

Multiple Regulation Effects of Ammonium Acetate on ZnO Growth Process in Chemical Bath Deposition

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Abstract: Chemical bath deposition method has been used to synthesize a variety of ZnO morphology structures. However, the specificity and interaction of acetate and ammonium ions with ZnO crystal during the growth process remain elusive. This study contributes to understand the roles of ammonium acetate on the growth mechanism of ZnO in Zn(NO₃)₂-HMTA system. The growth process indicates that the nucleation experienced Zn²⁺-layered basic zinc salts (LBZs)-ZnO process, while the self-assembled unit changed from urchin-shaped, rod-shaped to a fully coupled twin-shaped structure with increasing ammonium acetate concentration. Ammonium acetate dominates the growth process by combing the ligand-ligand interaction of acetate ions binding to the same Zn-rich (0001) polar surface and ammonium ions regulating

hexamethylenetetramine (HMTA) hydrolysis. Relatively regular hexagonal wurtzite structure and a dissolve-renucleation-regrowth process which retains the twin-shaped template and renucleates at the same position are observed at ~10 mM ammonium acetate. Photoelectrochemistry (PEC) measurements show that the uniform hexagonal ZnO rods (Y-10, the sample named as Y-x (x represents x mM ammonium acetate, herein, x is 10 mM)) have a maximum photocurrent density of 1.54 mA cm⁻² at 1.23 V (vs. RHE), much higher than that of the dumbbell-shaped ZnO rods (Y-50, 0.20 mA cm⁻²) at the same voltage. These results provide a further explanation of morphology regulation mechanisms on ZnO synthesis processes and pave the road for more practical applications.

Introduction

For novel functional materials, nanostructure and morphology are often designed to satisfy their aimed application in different fields.^[1] ZnO is well-known for its excellent multi-morphology-forming ability to facile growth of high quality nanostructures. Beyond well-known monolithic nanoribbons^[2] and nanocoils,^[3] there are micro-nanocrystal tetrapods,^[4] flexible transparent ultralarge nanopapers,^[5] monolithic ZnO quantum dots-on-nanoneedle hybrids^[6] and pyramid-shaped ZnO NPs,^[7] et al.^[8] However, it's still difficult to precisely fabricate functional ZnO nanostructures in chemical bath deposition (CBD) which is an economic and prospectively industrial mass production method.^[1,9] Therefore, it is necessary to understand its growth mechanism that generally involves nucleation, Ostwald ripening and self-assembly directed by oriented attachment.^[7,9c,10]

Some studies have proved ZnO precipitates directly from nutrient solution,^[10b] and revealed multistep transform pathways of intermediates known as layered basic zinc salts (LBZs)

during crystal growth.^[9c,10c] The subsequent self-assembly process is a complex phenomenon depending on multiple driving forces, including the shape and size effects, thermodynamic effects, free energy of activation and the solubility of the intermediates, defects formation and ligand-ligand interactions resulting in the final morphology.^[7,11] Some reporters attributed the coupling to the intrinsic polarity along the (0001) direction and van der Waals interaction,^[11a] while recently studies showed the coupling of ZnO twin-shaped structure based on well-developed facets and further driven by ligand-ligand interaction.^[7] The growth route is roughly clear, while it remains challenging in clarifying the contributions of each species on the growth process in the common CBD system, including the hexamethylenetetramine (HMTA), CH₃COO⁻ and NH₄⁺ ions in the commonly employed zinc salts (zinc nitrate and zinc acetate) and amines (HMTA and ammonium hydroxide), for each of them may play more than one roles.^[9c,12]

HMTA has been widely studied and proved to be not only as OH⁻ source but also as pH buffer reagent and encapsulation species.^[9c,12a,13] CH₃COO⁻ and NH₄⁺ ions also presents multiple regulatory effects including the Zn²⁺ (form [Zn(NH₃)₄]²⁺) and OH⁻ (NH₃ · H₂O → NH₄⁺ + OH⁻ and CH₃COO⁻ hydrolysis) ions concentration regulation and nanorods (NRs) encapsulation (NH₄⁺ and CH₃COO⁻ ions could coordinate with polar facets O²⁻ and Zn²⁺ ions respectively) in different systems.^[12,14] Some spectroscopy evidence also proved the regulation process of organic ligand coordination on ZnO crystal growth.^[15] However, the specific regulator effects of crystal growth process contributed by CH₃COO⁻ and NH₄⁺ ions are still lacking, especially when they are coexist, such as the Zn(CH₃COO)₂-NH₃ system. Ammonium hydroxide provides a high concentration of OH⁻

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Supporting information for this article is available on the WWW under <https://doi.org/10.1002/chem.202103064>

ions for c-axis orientation and ZnO etching effect leading to it difficult to clarify the effects of other ions.^[12b,c,15c] Ammonium acetate different from other amine substances, is a weak acid and alkali salt and has been successfully used as a morphological regulator. For example, Xu et al.^[16] reported a kinetically controlling the growth rates of various facets by ammonium acetate, and demonstrated that adsorption of CH_3COO^- ions takes places preferentially onto the (0001) plane to produce platelet-like crystals. Nur Kicir et al.^[17] synthesized ZnO nano-flowers by adding ammonium acetate to regulate the production rate of OH^- ions (acetate anions hydrolysis) and the diffusion rate of Zn^{2+} ions ($[\text{Zn}(\text{NH}_3)_4]^{2+}$ complex formed). Zhao et al.^[14d] suggested that ammonium acetate in the solution produced the effect on increasing the growth rate and decreasing the defect density of ZnO nanostructure arrays. The above results all illustrate partial regulations of the acetate and ammonium ions, while the specific roles and the regulator effect on growth route of ZnO are still elusive.

