Electronic supplementary information

Counter-ion influence on the mechanism of HMTA-mediated ZnO formation

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TABLE OF CONTENTS

ESI SECTION 1 EXPERIMENTAL

Materials

Ammonia (28 %, GPR rectapur) was acquired from VWR, hexamethylenetetramine (HMTA, >99.0 %, ACS reagent) was acquired from Sigma-Aldrich, Zinc acetate dihydrate ($ZnAc_2$, 98+ %, ACS reagent), zinc chloride ($ZnCl_2$, 97+ %, ACS reagent), zinc nitrate hexahydrate ($Zn(NO_3)_2$, 98 %, ACS reagent) and zinc sulphate heptahydrate ($ZnSO_4$, 99 %, ACS reagent) were acquired from Acros organics. All chemicals were used as received unless stated otherwise.

Methods

Synthesis

In a standard synthesis 50 mM of zinc salt and 25 mM of HMTA were dissolved in 50 ml pure water in a 100 ml three-neck round-bottom flask under reflux. The solution was magnetically stirred (vortexing at, 450 rpm) for at least 15 minutes the before start of the reaction. The reaction pH and temperature were registered using a Metrohm unitrode pH probe. The reaction flask was suspended in an oil bath and the reaction was subsequently initiated by gradually heating to 60 or 80 °C under continued stirring. The reaction was terminated after 6 h and the final dispersion was collected. In the case that the product formed dominantly on the flask wall, ultrasonication was used to remove parts of the formed products from the flask wall. All dispersions were subsequently purified by centrifugation using an Optima L-90K ultracentrifuge equipped with a Type 70 Ti rotor at 20.000 rpm for 20 min. The pellet was redispersed in pure water followed by another centrifugation step. This procedure was performed twice. After centrifugation the solid product was dried at room temperature.

For the SEM sampling experiments, the reactions were performed in 25 ml vials using 10 ml reaction solutions. A glass cover slide (precleaned with ethanol) was diagonally suspended in the vial. The vial was suspended in an oil bath and the reaction was subsequently initiate by gradually heating to 80 °C under stirring. The reaction was terminated by removing the cover slide and rising it with pure water several times.

Analysis

Cryogenic transmission electron microscopy (CryoTEM) samples were prepared by depositing 3 µl of reaction solution on a 200 mesh Cu grid covered with a Quantifoil R 2/2 holey carbon films (Quantifoil Micro Tools GmbH). An automated vitrification robot (FEI Vitrobot Mark III) preheated to 60 °C at 100% humidity was used for blotting and plunging in liquid ethane. All TEM grids were surface plasma treated for 40 seconds using a Cressington 208 carbon coater prior to use.

In case of discrete sampling at elevated temperatures the Vitrobot chamber and the used pipet tip were preheated to 60 °C to minimize sample preparation artifacts due to cooling. The TEM grid was placed in the Vitrobot several minutes before applying the sample to allow for thermal equilibration. Finally, the sample was taken directly from the reaction solution and rapidly transferred onto the grid in the Vitrobot followed by blotting and plunge freezing.

Cryo-TEM studies were performed on the TU/e cryoTITAN (FEI, www.cryotem.nl) which is equipped with a field emission gun (FEG), a postcolumn Gatan Energy Filter (model 2002) and a post-GIF 2k x 2k Gatan CCD camera (model 794). The microscope was operated at 300 kV acceleration voltage in bright field mode with zero-loss energy filtering using an electron flux between 2 – 24 $e^-/ Å^2s$. and a 1s image acquisition time.

Powder X-ray diffraction (pXRD) measurements were performed on a MiniFlex 600 diffractometer using Cu Kα radiation (1.54 nm), operating at 40 kV and 15 mA.

Scanning electron microscopy (SEM) was carried out on an 3D FEG Quanta (Thermo Fischer Scientific) equipped with a secondary electron detector and operated at 5.0 kV. SEM samples prepared on glass were sputter coated with a 10 nm gold layer using an Emitech K575X sputter coater to improve conductivity. The samples in powder form were dispersed in pure water, 10 µL dispersion was deposited on a continuous carbon coated TEM grid with copper or gold supports (200 mesh) followed by manual blotting after 40 seconds. Samples were loaded in the SEM using an in-house build custom SEM holder that can accommodate 6 TEM grids.

ESI SECTION 2 FIGURES

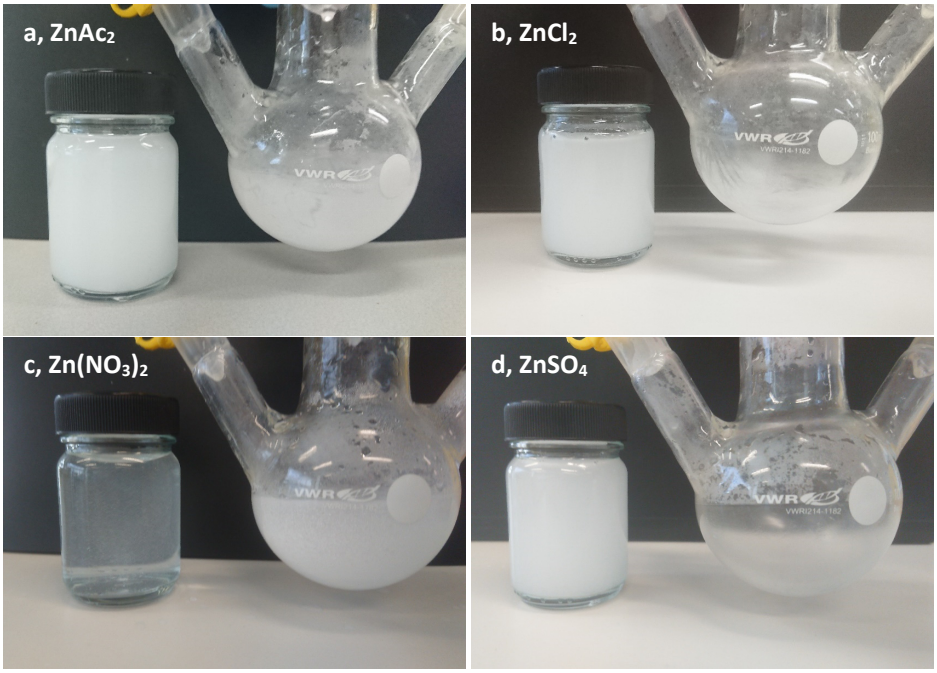


Figure S1 Pictures of the reaction flask and a storage jar containing the final dispersion for reactions performed with $ZnAc_2$ (a), $ZnCl_2$ (b), $Zn(NO_3)_2$ (c) and $ZnSO_4$ (d) at 80 °C.

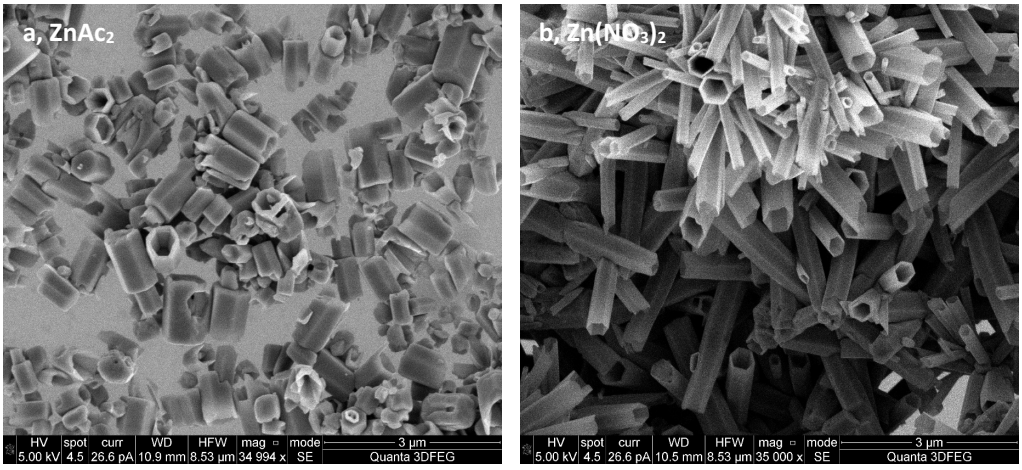


Figure S2 SEM images of hollow ZnO pillars synthesized from $ZnAc_2$ (a) and $Zn(NO_3)_2$ (b) purified at least 24 hours after the reaction was terminated.

