

Electronic supplementary information: Controlled Titration-based ZnO Formation

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ESI SECTION 1 EXPERIMENTAL

ESI 1.1. Materials

Acetic acid (99-100%, GPR rechapur) and ammonia (28 %, GPR rechapur) were acquired from VWR, hexamethylenetetramine (HMTA, >99.0 %, ACS reagent) and formaldehyde (37%, ACS reagent in water 10 – 15 % methanol as stabilizer) were acquired from Sigma-Aldrich, potassium hydroxide (pellets, pure) was acquired from Merck, zinc acetate dihydrate (ZnAc₂, 98+ %, ACS reagent) was acquired from Acros organics. All chemicals were used as received unless stated otherwise.

ESI 1.2. Methods

Reaction set-up, pH and temperature measurements

pH and temperature measurements were conducted, respectively, using a Metrohm 6.0234.100 and 6.1110.100 pH and temperature sensor, connected to an 809 Titrando unit equipped with two 800 dosino dosing devices (10 or 20 mL) controlled by TIAMO 2.5 software.

Determining the pH dependent HMTA hydrolysis rate

25 mM of HMTA was dissolved in 50 ml pure water in a 100 mL five-neck flask under reflux. The titration experiment was magnetically stirred (vortexing, 450 rpm). The titration unit was set to titrate acetic acid (0.25 M) to achieve a pH of 5.7, 5.8 or 6.0 using the optimal titration speed setting on the dosing device. 300 s after initiating the titration protocol, the reaction temperature was gradually increased to ~80 °C. The experiment was continued for 22200 s (6.2 h) during which time the added volume, the pH and the reaction temperature were monitored. From this data the released amount of ammonia and hydroxide by HMTA were calculated, see *ESI section 2*.

Table S1 Titration protocol including the titration solution composition and time specific titration rates for the HMTA imitation and control reactions.

Protocol	Added solution	0 – 1198 s (mL·min ⁻¹)	1200 – 2958 s (mL·min ⁻¹)	2960 – 5768 s (mL·min ⁻¹)	5770 – 10598 s (mL·min ⁻¹)	10600 – 22200 s (mL·min ⁻¹)
Measure	None					
IM	Pure water	0			0.02	
IM-73	73.35 mM NH ₃ or KOH	0			0.02	
IM-146	146.70 mM NH ₃ + 221.55 mM CH ₂ O	0			0.01	
IM-OH	0.0310 mM KOH	0	0.07	0.03	0.02	0.01

Table S2 Titration protocol including the titration solution composition and time specific titration rates used for reactions with an increased base concentration.

Protocol	pH set solution	Titrated solution	0 – 1198 s (mL min ⁻¹)	1198 - 22200 s (mL min ⁻¹)	1198 – 3600 s (Target pH)	3600 – 22200 s (Target pH)
pH 6.8	None	1 M ammonia	0	0.02	7.0	6.0
pH 5.3	0.25 mM acetic acid	1 M ammonia	0	0.02	5.5	5.5
pH 8.3	1 M NH ₃ or KOH	1 M ammonia	0	0.02	8.5	6.0

Titration-based synthesis of zinc oxide

50 mM zinc acetate (and when noted 8.33 or 25 mM of HMTA) was dissolved in 50 ml pure water in a 100 ml five-neck flask under reflux. The titration experiment was magnetically stirred (vortexing, 450 rpm). If stated, the pH was pre-set at RT by adding 1 M acetic acid, KOH or ammonia solution. After addition of the chemicals or the correction of the pH, the solution was stirred for 900 s. After this time titration unit was set to add base (ammonia or KOH) at a constant rate. The used titration protocol is sample specific and detailed in *Table S1 and S2*. 300 s after initiating the titration protocol, the reaction temperature was gradually increased to ~80 °C. After 22200 s (6.2. h) the reaction was terminated, and

the reaction dispersions were collected. These dispersions were subsequently purified by centrifugation using an Optima L-90K ultracentrifuge equipped with a Type 70 Ti rotor at 20k or 30k rpm for 20 min. The sediment was redispersed in pure water followed by another centrifugation step. This procedure was performed twice. After centrifugation the product was dried at room temperature. An overview of all experimental results is shown in *Table S3*.