In this paper, ammonium acetate was selected as morphological regulator in the zinc nitrate-HMTA system, and its multi-regulator effects were discussed. The SEM images were used to characterize the growth process of ZnO from the initial precipitation, nucleation and crystallization, self-assembly to the resulting morphology, to reveal the growth mechanism and contributions of ammonium acetate on ZnO morphology transformation. Finally, the synthesized ZnO were characterized by PEC measurements. It is anticipated that more efficiently functional ZnO structures could be designed and developed based on these insights into the growth mechanism.

Results and Discussion

The regulating effect of ammonium acetate

Figure 1(a) depicts the ideal ZnO morphology transform with different amounts of ammonium acetate as additives, and the corresponding SEM images of experimental data are shown in Figure 1(b–f) and Figure S1. The experiment details are shown in the experimental section. The ZnO rods composed into urchin-shaped stacked structures (Figure 1(b)) without ammonium acetate, assembled into branch-like structures (Figure 1(c)) with regular hexagonal ZnO rods at 10 mM, and transformed into dumbbell-shaped rods (Figure 1(e)) at 50 mM. There is an obvious transformation of ZnO rods from a top-cone shaped to a regular hexagonal and to a dumbbell-shaped structures, which implied a preferentially direction growth change from c-axis to the lateral direction. The diameter calculated from the SEM images (the value is the average of that measured more than 30 points through the SEM instrument software directly) coarsens obviously from $\sim 0.26 \mu\text{m}$ (0 mM), $\sim 1.12 \mu\text{m}$ (10 mM), $\sim 1.56 \mu\text{m}$ (30 mM) to $\sim 2.18 \mu\text{m}$ (50 mM), and aspect ratio (aspect ratio = length/diameter) reduces from ~ 12.33 (0 mM), ~ 5.76 (10 mM), ~ 2.50 (30 mM) to ~ 2.62 (50 mM), as shown in Figure 1(f and g). Both of them display an apparent lateral preferential growth.

XRD data (Figure 1(h) and Figure S3) show the strongest detected peaks are at 2θ values of $\sim 31.7^\circ$, $\sim 34.4^\circ$, $\sim 36.2^\circ$, $\sim 47.50^\circ$, $\sim 56.6^\circ$, and $\sim 62.8^\circ$, corresponding to the following hexagonal wurtzite structure lattice planes: $(10\bar{1}0)/(100)$, $(0001)/(002)$, $(10\bar{1}1)/(101)$, $(10\bar{1}2)/(102)$, $(11\bar{2}0)/(110)$ and $(10\bar{1}3)/(103)$,^[9c,18] respectively (JCPDS card No. 36–1451). The intensity of the peaks demonstrates high purity of the hexagonal ZnO

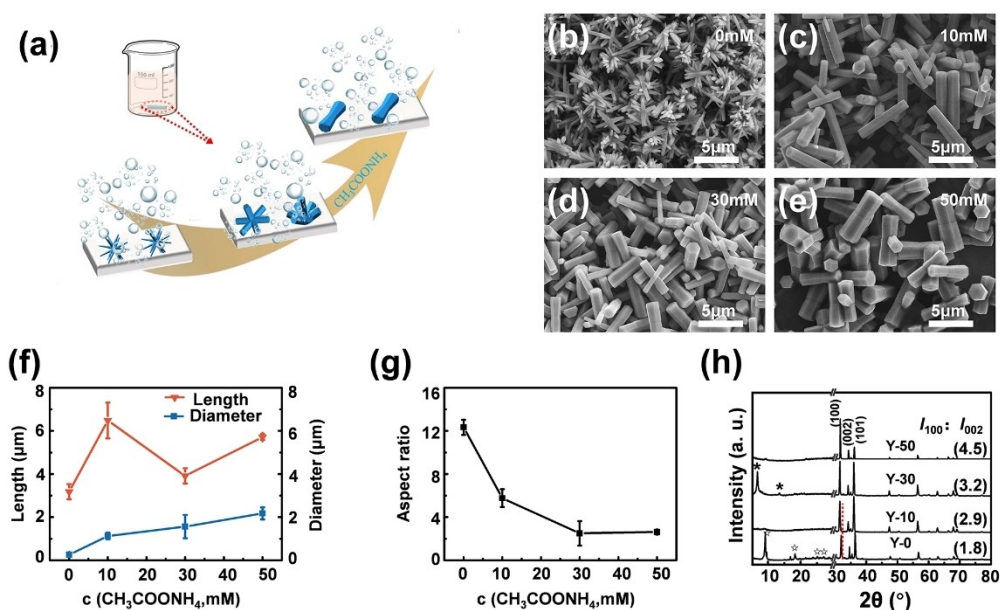


Figure 1. (a) The schematic of ZnO morphology transform; (b), (c), (d) and (e) are the SEM images of ZnO (Y-x) obtained with different amounts of ammonium acetate (b-0 mM, c-10 mM, d-30 mM, e-50 mM); the length and diameter (f) and aspect ratio (g) derived from the SEM images (aspect ratio = length/diameter); (h) the XRD patterns (*: Layered basic zinc acetate, $\text{Zn}_5(\text{OH})_8(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$; ☆: Layered basic zinc nitrate, $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$).