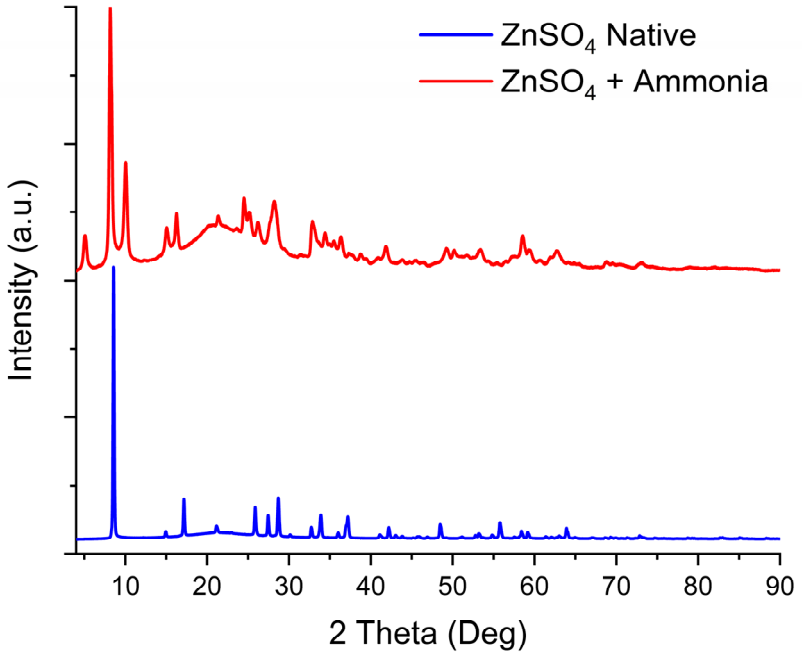


Figure S3 pXRD data of $Zn_4(OH)_6SO_4{\cdot}4H_2O$ (a) and a mixture of zinc sulphate hydroxy hydrate salts (b) formed from $ZnSO_4$ under native reaction conditions and with an initial addition of ammonia to increase the amount of base present, respectively.

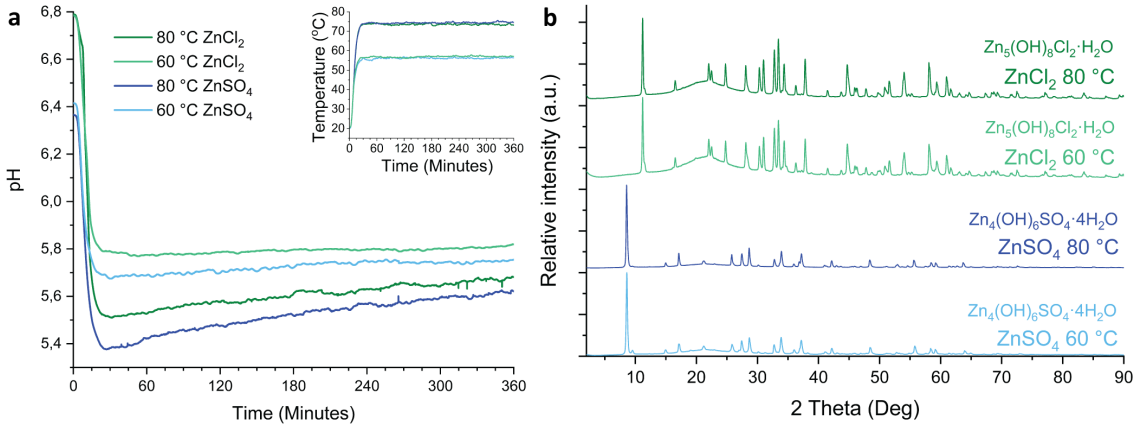


Figure S4 pH and temperature profiles (a) and pXRD data (b) of the reaction using $ZnCl_2$ and $ZnSO_4$ as zinc source at 60 and 80 °C reaction temperature.