Table S3 Overview of investigated samples, their yield, LBZA-ZnO transition time, initial pH, final pH, used titration protocol and diameter as measured by SEM.

Sample	Yield %	LBZA-ZnO transition (min)	Initial pH	Final pH	Titration-protocol	Diameter (nm)
25 mM HMTA	12.6	120	6.8	5.8	measure	400±150
8.33 mM HMTA	7.2	141	6.8	5.8	measure	410±160
25mM HMTA-H ₂ O	13.2	126	6.8	5.8	IM	430±140
146.70 mM NH ₃ + 221.55 mM CH ₂ O	3.7	51	6.8	5.8	IM-146	260±70
73.35 mM NH ₃	3.5	51	6.8	5.8	IM-73	250±40
3.1 mM KOH	0.4	64	6.8	5.7	IM-OH	270±110
73.35 mM KOH	4.3	40	6.8	5.9	IM-73	110±30
1 M KOH	31.8	41	6.8	6.0	pH 6.8	140±30
1 M NH ₃ STD	41.3	44	6.8	6.0	pH 6.8	240±90
1 M NH ₃ pH 8.3* ^I	63.6	21	8.3	6.6	pH 8.3	390±110
1 M NH ₃ pH8.3* ^{II}	74.5	22,42	8.4	6.8	pH 8.3	220±90
1 M NH ₃ pH 5.3* ^{III}	0	-	5.3	5.5	pH 5.3	No product
1M NH ₃ STD opti* ^{IV}	34.0	50	6.9	6.0	pH 6.8	200±50

*Either the starting pH was pre-set using 1M ammonia,^I KOH^{II} or acetic acid^{III} or 1mL 1M ammonia was gradually added at RT^{IV} before initiating the reaction by heating.

ESI 1.3. Analysis

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

Scanning electron microscopy (SEM) was carried out on a Quanta 3D (Thermo Fischer Scientific) equipped with a field emission gun, secondary electron detector and operated at 5.0 kV. The samples in powder form were dispersed in pure water, 10 μ L dispersion was deposited on a continuous carbon-coated TEM grid with copper or gold supports (200 mesh), followed by manual blotting after 40 s. Samples were loaded in the SEM using an in-house build custom SEM holder that can accommodate 6 TEM grids.

Size measurements were performed on SEM images using an in-house Matlab script. For each sample the diameter of 60 clearly identifiable particles was measured (3 images, 20 particles each). For these particles the diameter was measured either at the twinning location or if not possible at the end with visually the shortest diameter.

ESI SECTION 2 ACETIC ACID COUNTER TITRATION CALCULATIONS

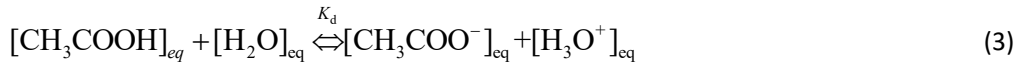
ESI 2.1. Calculations

Calculating the release of base from HMTA using zinc acetate counter titration requires several considerations. First the molar concentration of acetic acid in solution $[\text{CH}_3\text{COOH}]_{\text{total}}$ depends on the molarity of titrated acetic acid solution $[\text{CH}_3\text{COOH}]_{\text{titrated}}$ the initial volume (V_{initial}) and the titrated volume (V_{titrated}):

$$[\text{CH}_3\text{COOH}]_{\text{total}} = \frac{[\text{CH}_3\text{COOH}]_{\text{titrated}} \times V_{\text{titrated}}}{V_{\text{initial}} + V_{\text{titrated}}} \quad (1)$$

Acetic acid is a weak acid therefore only part of $[\text{CH}_3\text{COOH}]_{\text{total}}$ will be deprotonated to $[\text{CH}_3\text{COO}^-]_{\text{eq}}$ depending on the dissociation constant (K_d):

$$[\text{CH}_3\text{COOH}]_{\text{total}} = [\text{CH}_3\text{COOH}]_{\text{eq}} + [\text{CH}_3\text{COO}^-]_{\text{eq}} \quad (2)$$