phase and good crystallinity which can also be proved by the Raman (Figure S3) and TEM (Figure 2) data. The ratios of the intensities of diffraction peaks (10 $\bar{1}$ 0) and (0001) planes increase from ~ 1.8 (0 mM), ~ 2.9 (10 mM), ~ 3.2 (30 mM) to ~ 4.5 (50 mM), indicating a strong growth inhibition effect along the c-axis direction.^[19] The peaks at $\sim 6.7^\circ$ (001) and $\sim 12.8^\circ$ (002) are attributed to the intermediates LBZA (layered basic zinc acetate, $\text{Zn}_5(\text{OH})_8(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$). The peaks at $\sim 9.0^\circ$ (200), $\sim 18.3^\circ$ (400), $\sim 23.7^\circ$ (401), $\sim 25.1^\circ$ ($\bar{3}$ 11), $\sim 27.1^\circ$ (510), $\sim 28.7^\circ$ (020) and $\sim 32.9^\circ$ (021) are attributed to the intermediates LBZN (layered basic zinc nitrate, $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$),^[9c,10c] as shown in Figure 1(h). The peaks offset to lower positions (such as reduce the 2θ value from $\sim 31.9^\circ$ (0 mM) to $\sim 31.5^\circ$ (10 mM)), indicating lattice expansion and indirectly proving the ions coming from ammonium acetate or its derivative incorporated into the crystal structure.^[20] The regulatory effects of ammonium acetate on ZnO growth progress will be discussed in below.

In order to investigate in detail the crystal structure, TEM, high-resolution TEM (HRTEM) and XPS analyses were carried out on Y-0 and Y-10. Figure 2 shows the TEM images of Y-0 (Figure 2a) and Y-10 (Figure 2c). Their HRTEM images are shown in Figure 2b and Figure 2d, respectively. Figure 2b corresponds to the area marked as b in Figure 2a, and shows a single crystalline nature. The two-dimensional lattice patterns, with an interlayer spacing of ~ 0.26 nm, show the highly crystalline nature of Y-0, with growth occurring along the [0001] direction.^[7,21] The corresponding selected-area electron diffraction (SAED) patterns also confirm the single crystalline nature of it, as shown in insets. The area marked as d in Figure 2c shows the same single crystalline nature. Its HRTEM and SAED also confirm it, as shown in Figure 2c and the insets. The other TEM

images of them including the possible polycrystalline nature during growing process are shown in Figure S4.

Figure 3 compares the O 1s XPS spectra of Y-0 and Y-10. We fit O 1s envelope with two components, the lower binding energy (530.3 ± 0.1 eV) corresponding to ZnO, the other higher binding energy (531.6 ± 0.1 eV) can be attributed to oxygen defects and $\text{Zn}(\text{OH})_2$.^[10c,22] There was small amount of uncomplete converted $\text{Zn}(\text{OH})_2$, attributing to that some ZnO rods were still in growing states. This growing states was also observed in the TEM data (Figure S4). The insets in Figure 3 show the intense Zn 2p $_{3/2}$ (2p $_{1/2}$) feature at ~ 1021.5 eV (~ 1044.6 eV), indicating the presence of a single Zn²⁺ divalent state corresponding to both $\text{Zn}(\text{OH})_2$ and ZnO.^[22b,23]

The regulatory effects of ammonium acetate on ZnO NRs growth progress are schematic in Figure 4a, including: 1) the regulating effect of CH_3COO^- ions on OH^- ions; 2) the regulating effect of NH_4^+ ions on Zn²⁺ ions and HMTA; 3) The encapsulation effect of ammonium acetate on ZnO NRs. It will be discussed in the next part in detail, and the corresponding reaction are listed in equation (1–7).^[12b,c,13,17,20]

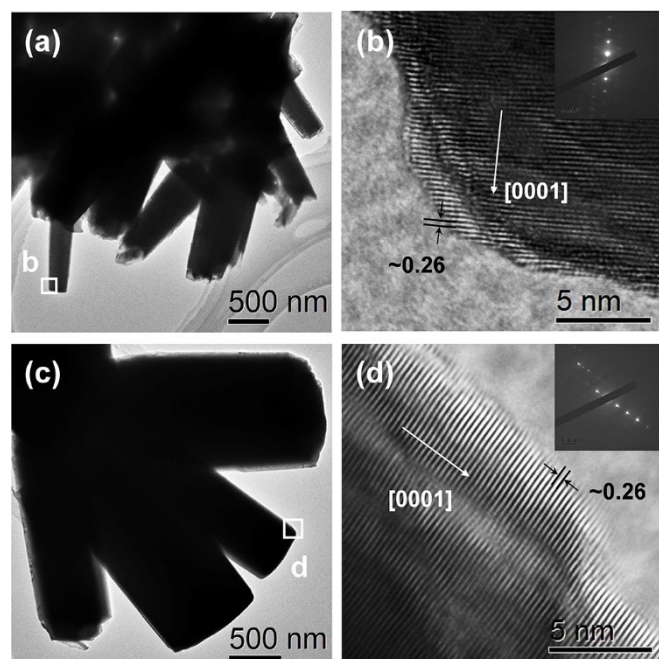
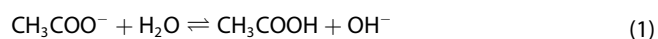


Figure 2. TEM images of Y-0 (a) and Y-10 (c). HRTEM images of Y-0 (b) and Y-10 (d). The insets show the corresponding SAED patterns.