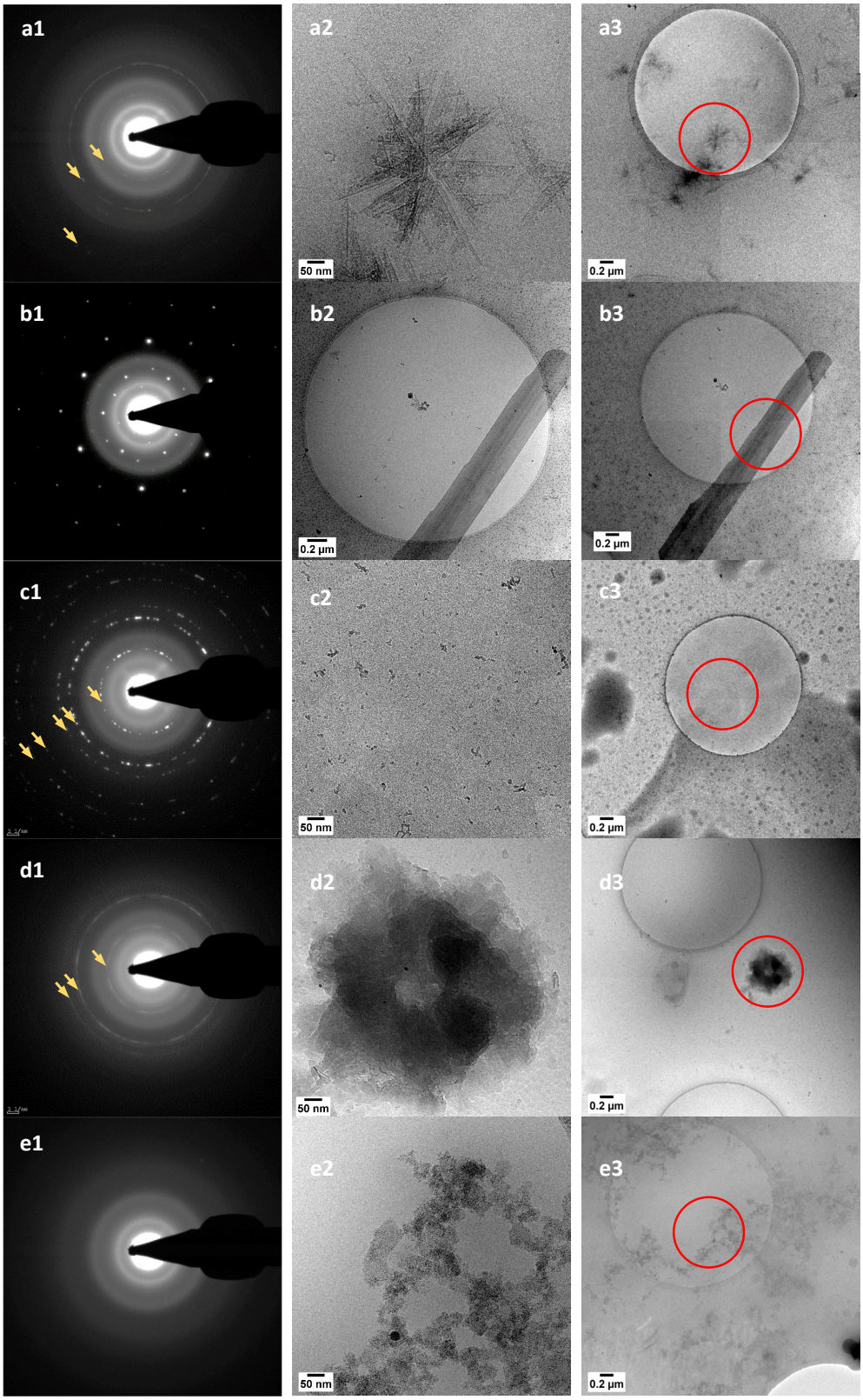


Figure S5 Low Dose Selected Area Electron diffraction (LDSAED) patterns (a1-e1),corresponding cryoTEM images (a2-e2) and the selected area location encircled in red (a3-e3) from the radial averaging plots showed in *Fig. 3.* LBZA sheets formed initially at RT (a), matured LBZA sheets (b), and species observed during the LBZA collapse; high contrast particulated regions (c), disorganized sheet clusters (d) and particle clusters (e). Diffraction rings are indicated with yellow arrows.

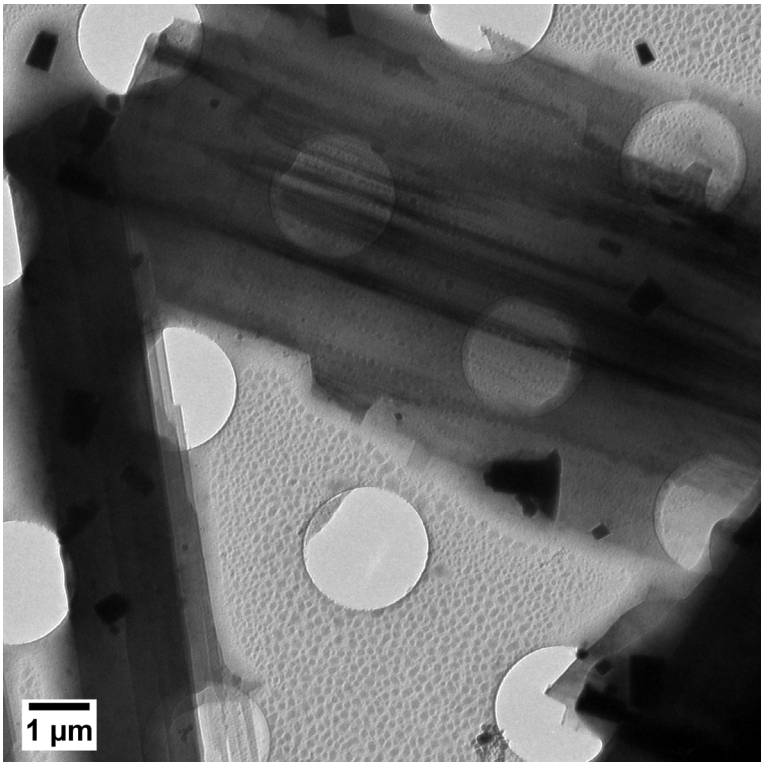


Figure S6 CryoTEM image of large LBZA sheets and small ZnO crystals observed in region II.

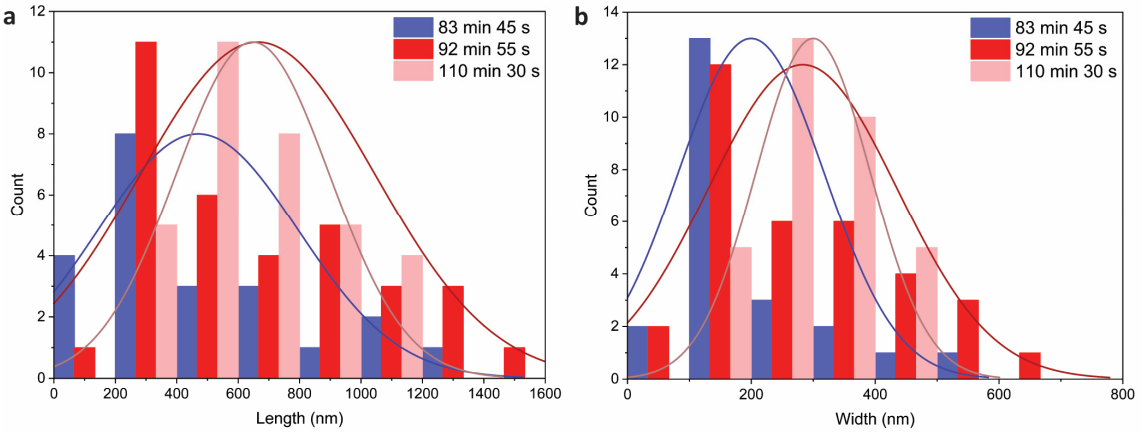


Figure S7 Histogram of the measured length (a) and width (b) of ZnO crystals observed by cryoTEM just before (83 min 45 s, blue), at the beginning (92 min 55 s, red) and at the end (110 min 30 s, pink) of the second $ZnAc_2$ pH drop. All data was taken from cryoTEM experiment 4 (ESI section 3). Using a two-sided independent t-test it is found that the average length (l) at 92 min 55 s (l = 660 nm, S_l = 380 nm, N = 34) and 110 min 30 s (l = 650 nm, S_l = 250 , N = 33) is not equal to the average length at 83 min and 45 s (l = 470 nm, S_l = 330 nm, N = 22) with a probability of 95.4 and 96.4 %, respectively. It was found that the average width (w) at 92 min 55 s (w = 280 nm, S_w = 150 nm, N = 34) and 110 min 30 s (w = 300 nm, S_w = 90 , N = 33) is not equal to the average width at 83 min and 45 s (w = 200 nm, S_w = 120 nm, N = 22) with a probability of 97.5 and 99.8 %, respectively.

