot extraction after 1, 2, 3, 4, 5, 10, 15, 20, 40, 60, 80, 100, 120, 140, 160, 180, 200, 220, and 240 min and evaluation of the corresponding particle sizes based on TEM image analyses (**Figs. S8-S11**). For the time-resolved experiments, the batch size was up-scaled by a factor of three to reduce the relative loss of reaction volume due to the removal of aliquots. The reproducibility of the NP size and shape in the larger batch additionally serves as proof for the scalability of the reaction and provides a facile route towards a larger number of NPs per batch.

2.7.1 Growth series for sample 100_{6mmol}^{4h}

The reaction corresponding to sample type $100_{2\text{mmol}}^{1\text{h}}$ as described above, was up-scaled by a factor of three to a total batch volume of 60 mL OLA, 6 mL EtOH, 6 mL NaOH solution (2M) and a Co(II) content of 6 mmol of Co(NO₃)₂·6 H₂O. Additionally, the duration of particle growth was increased from 1h to 4h to monitor the development of the NPs for a longer period of time. For brevity, this experiment is termed $100_{6\text{mmol}}^{4\text{h}}$. TEM micrographs of the extracted aliquots are displayed in **Figure S8**, and the corresponding particle sizes are summarized in **Table S4**. As apparent from the TEM images, the Co₃O₄ particles exhibit a pronounced tendency towards aggregation and agglomeration even in the early stages of the synthesis (onset after ca. 20 min). This may be a result of the low initial reagent concentration leading to rapid depletion of the precursor solution. Monomer depletion is expected to cause a broadening of the PSD due to Ostwald ripening. This process increases the tendency towards aggregation, since the monomer shell surrounding the individual particles shrinks, which makes direct inter-particle contact more probable.^{10–12}



Figure S8: TEM micrographs recorded for a series of extracted aliquots to generate a growth curve for Co_3O_4 NPs prepared at T = 100°C with a total growth time of 4h (${}^{100}_{6mmol}$). The time points of aliquot extraction are stated in the respective images.

Growth time	Particle size	PSD
[min]	[nm]	[%]
1	2.43 ± 0.65	26.7
2	2.15 ± 0.51	23.7
3	3.11 ± 0.77	24.7
4	3.88 ± 0.97	25.4
5	3.63 ± 0.76	21.0
10	4.84 ± 1.29	26.6
15	5.04 ± 1.46	29.0
20	6.46 ± 1.50	23.1
40	6.92 ± 1.80	26.0
60	8.23 ± 1.67	20.3
80	8.04 ± 2.37	29.7
100	8.25 ± 2.12	25.7
120	8.30 ± 1.90	23.0
140	8.12 ± 2.10	25.6
160	8.26 ± 2.71	33.0
180	7.94 ± 2.14	27.0
200	8.31 ± 2.40	28.7
220	8.13 ± 2.30	28.2
240	8.37 ± 1.96	23.4

Table S4: Time-dependent average nanoparticle sizes and particle size distributions of sample type 100_{6mmol}^{4h}

2.7.2 Growth series for sample ${100_{12}}^{4\mathrm{h}}_{\mathrm{12mmol}}$

The reaction corresponding to sample type $100_{4\text{mmol}}^{1\text{h}}$ as described above, was up-scaled by a factor of three to a total batch volume of 60 mL OLA, 6 mL EtOH, 6 mL NaOH solution (4M) and a Co(II) content of 12 mmol of Co(NO₃)₂·6 H₂O. Additionally, the duration of particle growth was increased from 1h to 4h to monitor the development of the NPs for a longer period of time. For brevity, this experiment is termed $100_{12\text{mmol}}^{4\text{h}}$. TEM micrographs of the extracted aliquots are displayed in **Figure S9**, and the corresponding particle sizes are summarized in **Table S5**.

Based on the examination of the TEM micrographs, the particles exhibit a substantial tendency towards aggregation/agglomeration after 120 min growth time, where this effect becomes even more apparent at a reaction duration of around 200 min.