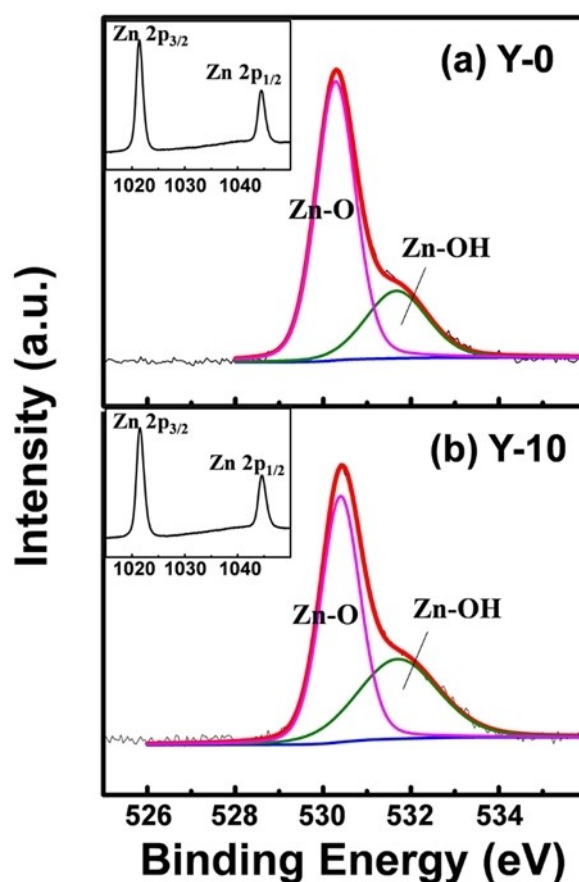


Figure 3. O 1s XPS spectra of (a) Y-0 and (b) Y-10. The insets show the corresponding Zn 2p spectra.

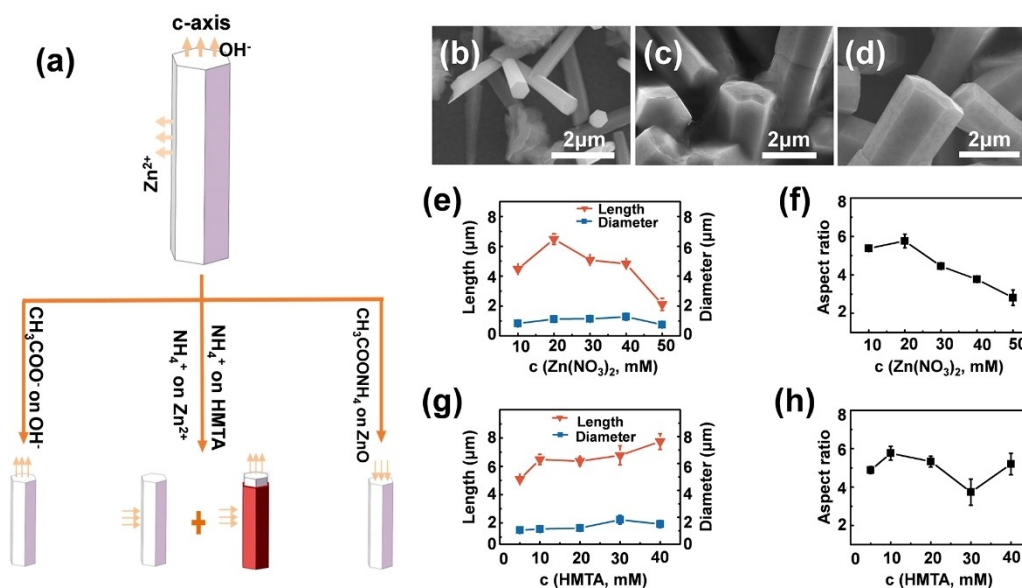
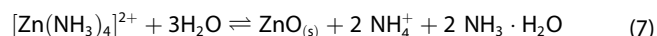
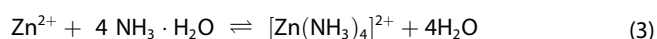


Figure 4. (a) The regulator effects of ammonium acetate on the growth process of ZnO; (b) the SEM image of ZnO obtained with CH₃COONa (20 mM) and Zn(NO₃)₂ (20 mM); (c) and (d) the top view of Y-40 and Y-50; (e), (f), (g) and (h) the length, diameter and aspect ratio of ZnO derived from the SEM data with different amount of Zn(NO₃)₂ (e, f) and HMTA (g, h), respectively.



The regulating effect of CH₃COO⁻ ions on OH⁻ ions

In order to investigate the contribution of CH₃COO⁻ ions hydrolysis on OH⁻ ions, we performed some reaction systems without HMTA. There are no ZnO generated (Figure S5(a and b)) with 20 mM zinc nitrate reacted with 10 mM or 20 mM ammonium acetate respectively under the same conditions. While a small amount of ZnO rods generated (Figure 4(b)) using 20 mM sodium acetate as a substitute, indicating the OH⁻ ions produced by the CH₃COO⁻ ions hydrolysis was sufficient to nucleate. No ZnO generated mainly due to the inhibition effect of NH₄⁺ ions, including OH⁻ ions generation or Zn²⁺ ions chelation.^[12c,14a] While no ZnO formed (Figure S5(c)) when increasing zinc nitrate to 50 mM, suggesting the NH₄⁺ ions mainly affect the production of OH⁻ ions rather than Zn²⁺ ions. The results above show that the OH⁻ ions produced by ammonium acetate hydrolysis are not sufficient to nucleate with Zn²⁺ ions without HMTA. Therefore, the OH⁻ ions produced by CH₃COO⁻ ions hydrolysis in the system could be ignored, and it will be further inhibited by HMTA hydrolysis.