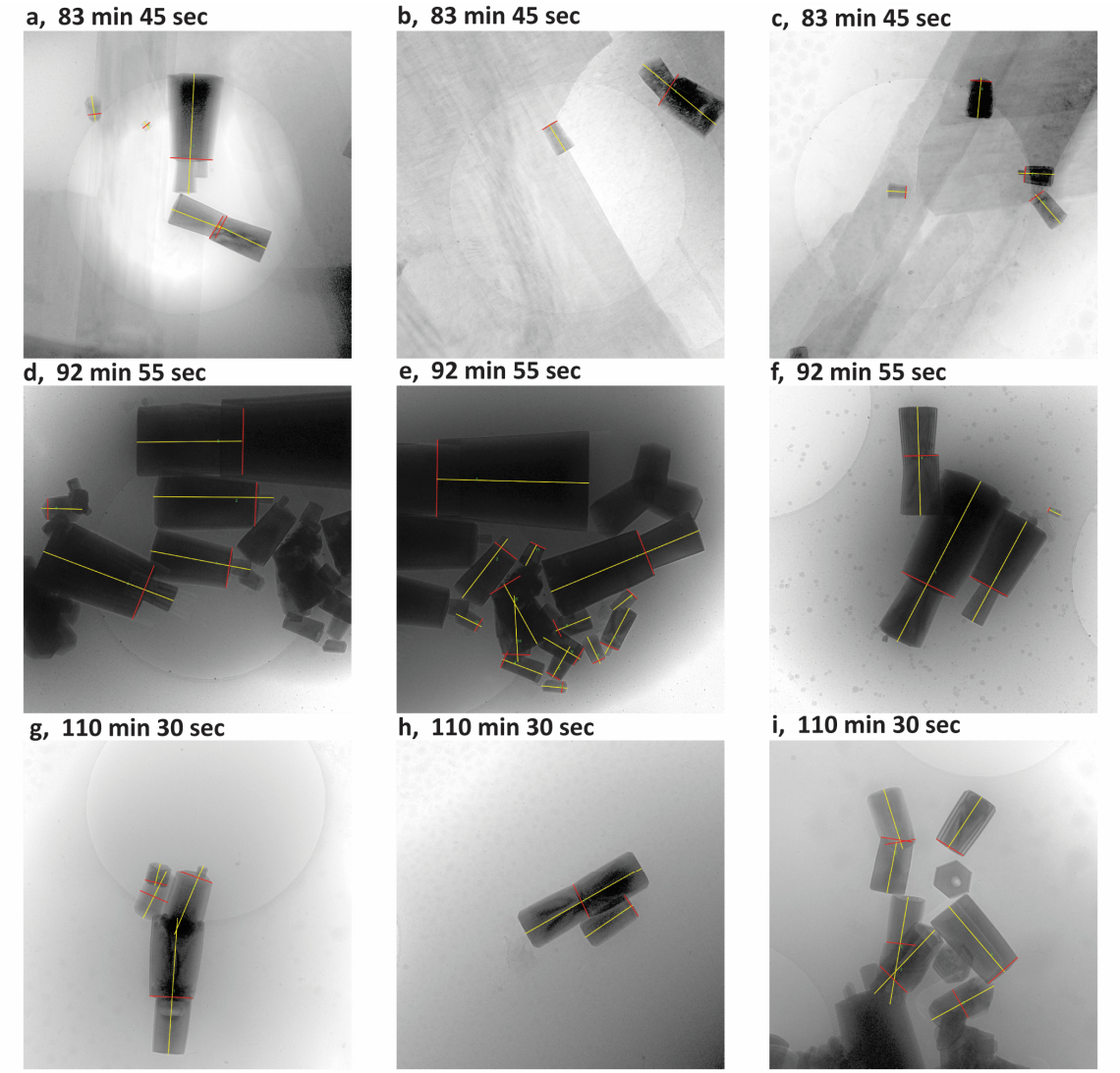


Figure S8 CryoTEM images at 83 min 45 s, 92 min 55 and at 110 min 30 s sampling time used for particle size analysis. The red lines indicate measured withs and the yellow lines indicate measured lengths. The contrast was modified to distinguish between individual ZnO particles. Data collected from these images and at least 4 additional images per sampling time were used to compose the histograms in *Fig. S7* and the particles sizes in the main text.

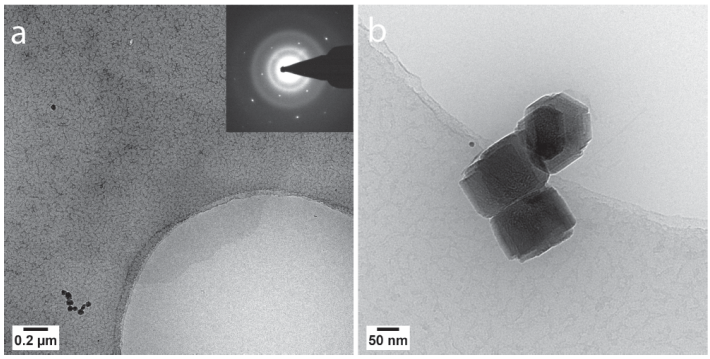


Figure S9 CryoTEM images of the $Zn(NO_3)_2$ reaction sampled at 15 min reaction time, showing incidentally observed particles including one LBZN sheet (a) and two twined ZnO crystals (b).

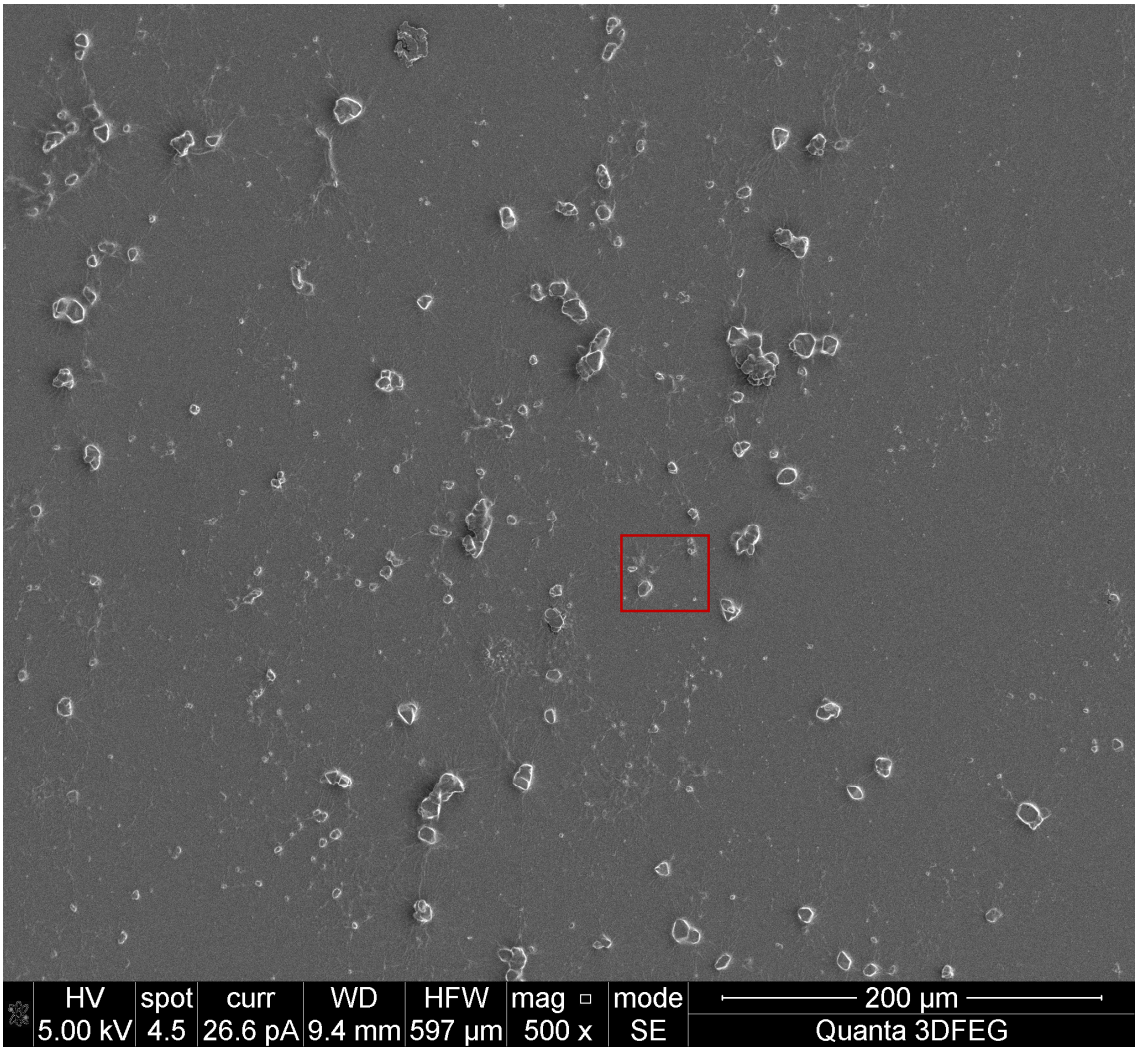


Figure S10 Lower magnification SEM image of the region showed in Fig. 5b. The location of Fig. 5b has been indicated in red.