This means the molar concentrations can be set against the K_d . This can be simplified by considering that the formed amount of $[\text{CH}_3\text{COO}^-]_{\text{eq}}$ is equal to the formed amount of $[\text{H}_3\text{O}^+]_{\text{eq}}$ and that in the case of a neutralization reaction with a constant pH $[\text{H}_3\text{O}^+]_{\text{eq}}$ reacts with an equal amount of released $[\text{OH}^-]_{\text{eq}}$:

$$K_d = \frac{[\text{CH}_3\text{COO}^-]_{\text{eq}} + [\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{CH}_3\text{COOH}]_{\text{eq}}} = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}^2}{[\text{CH}_3\text{COOH}]_{\text{eq}}} = \frac{[\text{OH}^-]_{\text{eq}}^2}{[\text{CH}_3\text{COOH}]_{\text{eq}}} \quad (4)$$

By substituting equation 4 into equation 2 we obtain equation 5:

$$\begin{aligned} [\text{CH}_3\text{COOH}]_{\text{total}} &= [\text{CH}_3\text{COOH}]_{\text{eq}} + [\text{CH}_3\text{COO}^-]_{\text{eq}} = [\text{CH}_3\text{COOH}]_{\text{eq}} + [\text{H}_3\text{O}^+]_{\text{eq}} = \\ &= [\text{CH}_3\text{COOH}]_{\text{eq}} + [\text{OH}^-]_{\text{eq}} = \frac{[\text{OH}^-]_{\text{eq}}^2}{K_d} + [\text{OH}^-]_{\text{eq}} \end{aligned} \quad (5)$$

Performing these calculations for ammonia will result in equation 6:

$$[\text{NH}_3]_{\text{total}} = [\text{NH}_3]_{\text{eq}} + [\text{NH}_4^+]_{\text{eq}} = [\text{NH}_3]_{\text{eq}} + [\text{OH}^-]_{\text{eq}} = \frac{[\text{OH}^-]_{\text{eq}}^2}{K_d} + [\text{OH}^-]_{\text{eq}} \quad (6)$$

To determine the amount of $[\text{OH}^-]_{\text{eq}}$ effectively released to the system, equation 5 can be solved for $[\text{OH}^-]$ using the quadratic formula:

$$[\text{OH}^-]_{\text{eq}} = \frac{-K_d \sqrt{K_d^2 + (4 \times K_d \times [\text{CH}_3\text{COOH}]_{\text{total}})}}{2} \quad (7)$$

The temperature dependence of K_d can be described by:

$$\text{Log } K_d = \frac{A}{T} + B \text{ Log } T + CT + D \quad (8)$$

$$K_d = 10^{\text{Log } K_d} = 10^{\frac{A}{T} + B \text{ Log } T + CT + D} \quad (9)$$

where A, B, C and D are constants, given in Table S4.

Table S4 The constants for acetic acid and ammonia in expressions 8 and 9. ¹⁻³

Compounds	A	B	C	D
Acetic acid	-1500.65	-6.50923	-0.0076792	18.67257
Ammonia	-1746.57	0	0.01706	-6.1848

In absence of counter titration, the released molar concentration of hydroxides $[\text{OH}^-]_{\text{eq}}$ by HMTA can be measured by the change in pH. This takes place at neutral pH, therefore, the decrease in free protons (pH) and the increase in free hydroxides (pOH) should be considered:

$$[\text{OH}^-]_{\text{eq}} = 10^{-\text{pOH}} - 10^{-\text{pH}} = 10^{-(14-\text{pH})} - 10^{-\text{pH}} \quad (10)$$

ESI 2.2. Collecting and transforming experimental data

During a typical ZnO reaction from 50 mM zinc acetate and 25 mM HMTA at $\sim 80^\circ \text{C}$, the pH remains constant, close to pH 5.8, for most of the reaction.⁴ To probe the release of hydroxide under these conditions, a reference reaction containing 25 mM HMTA in water was performed while titrating 0.25 M acetic acid targeting a pH of 5.8.

The reaction pH could be controlled by acetic acid titration (*Fig. S1a,b,d*). The released amount of hydroxide was calculated by correcting for the dissociation constant (K_d , *Fig. S1c*) while taking the reaction temperature into account.^{2, 3} As expected, hydroxide was released into the system at a gradually decreasing rate over time (*Fig. S1e,f*). This results in the release of 3.3×10^{-2} mmol hydroxide after 6 h reaction time, which is equivalent to 0.50 mmol ammonia (*Fig. S1g*) or $\sim 10\%$ of total amount of ammonia present in HMTA per 6 h.