The regulating effect of NH₄⁺ ions on Zn²⁺ ions and HMTA

The effect of NH₄⁺ ions on Zn²⁺ ions concentration is chelating to form [Zn(NH₃)₄]²⁺ complexes at pH = 7~12 which would be more favorable at higher pH values.^[12c,24] The pH value also determines the solubility and stability of ZnO in the growth process and even the final morphology.^[12c,15c,25] The pH values of the nutrient solution (20 mM Zn(NO₃)₂ and 10 mM HMTA) at 90 °C with different amounts of ammonium acetate (0~50 mM) are 6.65 ± 0.02 (0 min), 5.60 ± 0.02 (after reaction 10 min) and 6.50 ± 0.02 (after reaction 60 min). The results are unfavorable to forming [Zn(NH₃)₄]²⁺. The SEM data shown in Figure S6, also present the diameter of ZnO NRs coarsening obviously with increasing Zn(NO₃)₂ concentrations. The data derived from SEM data, as shown in Figure 4(e and f), including the aspect ratio decrease from ~5.78 (20 mM) to ~2.81 (50 mM), the length reduce from ~6.48 μm (20 mM) to ~2.11 μm (50 mM), and the diameter vary from ~1.12 μm (20 mM) to ~0.75 μm (50 mM), demonstrate a restrained growth trend along c-axis. This is because the ratio between OH⁻ ions generation and Zn²⁺ ions diffusion is the key parameter determining the length and diameter of ZnO. Higher concentration of Zn²⁺ ions promotes lateral growth, while higher OH⁻ ions concentration inhibits lateral growth as Zn²⁺ ions is rapidly consumed once it approaches the top of the NRs.^[23] The apparent Zn²⁺ ions response further indicates that the addition of ammonium acetate has little effect on Zn²⁺ ions.

The second regulatory effect of NH₄⁺ ions is the inhibition of HMTA hydrolysis (Eq. (2) and (4)) giving rise to two competitive effects: 1) Higher NH₄⁺ ions concentration means lower OH⁻ ions generation rate which will restrain the growth along c-axis; 2) The slower HMTA hydrolysis causes more chelating HMTA molecules binding to the lateral faces of ZnO NRs leading to

preferential growth along the *c*-axis.^[13] A tapering tendency from center to top at low ammonium acetate concentration (0, 2 mM and 5 mM), as shown in Figure 1(b) and Figure S1(Y-2 and Y-5), which represents the growth of NRs *c*-axis dominant meaning a relatively weak inhibition of HMTA hydrolysis. The ZnO rods show an obviously coarser top after 30 mM (Figure 1(d and e) and Figure S1(Y-40)). And the other crystal facets around the (0001) face could be seen from the top figure of ZnO (Figure 4(c and d)). It indicates an obvious lower OH[−] ions generation rate resulting from the inhibitory effect of HMTA hydrolysis.^[12a,16] Although the high concentration HMTA chelating on ZnO could enhance a preferential growth along *c*-axis at this time, the low OH[−] ions dominates the crystal growth.^[23] Therefore, two competitive effects introduced by NH₄⁺ ions on HMTA hydrolysis dominant the growth together, and the inhibitory effect on OH[−] ions is primary. The top poly-crystal face structures attribute to that the OH[−] ions produced from the HMTA adsorbing around ZnO rods consumed directly by the Zn²⁺ ions, leading to an obvious nonpolar facets growth.^[23] Figure 1(c) presents relatively regular hexagonal wurtzite structure at 10 mM, indicating the two competitive effects reach a balance. It needs to be noted that the regular hexagonal structure isn't influenced by Zn(NO₃)₂ or HMTA concentration, as shown in Figure (S6-S7), which implies other regulate effect including ammonium acetate attaching to the polar terminated ions, it will be discussed in detail below.

The encapsulation effect of ammonium acetate on ZnO

A typical ZnO wurtzite structure composes of a basal polar oxygen plane (000 $\bar{1}$), a top tetrahedron corner-exposed polar zinc plane (0001) and low-index nonpolar {10 $\bar{1}$ 0} face.^[26] The CH₃COO[−] ions preferentially adsorb on the positive polar plane (0001), for its electrostatic force is much stronger than the growth unit [Zn(OH)₄][−], which restrains the crystal growth along *c*-axis and is a reversible adsorption-desorption process.^[16,27] Ammonia also shows evidence of capping behavior.^[12c] Figure (S6–S7) present the ZnO keep urchin-shaped by simply changing zinc nitrate or HMTA without ammonium acetate and transform into regular hexagonal rods after adding 10 mM ammonium acetate. The length of ZnO rods increases from ~5.08 μ m (5 mM) to ~6.48 μ m (10 mM), ~6.36 μ m (20 mM), ~6.78 μ m (30 mM) and ~7.75 μ m (40 mM) with the increased HMTA concentration (Figure 4(g)) due to OH[−] ions generated and HMTA formed a shell around ZnO rod induce the vertical growth along the *c*-axis.^[12a,16,23,28] While the aspect ratio varies from ~4.88 (5 mM) to ~5.76 (10 mM), ~5.33 (20 mM), ~3.73 (30 mM) and ~5.20 (40 mM), as shown in Figure 4(h), indirectly indicating the growth along *c*-axis was inhibited. This effect can only be attributed to the inhibitory effect of NH₄⁺ and CH₃COO[−] ions coordinated with O^{2−} and Zn²⁺ of ZnO polar (0001) surface, respectively.^[16,29] And the additive ions coordinated into the ZnO crystal were also demonstrated by the XRD peak positions shifting to lower angles (Figure 1(h)) with the increasing of ammonium acetate.^[20] A higher mole percent at the higher binding energy (531.6 $\pm$ 0.1 eV) of the O1s spectra at 10 mM

ammonium acetate also evidently show a slower complete conversion of the formation of Zn(OH)₂ to ZnO, which could be resulted from the O^{2−} and Zn²⁺ nucleation sites were occupied by adsorbate, as shown in Figure 3. Some spectroscopy evidence also proved the regulation process of organic ligand and ions coordination on ZnO crystal growth.^[15] The ions coordination not only affects the facet growth direction, but dominates the whole growth process from crystallization nucleation to self-assemble into final morphology.^[30] It will be further discussed in next part.