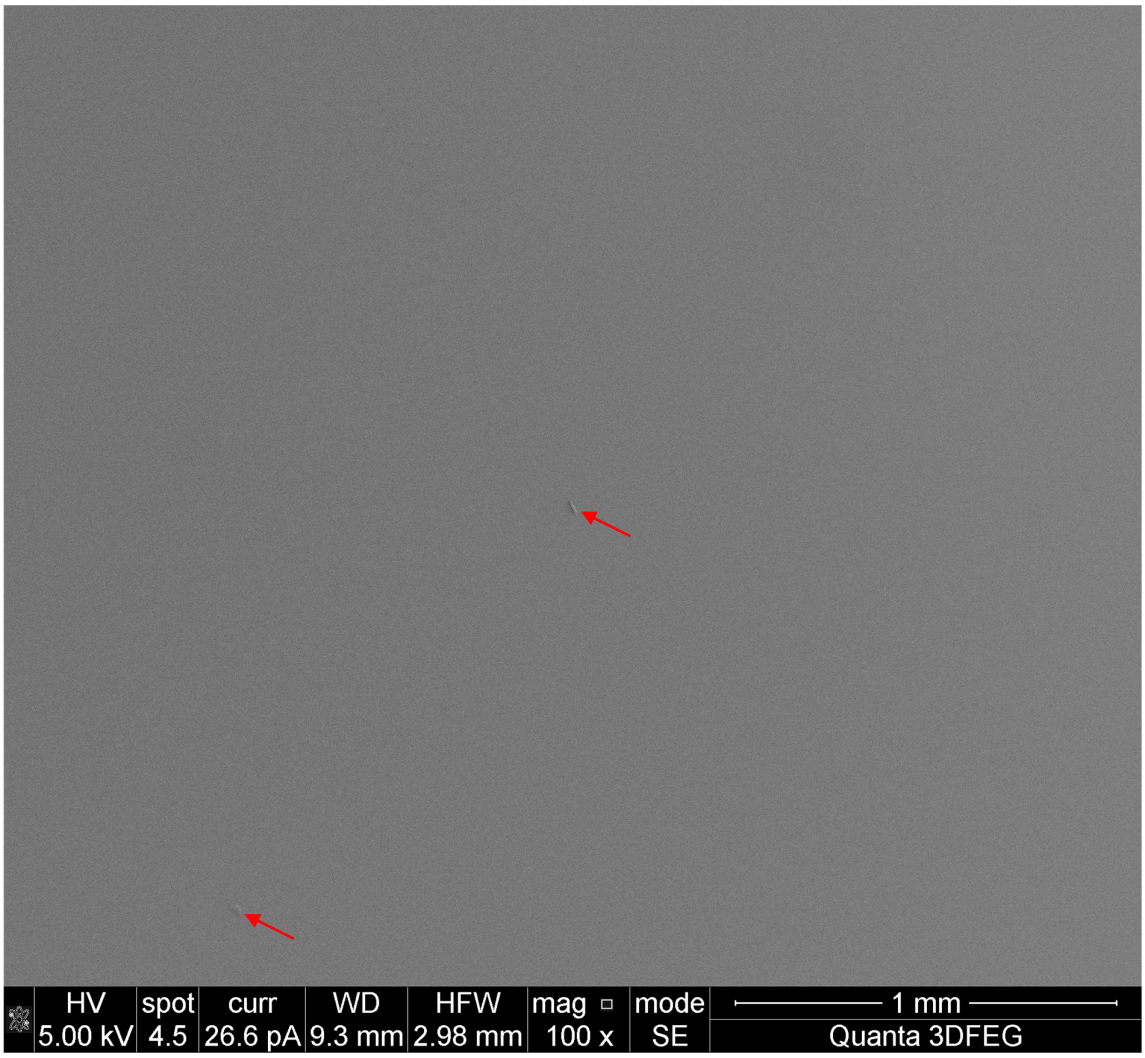


Figure S11 SEM images of a glass surface suspended in a $ZnAc_2$ reaction for the first 30 minutes, showing two particles (red arrow) in a field of roughly 9 mm^2. This shows that the image is in focus and no significant surface growth occurs at this time point.

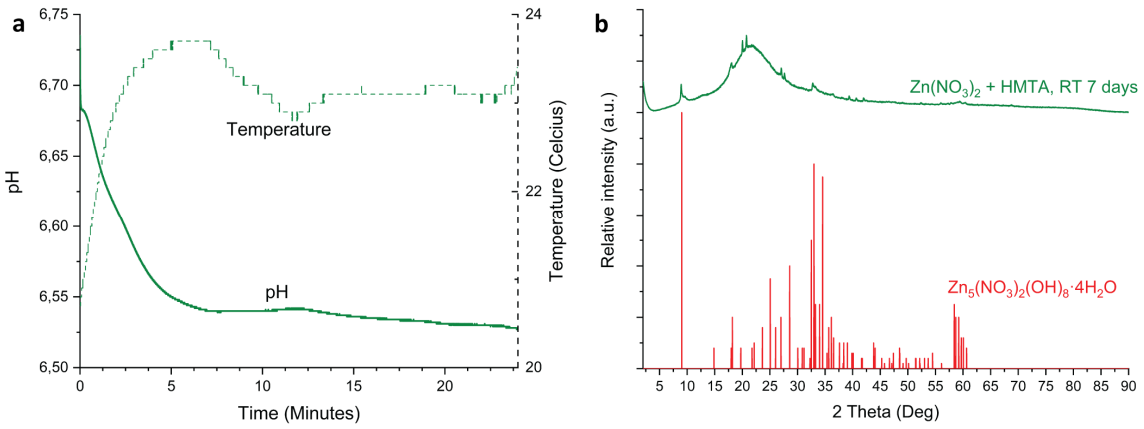


Figure S12 pH and temperature (a) profile of $Zn(NO_3)_2$ and HMTA in water incubated for 24h at RT. pXRD data (b) collected of the product obtained after >7 days of incubation at RT.

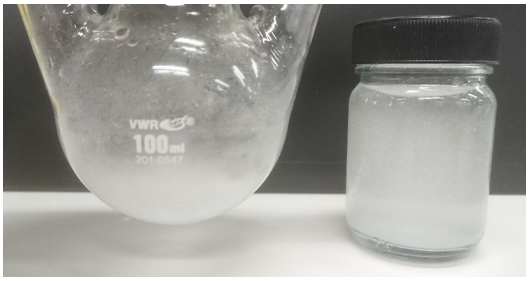


Figure S13 Pictures of the flask and isolated reaction product dispersion for the reaction performed with $Zn(NO_3)_2$ with an additional 24 hours incubation time.