Figure S9: TEM micrographs recorded for a series of extracted aliquots to generate a growth curve for Co_3O_4 NPs prepared at T = 100°C with a total growth time of 4h (100_{12mmol}) . The time points of aliquot extraction are stated in the respective images.

Growth time	Particle size	PSD
[min]	[nm]	[%]
1	2.75 ± 0.93	34.0
2	2.35 ± 0-60	25.5
3	2.75 ± 0.46	16.8
4	3.36 ± 0.84	25.0
5	3.61 ± 0.80	22.1
10	3.72 ± 0.76	20.4
15	3.67 ± 0.61	16.7
20	4.13 ± 0.86	21.0
40	6.12 ± 0.97	16.0
60	8.02 ± 1.07	13.4
80	8.42 ± 1.83	21.7
100	8.03 ± 1.25	15.6
120	8.20 ± 1.70	21.0
140	8.94 ± 2.00	22.2
160	8.80 ± 1.90	21.6
180	9.02 ± 2.23	24.7
200	8.73 ± 1.90	22.0
220	8.97 ± 2.11	23.5
240	9.55 ± 2.40	25.0

Table S5: Time-dependent average nanoparticle sizes and particle size distributions of sample type 100_{12mmol}^{4h}

2.7.3 Growth series for sample $100_{18 \text{mmol}}^{4\text{h}}$

The reaction corresponding to sample type 100_{6mmol}^{1h} . as described above, was up-scaled by a factor of three to a total batch volume of 60 mL OLA, 6 mL EtOH, 6 mL NaOH solution (6M) and a Co(II) content of 18 mmol of Co(NO₃)₂·6 H₂O. Additionally, the duration of particle growth was increased from 1h to 4h to monitor the development of the NPs for a longer period of time. For brevity, this experiment is termed 100_{18mmol}^{4h} . TEM micrographs of the extracted aliquots are displayed in **Figure S10**, and the

corresponding particle sizes are summarized in **Table S6**. Contrarily to samples 100_{6mmol}^{4h} and 100_{12mmol}^{4h} , the particles appear to be stable in dispersion until the end of the experiment.



Figure S10: TEM micrographs recorded for a series of extracted aliquots to generate a growth curve for Co_3O_4 NPs prepared at T = 100°C with a total growth time of 4h $(100_{18 \text{mmol}}^{4\text{h}})$. The time points of aliquot extraction are stated in the respective images.

Growth time	Particle size	PSD
[min]	[nm]	[%]
1	3.44 ± 0.86	25.0
2	3.65 ± 0.77	21.1
3	3.04 ± 0.57	19.0
4	3.68 ± 1.03	28.1
5	3.73 ± 0.83	22.4
10	4.13 ± 1.15	28.0
15	4.41 ± 1.00	22.5
20	5.80 ± 1.10	19.0
40	8.36 ± 1.40	16.5
60	9.21 ± 1.76	19.1
80	9.10 ± 1.77	19.4
100	9.51 ± 1.85	19.5
120	10.70 ± 1.50	14.0
140	10.43 ± 1.73	16.6
160	11.31 ± 1.91	17.0
180	11.51 ± 1.81	15.7
200	11.70 ± 2.04	17.5
220	11.38 ± 1.70	15.0
240	11.98 ± 2.04	17.0

Table S6: Time-dependent average nanoparticle sizes and particle size distributions of sample type $100_{18 mmol}^{4h}$

2.7.4 Growth series of sample ${100_{24}}^{4h}_{mmol}$

The reaction corresponding to sample type 100_{8mmol}^{1h} as described above, was up-scaled by a factor of three to a total batch volume of 60 mL OLA, 6 mL EtOH, 6 mL NaOH solution (8M) and a Co(II) content of 24 mmol of Co(NO₃)₂·6 H₂O. Additionally, the duration of particle growth was increased from 1h to 4h to monitor the development of the NPs for a longer period of time. For brevity, this experiment is termed 100_{24mmol}^{4h} . TEM micrographs of the extracted aliquots are displayed in **Figure S11**, and the

corresponding particle sizes are summarized in **Table S7**. Similar to sample $100_{18\text{mmol}}^{4\text{h}}$, the particles do not appear to aggregate until the end of the experiment.