The discussions of growth mechanism

To further identify the regulate effect of ammonium acetate on ZnO synthesis, SEM were used to characterize the whole growth process. Sampling every minute started from 3 min to 20 min after immersing in the water bath, and the reaction was stopped immediately by ice. Figure 5(a1-a4) shows the amorphous precursor precipitates directly from the solution firstly, then transformed into intermediates LBZs which were also observed on the XRD data (Figure 1(h) and Figure S3), and converted into small ZnO crystalline grain in the end (Figure 5(a4)).^[10c] Initially, nucleation were understood as an isotropic growth combined Ostwald ripening and coalescence.^[10b] The small particles agglomerate due to the high surface energy after nucleation, and form spherical structures through a free-orientation self-assembly of different adjacent crystal faces, which could also be explained by Ostwald ripening.^[11b,31] The other nucleation and EDX data also indicate that the nucleation underwent the Zn²⁺-LBZs-ZnO process (Figure S8-S12), which have been proved by C. C. Perry et al.^[10c] These particles begin to agglomerate and grow anisotropic after nucleation, however, the formation of the final morphology was not simply by self-assembly.^[10b,24]

Figure 5(b1-b5) shows the ZnO spherical unit grows into an urchin-shaped unit structure. It continues to grow along the existing urchin structure and stack with adjacent units to form the final structure. The driving force of stack results from the covered LBZs (Figure 5(b2) and Figure S8(a4)). The formation of urchin-shaped unit is explained by the surface-dissolved mechanism.^[30a] The surface of ZnO particles is hydrolyzed by OH[−] to form [Zn(OH)₄]^{2−}, and then lose proton to generate [ZnO₂]^{2−}, the sum effects of growth and etching form the final morphology.^[30a] Wang et al.^[30a] pointed out a high HMTA concentration would induce a reaction-limited leading to a dendrite-like structure, otherwise there would be a spherical structure resulting from a diffusion-limited growth. The urchin-shaped unit may correspond to a higher HMTA reaction concentration, while the rod-shaped structure formed after adding ammonium acetate further illustrates a limitation on HMTA hydrolysis.

Figure 5(c1–c3) shows that the spherical grains gradually become rod-like unit. Although there is no direct contact between the rods, symmetric coupling can be observed. Some coupling are completely symmetrical, some are misaligned, and some uncoupling units are self-existed, suggesting the sym-

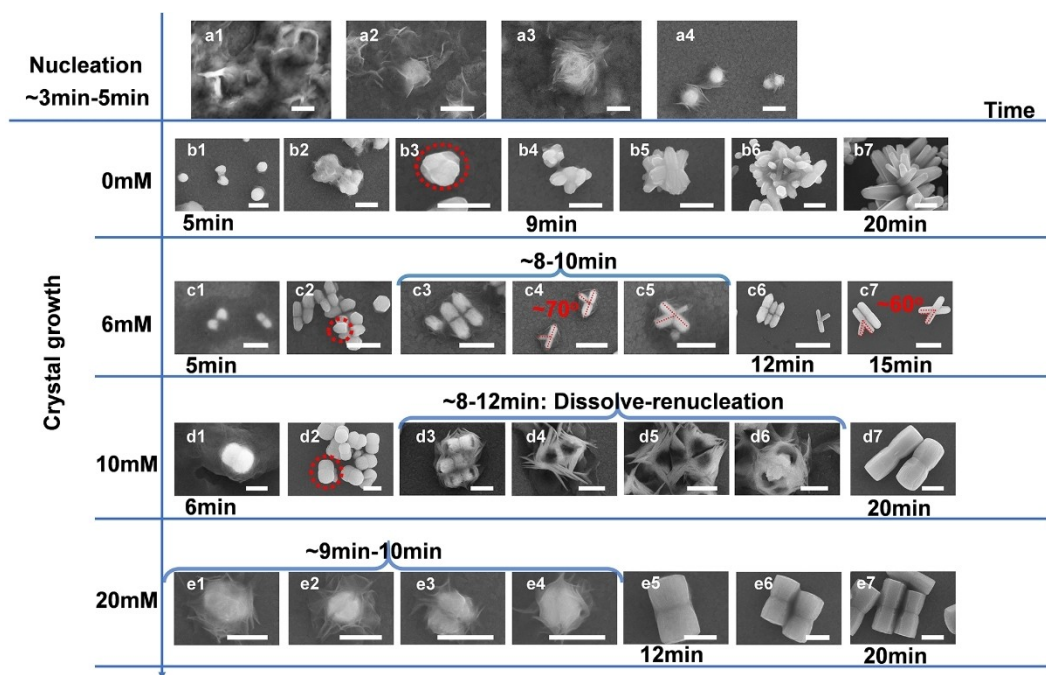


Figure 5. The SEM images of growth mechanism with different reaction time at specific amounts of ammonium acetate (a represents the nucleation process; b, c, d and e are the crystal growth and self-assembly process with 0 mM, 6 mM, 10 mM and 20 mM ammonium acetate, respectively. The scale bar is 1 μm).