The influence of slight pH deviations on the hydrolysis rate of HMTA was investigated by repeating the experiment at pH 5.7 and 6.0 (*Fig. S1a-b,d-g*). This resulted in the release of respectively 0.62 ($\sim 13\%$) mmol and 0.36 mmol ($\sim 6\%$) ammonia per 6 h. This shows clearly that slight variations in pH will have a notable influence on the hydrolysis rate of HMTA.

Both Strom et al.⁵ and Ashfold et al.⁶ used 50 mM HMTA to investigate the pH dependent hydrolysis rate of HMTA. Ashfold et al. predicts a HMTA hydrolysis rate (k) of 0.055 h^{-1} at a constant reaction pH of 5.64 at 90°C . After 2 h reaction time during the formation of ZnO, a rate (k_{obs}) of 0.059 h^{-1} is measured. To compare data, the concentration of HMTA (*Fig. S1i*) and the natural logarithm of the HMTA concentration (*Fig. S1h*) were determined from the calculated release of ammonia and set against the time. From this the k_{obs} could be calculated: at pH 5.7, $k_{\text{obs}} = 0.0230 \text{ h}^{-1}$, at pH 5.8, $k_{\text{obs}} = 0.0181 \text{ h}^{-1}$ and at pH 6.0, $k_{\text{obs}} = 0.0127 \text{ h}^{-1}$. Given that k_{obs} is concentration dependent the data from Ashfold et al. was corrected with a factor two presuming no difference in activity between 25 mM and 50 mM HMTA in solution. When plotting the obtained data and the corrected data from Ashfold et al. against the number of protons in solution ($10^{-\text{pH}}$), a clear match can be observed (*Fig 1b*). Using the experimental data provided by Ashfold et al. the initial hydrolysis rate of HMTA over the first 1.5 h was calculated. During this time the HMTA concentration decreased from 0.05 M to under 0.03 M. This results in a $k_{\text{obs}} = 0.51 \text{ h}^{-1}$, close to a nine-fold increase from $k_{\text{obs}} = 0.059 \text{ h}^{-1}$ obtained after 2 h reaction time. This shows that the HMTA hydrolysis rate is significantly higher during the initial 1.5 h of the reaction.