ESI SECTION 3 CRYOTEM SERIES ON ZNAC ZNO FORMATION

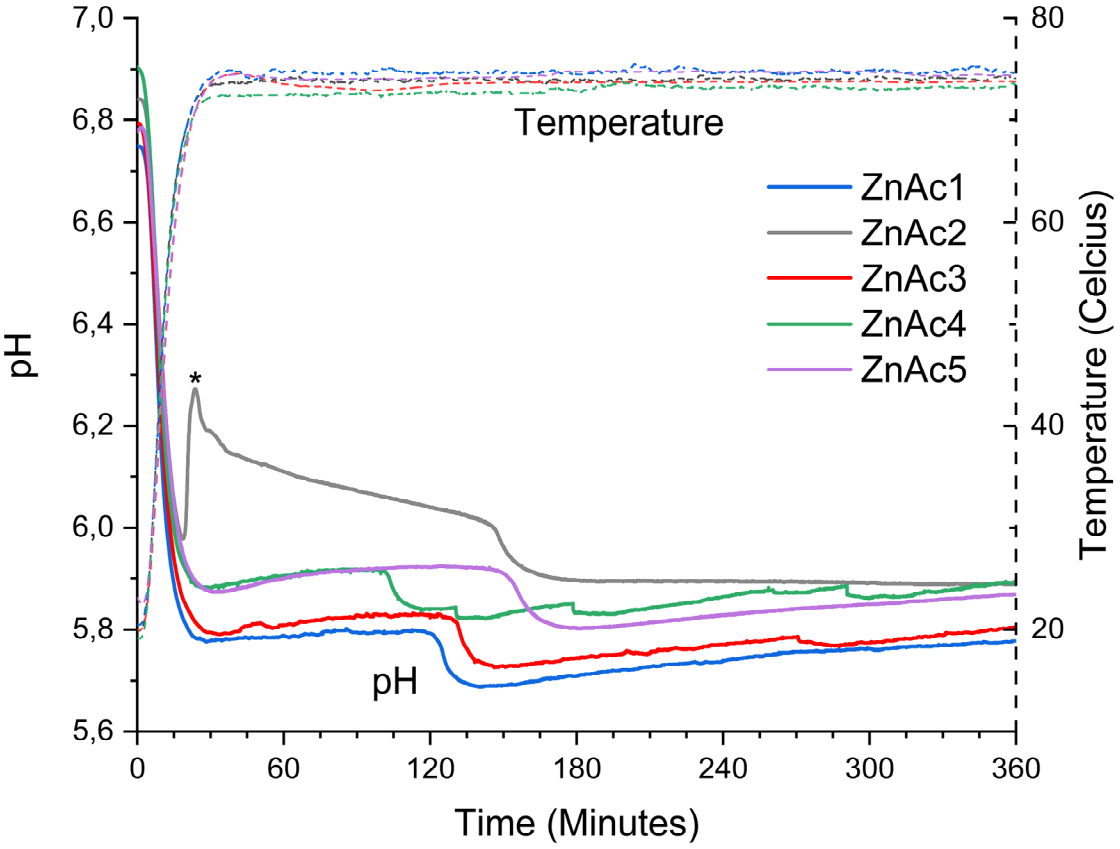
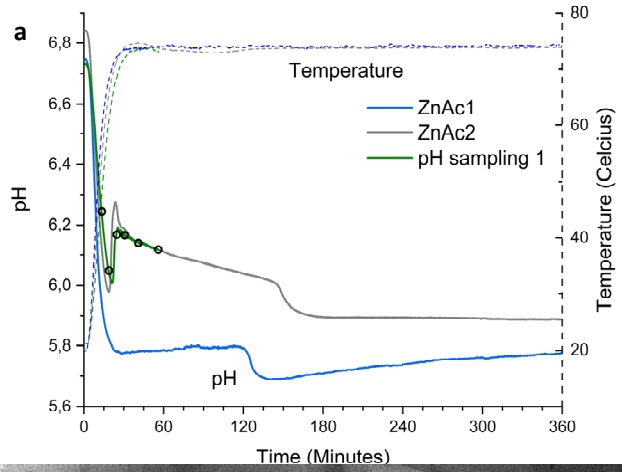


Figure S14 pH and temperature profiles for multiple reaction using 50 mM ZnAc and 25 mM HMTA in 50 ml water. The asterisk indicates a measurements artifact which is discussed in more detail below.

In ZnAc2 (*Fig. S14*) a sharp rise in pH can be observed after about 20 min, close to the moment when the reaction temperature reached approximately 60 °C. This spontaneous increase in pH is an artifact of the pH probe used for that experiment and two of the cryoTEM sampling experiments. Upon reaching this temperature this probe reports a slight increase in pH of ~0.3 points. This pH increase is gradually corrected out of the measurement over hours, meaning that the pH slope is not fully reliable. After the initial increase in pH, no spontaneous changes in pH are falsely reported by this probe. ZnAc3 and 4 show some drop of 0.02 pH points, these are small drift corrections and not representative of changes in reaction pH.

3.1 CryoTEM sampling experiment 1

a



b

Sample time Min:sec	Species
13:20	LBZA
19:00	LBZA
24:30	LBZA
30:20	LBZA
41:20	LBZA
54:40	LBZA + particle clusters

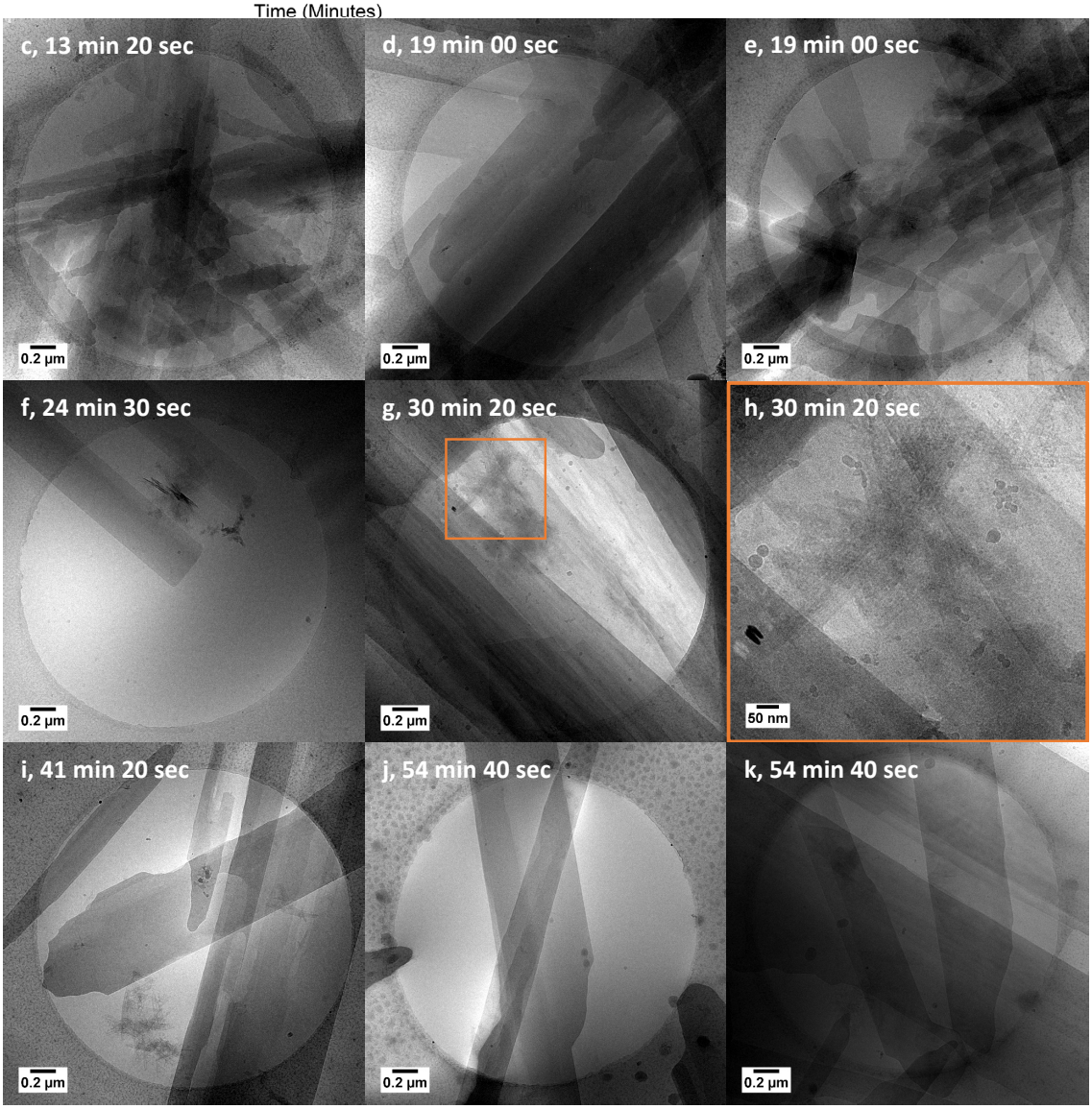
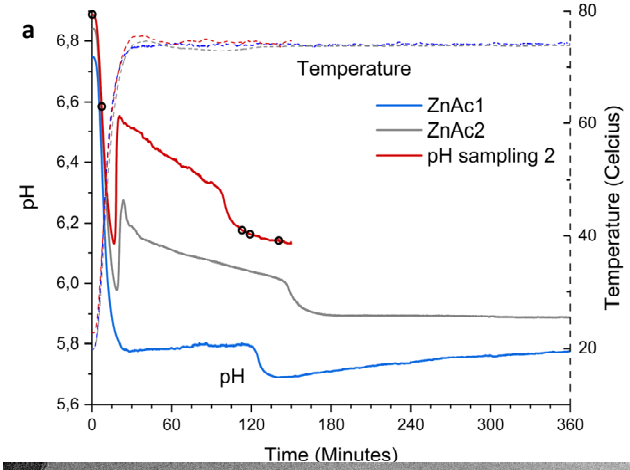