metrical coupling structure firstly occurred by growing along a well-defined base surface.^[7] Figure 5(c3–c7) shows that further coupling only occurs in polar planes, and the coupling planes of symmetric structures are basically the same. The coupling of three and four units could also be seen in Figure 5(c4–c7), a certain coupling angle ($\sim 60^\circ$) resulting from the necessary of lowest energy of the growth. The coupling of three units in all systems in our experiment occurs at about the same angle ($\sim 60^\circ$), even if the third unit is a later nucleated and reassembled structure (Figure S8(e)). The misaligned of symmetric coupling and multiple units illustrating the self-assembly process is independent of possible linear array and coupling is not along intrinsic polarity of [0001] direction.^[11a] Asymmetry between three and four unit coupling is different from a perfect flat coupling, suggesting that the coupling may mainly come from the interaction between ligand-ligand.^[7] E. Javon et al. detected a distinct organic layer (1.5–2.0 nm) connecting in the growth basal planes, and combining simulation showed a bidentate anchoring mechanism of stearate carboxyl group deprotonated on the surface of an effective Zn atom.^[7] ZnO's wurtzite structure is a 4-fold tetrahedrally planes alternation combination of O^{2-} and Zn^{2+} ions stacked along c-axis. It determines whether its top points to a polar Zn-rich (0001) or an oxygen-rich (000 $\bar{1}$) surface along c-axis. The polarity of the exposed polar surface determines its binding to organic ligand. The forces between the two facets are both repulsive without ligand. And a stable bidentate anchoring mechanism can be formed after the ligand is introduced, leading to the rods to attract each other until the minimum energy distance relative to the ligand thickness is reached.^[7] Attraction is mainly based

on ligand-ligand interaction. There is no obvious coupling structure without ammonium acetate (Figure 5(b)).

The symmetrical coupling structure increased and the coupling gap reduced apparently with the increasing of ammonium acetate, and no single unit rod were observed after 10 mM, as shown in Figure 5(d–e) and Figure S8–S9, further illustrating the ligand-ligand coupling interaction result from ammonium acetate. The twin-shaped structures were also obtained with sodium acetate (Figure 4(b)), further suggesting the ligand-ligand coupling interaction of acetate ions. The apparent gap between the coupled structures and the significantly slower growth rate compared with the opposite direction indicate the existence of repulsive force between the coupling surfaces, suggesting the coupling surface may have the same polarity.^[7,32]

The obvious nanopyramids-type protrusions at the center of the rod tip (Figure 5(c)) indicate that the growth starts from the conical tip along the polar $\langle 0001 \rangle$ direction. The tip has the highest defect density attributing to its growth characteristics, and corresponding to the highest binding energy, which is most conducive to binding the reactant molecules and most easily to be etched.^[12b] A significant dissolve - renucleation - regrowth process of the twin-shaped rod is observed at 10 mM ammonium acetate, as shown in Figure 5(d3–d6).

Etching is considered to be the reaction between exposed negative charge O^{2-} (000 $\bar{1}$) surface and $\text{NH}_3 \cdot \text{H}_2\text{O}$ and NH_4^+ (equation (7)).^[12b] This process started from the center of the exposed polar surface where has the highest defect density to form a ring hollow structure nearly parallel to $\langle 2\bar{1}\bar{1}0 \rangle$,^[12a,b] as shown in Figure 5(d3–d4). The twin-shaped template structure

would be retained after the ZnO crystal was completely dissolved, as shown in Figure 5(d5). The subsequent growth started from the coupling connection part where could see a gap (Figure 5(d5)) corresponding to the highest defect density center and grow along the twin-shaped template (Figure 5(d6)).^[33] The EDX data (Figure S11) also represent a higher O and N atomic content (atomic ratio C:N:O:Zn = ~ 1:13:66:20) in the template, implying the bond of acetate and ammonium ions. Eventually the atomic ratio of zinc and oxygen was about 1:1 (Figure S12), implying the adsorbed ions replaced by the ZnO crystal.

No significant etching process was observed with a higher ammonium acetate concentration, probably due to a relatively low amount of $\text{NH}_3 \cdot \text{H}_2\text{O}$, further indicting the etching is not only resulting from the effect of NH_4^+ ions and demonstrating the inhibition effect of NH_4^+ ions on OH^- generation. The zinc oxide growth will be controlled by the minimum concentration of HMTA and gradually changed to diffusion-limited growth under such condition.^[30a] Figure 5(e1–e4) shows the twin-shaped structure crystallized directly from the flower-like intermediates of LBZs. Initially, the growth was c-axis preferentially along a certain crystal plane (Figure 5(e1–e2)). The two units weren't completely connected or symmetrical on account of the repulsion between the same polarity facets and adsorbed ions. Then they coupled into a perfectly symmetrical twin-shaped structure (Figure 5(e5–e7)). The dumbbell-shaped structure (Figure 5e and Figure S9) and $(10\bar{1}0)$, $(0\bar{1}10)$, $(1\bar{1}00)$, $(\bar{1}010)$, $(01\bar{1}0)$, $(\bar{1}100)$ and (0001) around the middle (0001) face could be seen from the top view figure (Figure 4(c and d)). It indicates that the growth of the top facet of ZnO is not only the traditional over-saturated growth mechanism but the layer-layer procreation stage.^[34]

In addition, the PEC performances of ZnO rods were measured. The results and analysis are displayed in Supporting Information, as shown in Figure (S13–S18) and Table S1. The uniform hexagonal wurtzite ZnO structures show a higher photocurrent density during the PEC measurements, which mainly benefit from the lower resistance of photoanode/electrolyte interface.

Conclusion

The roles of ammonium acetate on ZnO growth process have been investigated. The contribution of CH_3COO^- ions hydrolysis and NH_4^+ ions chelating to form $[\text{Zn}(\text{NH}_3)_4]^{2+}$ complexes can be negligible. The primary roles of acetate and ammonium ions are that affect the coupling process via binding to the Zn-rich (0001) face and control the OH^- generation rate by inhibiting HMTA hydrolysis, respectively. The regulation effect ultimately expressed as the ZnO self-assembled unit changed from urchin-shaped, rod-shaped to a fully coupled twin-shaped structure with the increasing ammonium acetate concentration. Moreover, undergo an obvious dissolve-renucleation-regrowth process at a specific concentration of ammonium acetate. And the uniform hexagonal wurtzite ZnO structures display a better PEC performance. These results provide a few insights for the

regulation of ZnO morphology and the application in PEC water splitting.