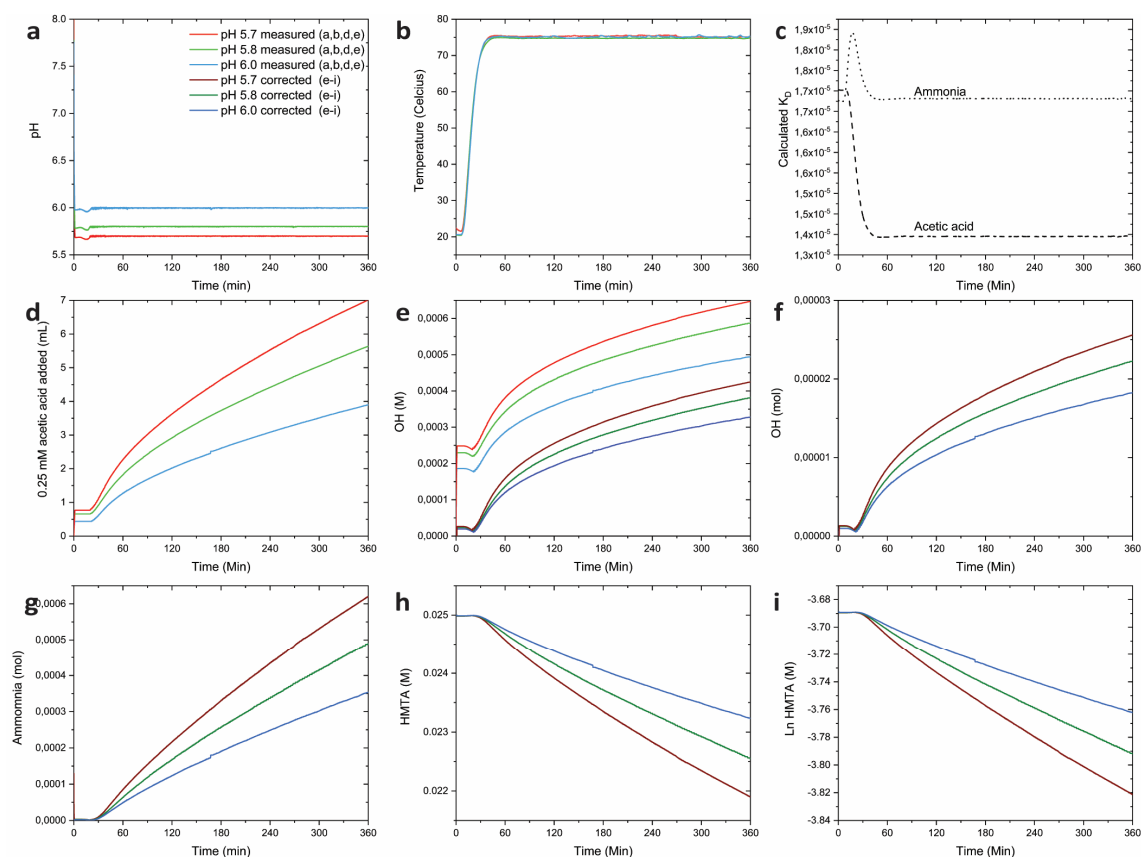


Figure S1 Hydrolysis of 25 mM HMTA at a constant pH of 5.7, 5.8 and 6.0, showing the evolution of pH (a) and temperature (b) of the acetic-acid counter titration as a function of time. Using the temperature evolution, the dissociation constant K_d of acetic acid and ammonia can be calculated (c). The titrated volume of acetic acid (d) is combined with the dissociation constant to calculate amount of hydroxide in M and mol (e, f), the amount of ammonia in mol released by the HMTA during the reaction (g), the concentration in M of HMTA present in solution (h) and finally the natural logarithm of the HMTA concentration (i).

ESI SECTION 3 THEORETICAL YIELD CALCULATIONS

The amount of hydroxide consumed during the reaction results from two sources: the original reaction solution (via the decrease in reaction pH) and the amount of base titrated into the system. During the investigated HMTA reference reaction and the titration reactions without an initial pH correction, the pH decreases from 6.8 to 5.8. For this pH decreases, equation 10 from ESI section 2 shows the release of 1.48×10^{-3} mM hydroxide, which is a negligible amount. The amount of hydroxide released to the system via ammonia titration is dependent on the K_d of ammonia. Using data from Fig. 1 and taking K_d of ammonia into account, it is expected that 0.380 mM hydroxide is released over a 6 h reaction period at pH 5.8. When presuming that all the ammonia is converted into ammonium, 8.771 mM hydroxide is released (0.489 mmol ammonia in 55.64 mL). When 50 mM zinc acetate is used in the reaction after titration (7 mL to 50 mL), 43.86 mM ZnO is the maximal attainable. The formation of 1 mol ZnO requires 2 mol hydroxide. This allows for a maximum formation of 0.190 mM ZnO, a yield of 0.433% when taking the K_d of ammonia into account or a maximum formation of 4.385 mM ZnO equal to a yield of 10.00% when a full transformation of ammonia into ammonium is presumed.