Figure S15 pH and temperature profile (a), sampling time and observed morphologies (b) and, cryoTEM images at the different sampling times (c-k) for cryoTEM sampling series 1.

3.2 CryoTEM sampling experiment 2

a



b

Sample time Min:sec	Species
00:10	LBZA
07:10	LBZA
112:45	PP + ZnO
118:10	ZnO
140:30	ZnO

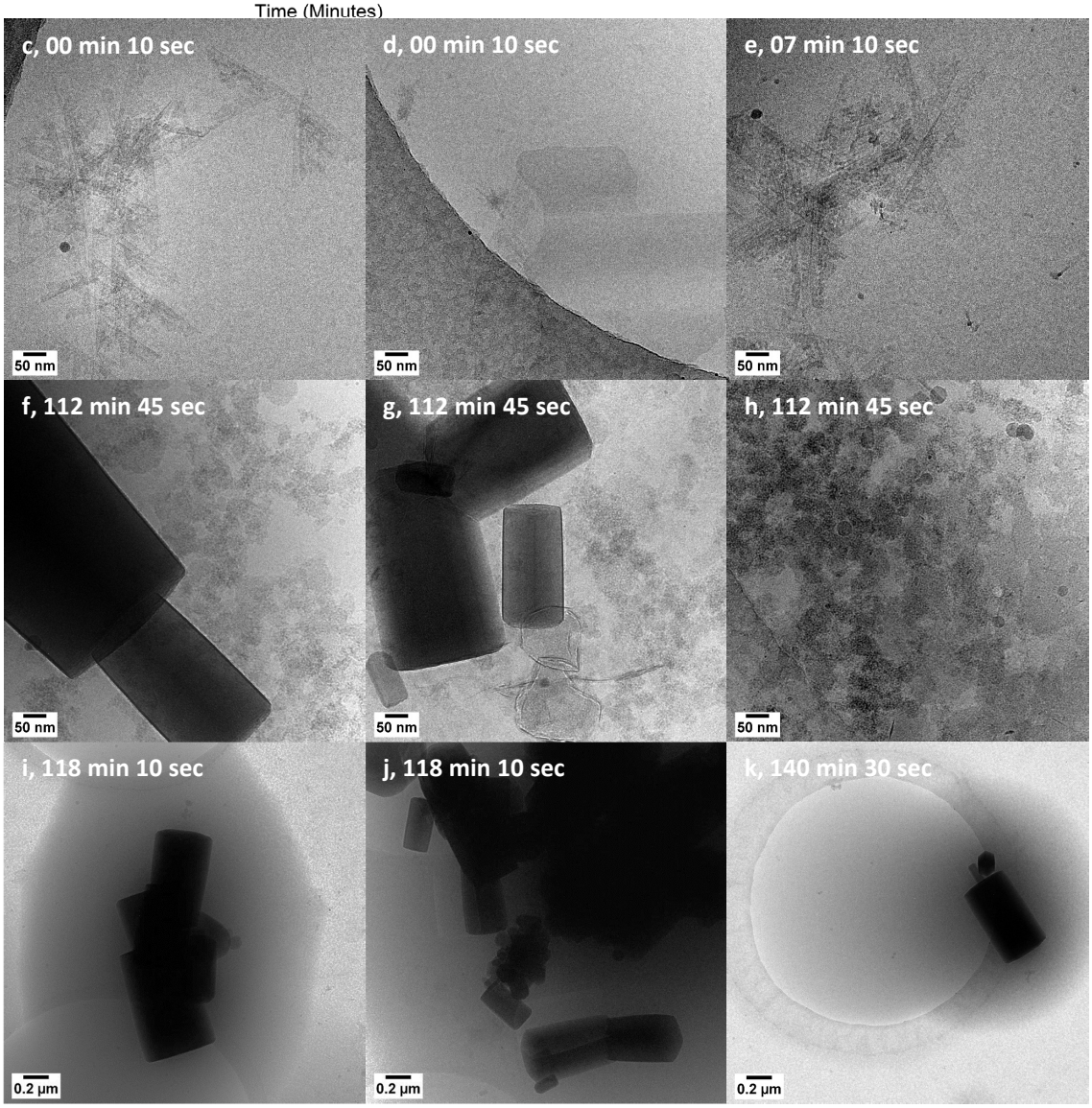
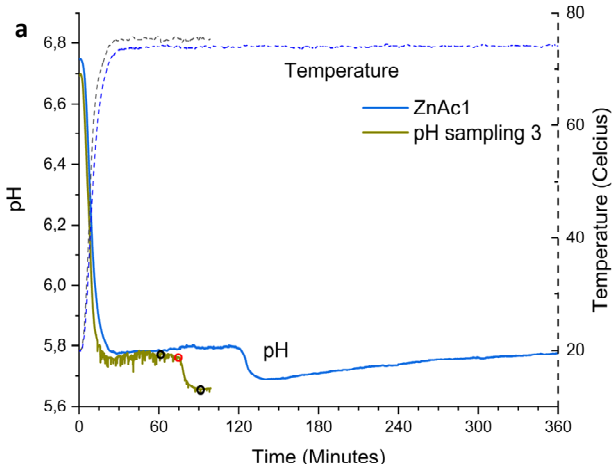


Figure S16 pH and temperature profile (a), sampling time and observed morphologies (b) and, cryoTEM images at the different sampling times (c-k) for cryoTEM sampling series 2.