Experimental Section

Materials: All chemicals used in this work were of analytical reagent grade and used as received without further purification. All the aqueous solutions were prepared using deionized water and reagents (zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, CAS#:10196-18-6, AR, 99%), hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$, CAS#:100-97-0, AR, 99%+), ammonium acetate ($\text{CH}_3\text{CO}_2\text{NH}_4$, CAS#:631-61-8, AR), sodium acetate ($\text{CH}_3\text{CO}_2\text{Na}$, CAS#:6131-90-4, AR, 99%), ethanol were bought from Aladdin (Shanghai Aladdin Bio-Chem Technology Co., LTD).

Synthesis of ZnO: ZnO crystals were synthesized in aqueous solution using precursors $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and HMTA following previously described hydrothermal synthesis methods.^[10c] The ITO conducting glass (1 cm × 2 cm) used as substrate was washed with acetone, absolute ethanol and deionized water to remove impurities prior to the CBD. Thereafter, the ITO glass were located in the bottom of the cell with various concentrations of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, HMTA and $\text{CH}_3\text{CO}_2\text{NH}_4$ aqueous solutions as nutrient solution (Table 1). The obtained ZnO were rinsed with deionized water and dried in air, and characterized directly except the PEC measurement which was annealed at 450 °C in air for 2 h before test.

The ITO conducting glass (1 cm × 0.5 cm) was washed with the same procedure and reaction conditions above. The study of growth process started sampling every minute from 3 min to 20 min after the nutrient solution (20 mM $\text{Zn}(\text{NO}_3)_2$, 10 mM HMTA and different amounts of $\text{CH}_3\text{COONH}_4$) immersed into the water bath. The samples were put on the ice to stop the reactions immediately, then took away from the ice and dried in the air after 10 min. The samples were rinsed with deionized water and dried in air again, and characterized by SEM directly.

Characterization: The surface morphology and crystallinity of the samples were characterized by scan electron microscope (SEM, SU3500, Hitachi, Japan), Energy Dispersive Spectrometer (EDX, Model 550i, IXXF, America) and transmission electron microscope (TEM, Tecnai G2 F20, FEI, Netherlands & America) operated at 200 kV. The X-ray diffractometer (XRD) scan of crystal structure was recorded by a D/MAX-2500 system using $\text{Cu-K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) at a scan rate of 5° min^{-1} . The chemical-state surface composition of the ZnO nanostructures was analyzed by X-ray optical electron spectroscopy (XPS, PHI 1600, ESCA system). The UV-Vis absorption spectrum was measured by a UV-Vis spectrophotometer (UV-3900, Hitachi, Japan). The transmittance (T , %) and reflectance (R , %) of the ZnO nanostructured samples were

Table 1. The ions concentration of nutrient solution (the samples prepared using 20 mM $\text{Zn}(\text{NO}_3)_2$, 10 mM HMTA and different amounts of $\text{CH}_3\text{COONH}_4$ are named as Y-x, x represents x mM $\text{CH}_3\text{COONH}_4$).

Sample	$\text{Zn}(\text{NO}_3)_2$ [mM]	HMTA [mM]	$\text{CH}_3\text{COONH}_4$ [mM]	CH_3COONa [mM]
Y-x	20	10	0 ~ 10, 20, 30, 40, 50	–
–	10, 20, 30, 40, 50	10	0, 10	–
–	20	5, 10, 20, 30, 40	0, 10	–
–	20, 50	–	10, 20	–
–	20	–	–	20

measured over the wavelength range of 300–800 nm. The absorption plus scattering ($A + S$, %) were calculated according to the formula $A + S = 100 - T - R$. The pH values were measured by a pH meter (S210, Mettler Toledo Instruments (Shanghai) Co., LTD). The Raman spectra were recorded by the Raman spectrograph (RTS-2, Titan Electro-Optics (Hong Kong) Co. Ltd) at 532 nm laser wavelength.

Photoelectrochemical testing: PEC measurements for water splitting were performed in a standard three-electrode electrochemical cell configuration using the prepared ZnO rods loaded on ITO as the working electrode, a platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. A 0.5 M Na_2SO_4 solution was employed as the electrolyte and purged with N_2 for 30 min before the measurements. PEC measurements and electrochemical impedance measurements were recorded under a solar simulator Xenon lamp (CEL-HXF300, Au Light, China) with AM 1.5G optical filter and optical power meter (NP2000, Au Light, China) were used to simulate sun light (100 mW cm^{-2}). The potential was measured against an Ag/AgCl reference electrode and converted to reversible hydrogen electrode (RHE) potential by the equation $E(\text{RHE}) = E(\text{Ag}/\text{AgCl}) + 0.225(\text{V}) + 0.059 \times \text{pH}$.^[35] All PEC measurements were tested with illumination from the front side of the ITO glass substrate covered with the ZnO nanostructures (NSs). For each group of samples, tests were performed in triplicate in order to exclude accidental phenomena and prove reproducibility.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 11774255), the National Basic Research Program of China (No. 2020YFC2004602) and the Key Project of Natural Science Foundation of Tianjin City (No. 17JCZDJC30100).

Conflict of Interest

The authors declare no conflict of interest.

Keywords: ammonium acetate · crystal growth · morphology regulation · PEC catalysis · ZnO

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Manuscript received: August 24, 2021

Accepted manuscript online: October 20, 2021

Version of record online: November 10, 2021