ESI SECTION 4 FIGURES

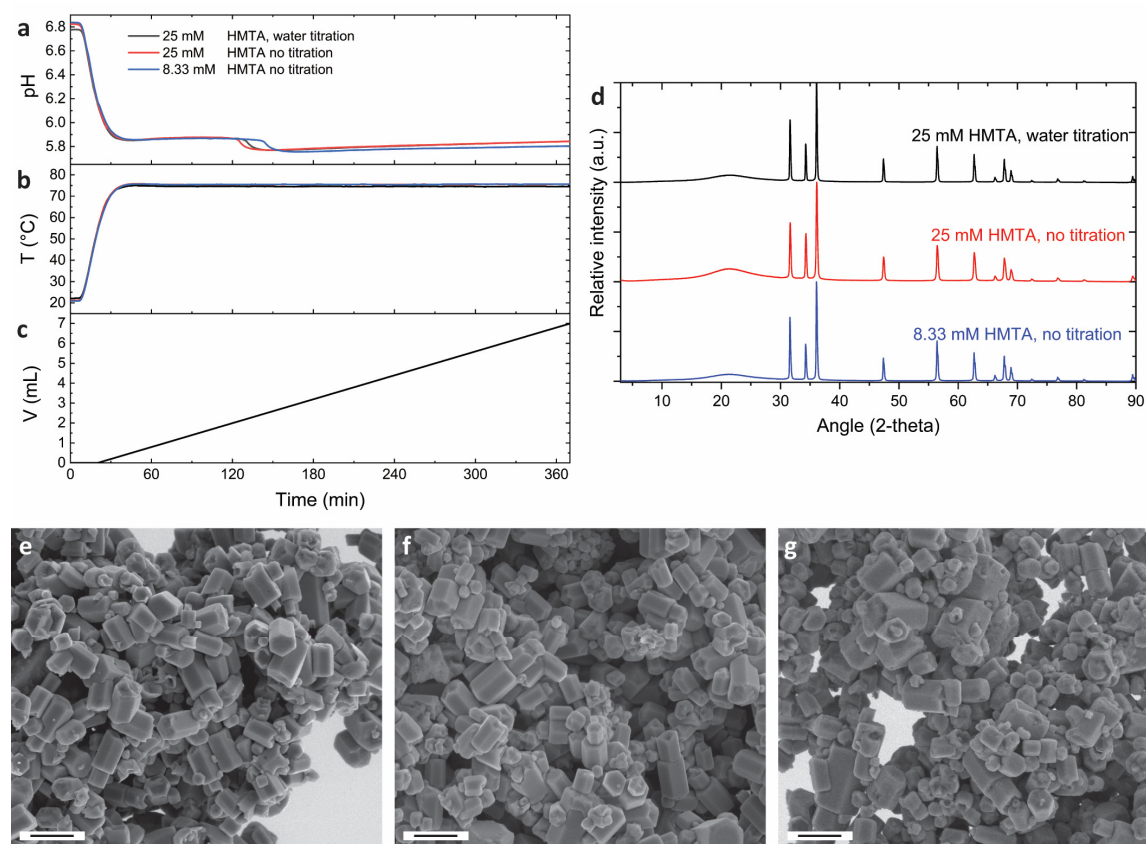


Figure S2 HMTA-mediated synthesis of ZnO from zinc acetate showing the evolution of pH (a), the temperature T (b) and the titration volume V (c) as a function of time combined with the pXRD results (d) and SEM images when using 25 mM HMTA with water titration (e), 25 mM HMTA without water titration (f) and 8.33 mM HMTA without water titration (g).