3.3 CryoTEM sampling experiment 3

a



b

Sample time Min:sec	Species
61:15	LBZA + ZnO
76:45	Grid too damaged
89.25	ZnO

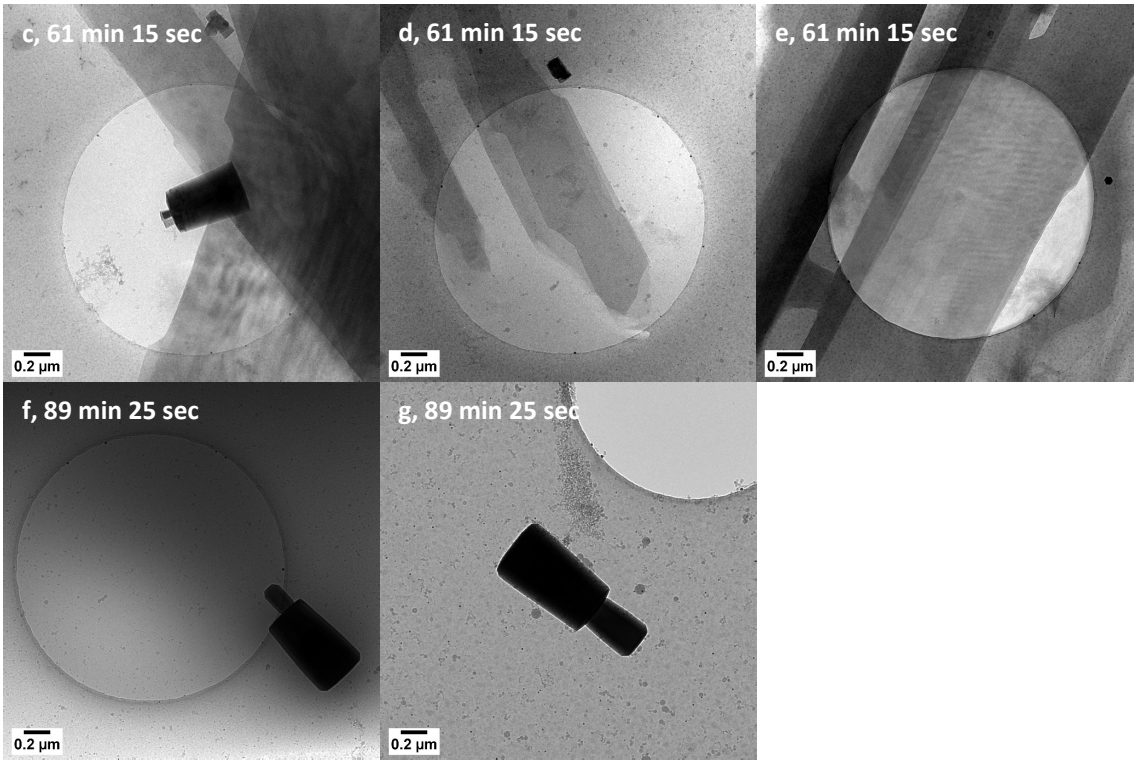
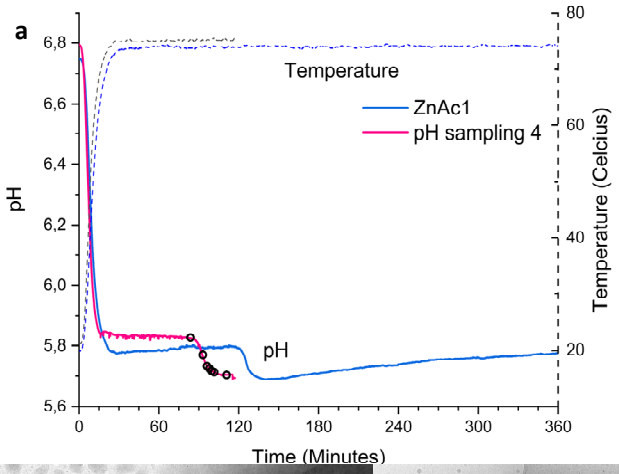


Figure S17 pH and temperature profile (a), sampling time and observed morphologies (b) and, cryoTEM images at the different sampling times (c-g) for cryoTEM sampling series 3.

3.4 CryoTEM sampling experiment 4

a



b

Sample time Min:sec	Species
83:45	LBZA + ZnO
92:55	ZnO mainly
95:05	ZnO mainly
97:35	Particulated zones
99:45	ZnO mainly
102	ZnO mainly
104:30	ZnO mainly
110:30	ZnO mainly

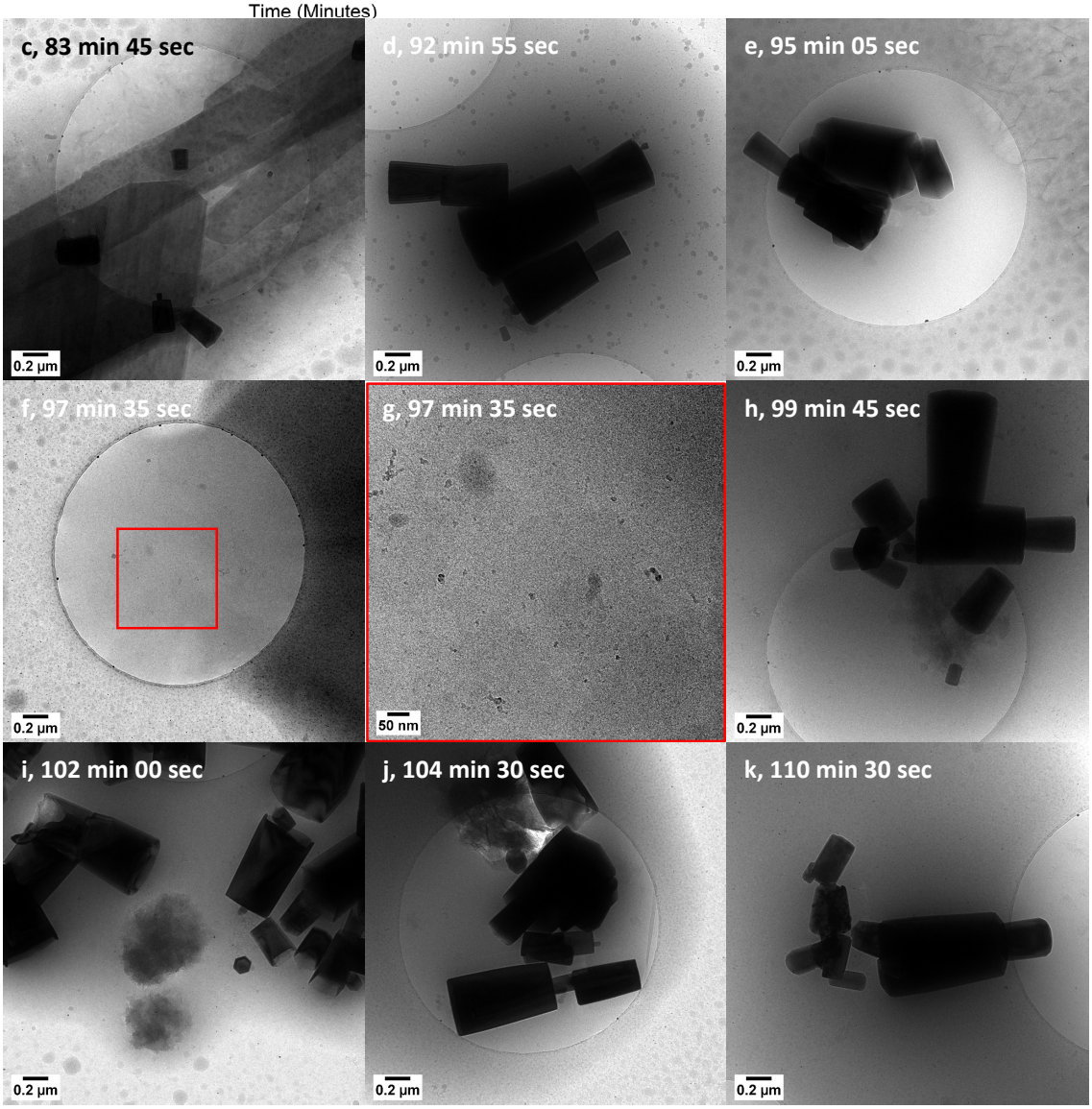


Figure S18 pH and temperature profile (a), sampling time and observed morphologies (b) and, cryoTEM images at the different sampling times (c-k) for cryoTEM sampling series 4.