Figure S11: TEM micrographs recorded for a series of extracted aliquots to generate a growth curve for Co_3O_4 NPs prepared at T = 100°C with a total growth time of 4h $(100_{24 \text{mmol}}^{4\text{h}})$. The time points of aliquot extraction are stated in the respective images.

Growth time	Particle size	PSD
[min]	[nm]	[%]
1	2.80 ± 0.55	20.0
2	3.24 ± 0.80	24.3
3	4.04 ± 1.04	25.6
4	3.97 ± 1.06	26.6
5	4.46 ± 1.11	25.0
10	4.63 ± 1.51	32.6
15	4.93 ± 1.00	20.3
20	6.00 ± 1.22	20.4
40	7.72 ± 1.40	18.1
60	10.30 ± 2.32	22.6
80	10.56 ± 2.02	19.2
100	11.47 ± 2.60	22.6
120	11.54 ± 2.63	22.0
140	12.57 ± 2.33	18.5
160	12.57 ± 2.16	17.2
180	11.78 ± 2.25	19.1
200	12.31 ± 2.90	23.4
220	12.82 ± 2.49	19.4
240	13.39 ± 2.46	18.4

 $\textbf{Table S7}: \textbf{Time-dependent average nanoparticle sizes and particle size distributions of sample type} \ \frac{100_{24 \text{mmol}}^{4 \text{h}}}{100_{24 \text{mmol}}}.$

2.8 Evaluation of the concentration-dependent particle size distribution during a four-hour growth experiment

To qualitatively compare the concentration-dependent particle size distributions, the average PSD values were calculated for each NP growth series from all data points with growth periods > 60 min as displayed in **Table S8** (*cf.* **Tables S4-S7** for individual PSD values used as input). Since TEM data show that particles obtained at reaction times below 60 min exhibit a relatively low count along with a slightly broader PSD (*cf.* **Figures. S8-S11**), only the data points recorded at longer growth periods > 60 min are evaluated. Furthermore, the particle growth is slow and steady at reaction stages after 60 min which makes the values more comparable.

As an overall trend, the averaged PSD for sample type $100_{6\text{mmol}}^{4\text{h}}$ is clearly higher than the values obtained for the other samples prepared at higher reagent concentrations. Interestingly, though, the PSD observed in sample $100_{18\text{mmol}}^{4\text{h}}$, was even slightly lower than in sample $100_{24\text{mmol}}^{4\text{h}}$.

Based on these growth series experiments, the most reliable concentration to achieve narrow PSDs in a standard reaction (*i.e.* 20 mL reaction volume) seems to be 6 mmol of $Co(NO_3)_2 \cdot 6 H_2O$ per 20 mL of OLA for variable growth times. As displayed in **Table 1** (in the main text), however, a concentration of 8 mmol/20 mL OLA may lead to narrower size distributions and should in practice not be inferior while offering a higher yield.

Table S8: Average PSD [%] of data points recorded for reaction times between 60-240 min in concentration-dependent growth experiments.

100 ^{4h} _{6mmol}	4h	4h	4h
	100 _{12mmol}	100 _{18mmol}	100 _{24mmol}
26.5 ± 3.5	21.1 ± 3.6	17.1 ± 1.8	20.2± 2.1

2.9 Development of edges and corners at higher concentrations

After long growth periods (*i.e.* 220 min), significant morphological differences are observed between samples prepared at different reagent concentrations (*cf.* **Figure S12**). The contribution of edges and corners to the particle surface energy is comparably high, which renders these features more difficult to stabilize.^{13–15} Therefore, well-developed, clearly faceted nanoparticles are more readily achieved at higher reagent concentrations. Consequently, the edges and corners of the samples 100_{6mmol}^{4h} and 100_{12mmol}^{4h} appear blunted. Curiously, however, slightly more faceted particles seem to be present in the specimen prepared at the lowest evaluated Co(II) concentration (100_{6mmol}^{4h}).