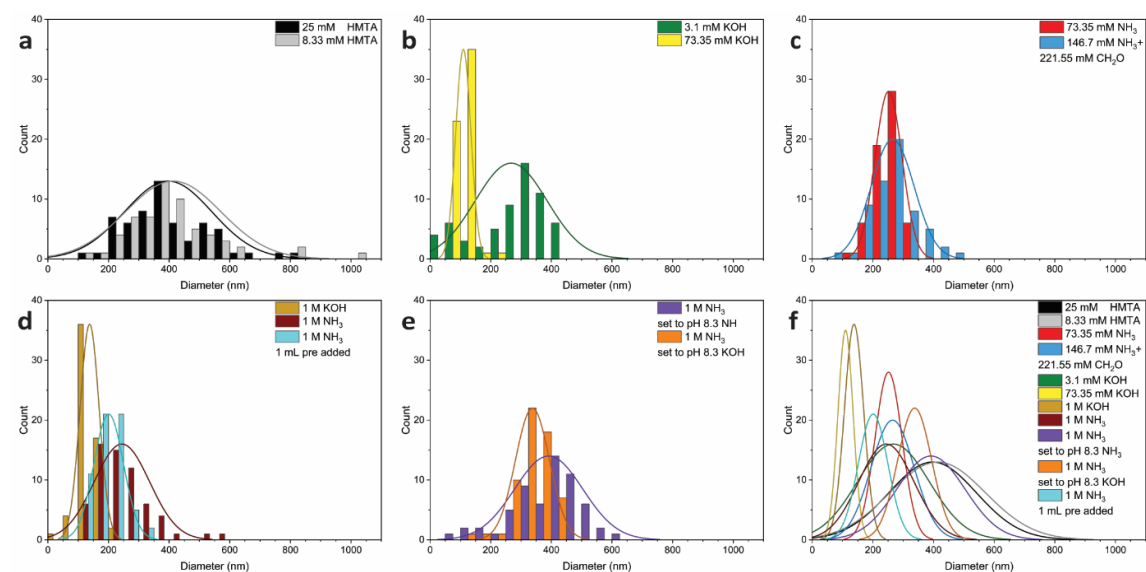


Fig. S3 Histograms (a-e) and size distribution plots (a-f) of diameter measurements on SEM images used to calculate the given diameter \pm sample standard deviation displayed in Table S3. This includes the HMTA references (a), the HMTA-inspired KOH titration strategy (b), the HMTA-inspired NH_3 titration strategy (c), the titration strategies with an increased base concentration at native pH (d) and at pH 8.3 (e), followed by an overview of all results (f).

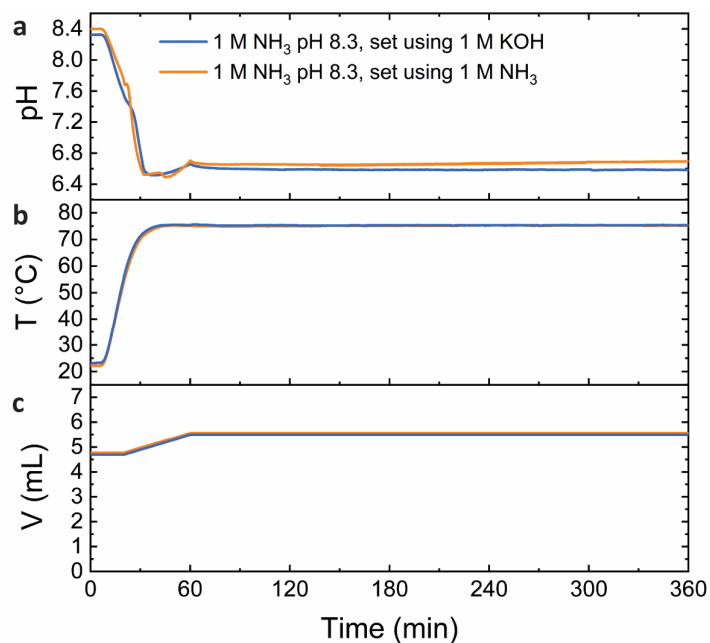


Figure S4 High pH titration-based synthesis of ZnO from zinc acetate showing the evolution of pH (a), temperature T (b) and titration volume V (c) as a function of time.

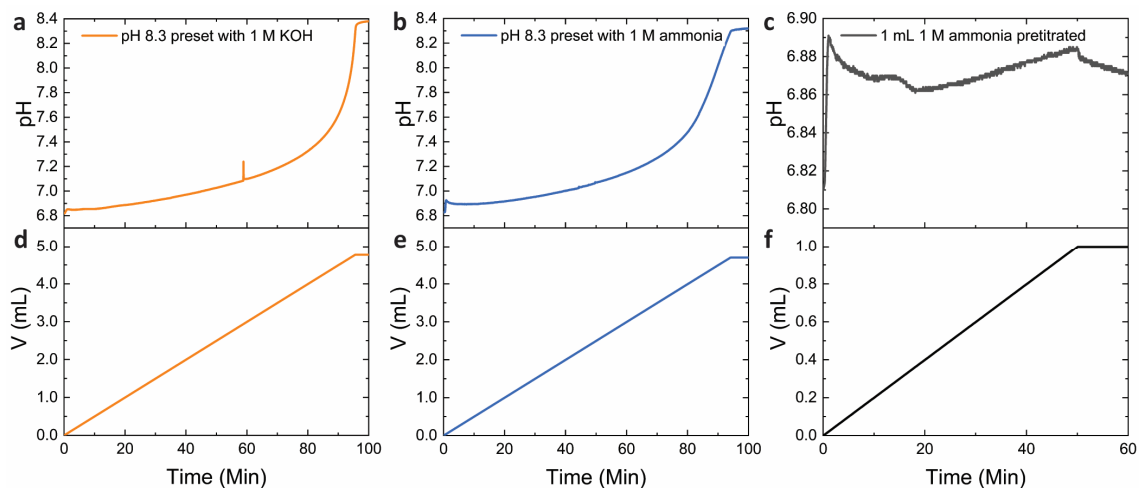


Figure S5 Evolution of pH (a-c) and titration volume V (d-f) as a function of time for the presetting of the zinc acetate solution to pH 8.3 using 1 M ammonia (a,d) or 1 M KOH (b,e) and for the initial addition of 1 mL ammonia (c,f). The pH was set titrating base at a rate of 0.05 mL min^{-1} (d,e). For the preformation of LBZA (c,f) a similar titration rate as the reaction of 0.02 mL min^{-1} was chosen.

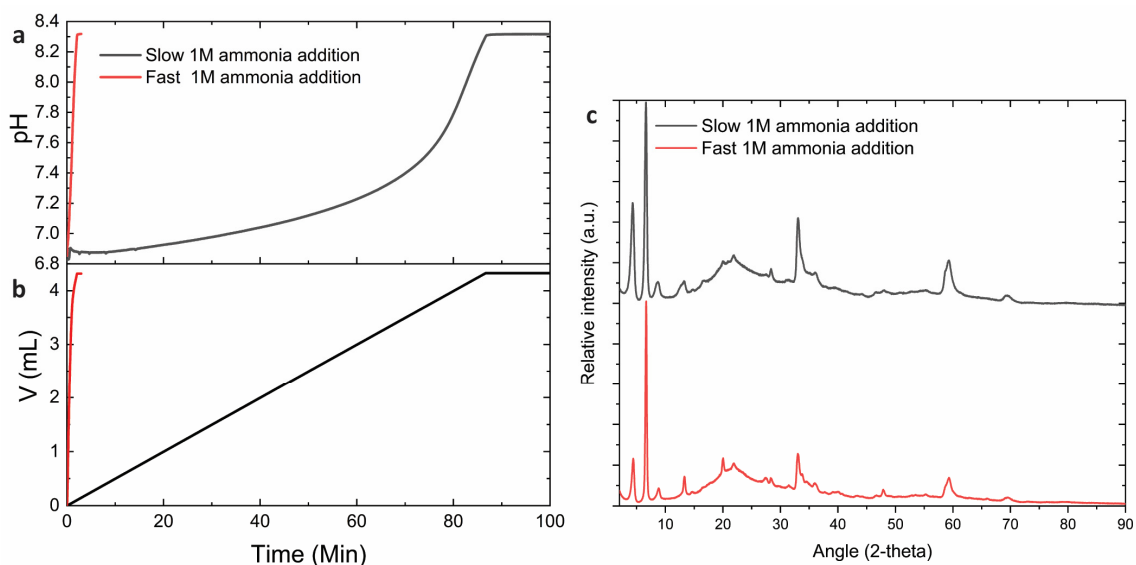


Figure S6 Controlled addition of 1 M ammonia to 25 mM HMTA solution showing the evolution of pH (a) and titration volume V (b) as a function of time and the pXRD (c) results of the products showing the formation of LBZA in both cases. It should be noted that sharper signals are obtained when using a faster addition rate suggesting more defined crystals with a more even crystal spacing.

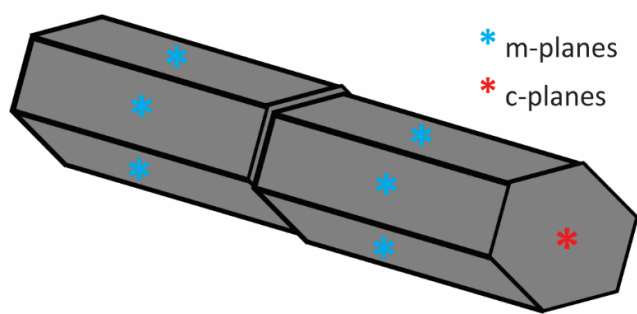


Figure S7 Sketch of a twin pillar ZnO structure indicating the c- and m-planes using red and blue asterisks, respectively.

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