Figure S12: Comparison of TEM micrographs recorded at a growth time of 220 min from samples with increasing reagent concentration: a) $100_{6\text{mmol}}^{4\text{h}}$ b) $100_{12\text{mmol}}^{4\text{h}}$ c) $100_{18\text{mmol}}^{4\text{h}}$ and d) $100_{24\text{mmol}}^{4\text{h}}$.

This observation might be related to the fact that the monomer pool is thoroughly exhausted in this case, based on the growth curve (*cf.* **Figure 2**). Therefore, NPs may only change their shape when ions transition between individual particles and not by monomer addition.^{12,16} In the case of monomer-mediated mass transfer (Ostwald ripening), edges and corners would be expected to redissolve first.

Samples $100_{18\text{mmol}}^{4\text{h}}$ and $100_{24\text{mmol}}^{4\text{h}}$, by contrast, are composed of facetted NPs with well-developed nanocube morphologies and it is readily apparent from a comparison between **Figures S12 c** and **d** that the NPs in sample $100_{24\text{mmol}}^{4\text{h}}$ exhibit even more clearly defined crystal facets. The latter indicates that experiment $100_{18\text{mmol}}^{4\text{h}}$ needs to be terminated after a shorter NP growth period (*i.e.* 180 min) when a regular cube shape is desired for the envisaged applications of the NP product.

3. References

- J. Kießling, S. Rosenfeldt and A. S. Schenk, *Nanoscale Adv.*, 2023, 5, 3942–3954.
- J. Schindelin, I. Arganda-Carreras, E. Frise, V. Kaynig, M. Longair, T. Pietzsch, S. Preibisch, C. Rueden, S. Saalfeld, B. Schmid, J.-Y. Tinevez, D. J. White, V. Hartenstein, K. Eliceiri, P. Tomancak and A. Cardona, *Nat. Methods*, 2012, 9, 676–682.
- 3 C. T. Rueden, J. Schindelin, M. C. Hiner, B. E. DeZonia, A. E. Walter, E. T. Arena and K. W. Eliceiri, *BMC Bioinformatics*, 2017, **18**, 529.
- 4 M. Klinger, J. Appl. Crystallogr., 2017, 50, 1226–1234.
- 5 Z. Wei, T. Xia, J. Ma, W. Feng, J. Dai, Q. Wang and P. Yan, *Mater. Charact.*, 2007, **58**, 1019– 1024.
- 6 C. F. Holder and R. E. Schaak, *ACS Nano*, 2019, **13**, 7359–7365.
- 7 A. M. Abdallah and R. Awad, J. Supercond. Nov. Magn., 2020, **33**, 1395–1404.
- 8 O. Seo, O. Sakata, J. M. Kim, S. Hiroi, C. Song, L. S. R. Kumara, K. Ohara, S. Dekura, K. Kusada, H. Kobayashi and H. Kitagawa, *Appl. Phys. Lett.*, DOI:10.1063/1.5006830.
- 9 D. R. Lide and G. Baysinger, *CRC Handbook of Chemistry and Physics*, CRC Press, 90th edn., 2010.
- 10 I. M. Lifshitz and V. V. Slyozov, J. Phys. Chem. Solids, 1961, **19**, 35–50.
- 11 C. Wagner, Zeitschrift für Elektrochemie, Berichte der Bunsengesellschaft für Phys. Chemie, 1961, **65**, 581–591.
- 12 C. L. Kuo and K. C. Hwang, *Chem. Mater.*, 2013, **25**, 365–371.
- 13 N. Moll, M. Scheffler and E. Pehlke, *Phys. Rev. B*, 1998, **58**, 4566–4571.
- 14 A. S. Barnard and P. Zapol, J. Chem. Phys., 2004, **121**, 4276–4283.
- 15 J. M. Rahm and P. Erhart, *Nano Lett.*, 2017, **17**, 5775–5781.
- 16 L. Ratke and P. W. Voorhees, *Growth and Coarsening*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2002.