# Promotional effect of carbonate ions on growth of 1D ZnO crystals

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A series of ZnO crystals were fabricated by two separate steps including precursor precipitation and hydrothermal post-treatment to compare the influence of precursor anions on morphologies of ZnO crystals. Sharp-tip rod and flat-end hexagonal column could be synthesized through hydrothermally treating the zinc hydroxide precursor containing carbonate ions, $Zn_5(CO_3)_2(OH)_6$, in NaOH and $NH_3 \cdot H_2O$ solutions, respectively, whereas just irregular ZnO nanoparticles were obtained through hydrothermally treating the precursor containing chloride ions, $Zn_5(OH)_8Cl_2 \cdot H_2O$, in both of the alkaline solutions. Combining with the XRD, SEM and FTIR characterizations, it was proved that carbonate ions of the precursor promoted the formation of ZnO crystals with well-defined morphologies, and the alkaline solutions used in hydrothermal treatment also played the key role in anisotropic growth towards one-dimensional ZnO through controlling the growth rate.

## 1. Introduction

One-dimensional (1D) materials have attracted intensive research interest owing to their unique properties and diverse applications [1]. ZnO, a compound semiconductor with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV, has been demonstrated to have broad applications in electronic, piezoelectric, optical, optoelectronic, electrochemical and electromechanical devices [2]. So large effort has been focused on the synthesis of 1D ZnO structures through developing many methods, such as solution phase synthesis, physical or chemical vapour deposition, molecular beam epitaxy (MBE), sputtering and electrospinning [3,4]. Up to now, the growth of 1D ZnO in alkaline solution environment with or without surfactants has been extensively studied due to its low cost and easy operation [3-7]. However, the mechanism of solution phase route has not been fully understood and need further investigation.

The literatures [3,8] proposed that synthesis of ZnO structure was necessary to utilization of OH⁻ provided by alkaline solutions to hydrolyse zinc ion and consist of $Zn(OH)_4^{2-}$ aggregate. $Zn(OH)_4^{2-}$ was thought as the growth unit and was directly incorporated into ZnO crystal lattice at the interface with continuous association and dehydration of $Zn^{2+}$ and OH⁻ ions. We noticed that 1D ZnO structure could be synthesized though alkaline solutions containing $CO_3^{2-}$ anion, e.g. $Na_2CO_3$, $NH_4(CO_3)_2$, as precipitators and without surfactants or structure-directing agents in the previous literatures [5-7]. These literatures generally attributed the 1D structure to the influence of OH⁻ anions on the nucleation and growth rate, as well as the intrinsic feature of wurtzite ZnO, which has high energy polar surface {0001} and is preferential to orientation along the c axis. The function of carbonate ion was considered to simply provide and adjust OH⁻ concentration. To gain insight into the effect of carbonate ion on the structure and morphology of ZnO crystals, in this paper, we synthesized ZnO crystals by two separate steps including precursor precipitation and hydrothermal post-treatment, thus the influence of precursor anions on morphologies of ZnO crystals could be directly compared under more controllable conditions.

## 2. Experimental section

All chemicals used in the presented synthesis process were of analytical reagent grade. In a typical synthesis, 36 mmol of anhydrous $ZnCl_2$ was dissolved in deionized water and then added into a certain amount of $Na_2CO_3$ or NaOH alkaline solution with the control of the final pH value of the solution at 6.0. The precursor precipitates were immediately collected by filtration, washed with distilled water, and dried at 80 °C. 4 mmol of the pre-synthesized precursors and a certain amount of NaOH or $NH_3 \cdot H_2O$ solution with a pH value of 13.5 were added into a reaction kettle and heated at 160 °C for 4 h. The products were collected by filtration, washed with distilled water, and dried at 80 °C.

A Rigaku Ultima IV powder diffractometer was used to obtain powder X-ray diffraction (XRD) patterns in the 2θ range of 20-80° using Cu Kα radiation and rate 5 °/min. A Nicolet 6700 Fourier transform infrared (FTIR) spectrometer were operated in the wavenumber range of 400-4000 cm⁻¹ at room temperature with the precursors tablets diluted 20-fold with KBr. A Hitachi SU8010

scanning electron microscope (SEM) was used to determine the morphologies of the samples. The powder samples were supported on silicon slices prior to measurement.

## 3. Results and discussion

The powder XRD patterns of pre-synthesized precursors are shown in Fig. 1a. All the X-ray diffraction peaks of the precursors could be indexed to the corresponding standard spectra. The obtained precursor precipitated by $Na_2CO_3$ solution at final pH value of 6.0 was monoclinic hydrozincite $Zn_5(CO_3)_2(OH)_6$ (JCPDS 19-1458) [9,10]. When the NaOH solution was used as precipitator instead of $Na_2CO_3$, the precursor obtained at the same pH value of 6.0 was hexagonal $Zn_5(OH)_8Cl_2 \cdot H_2O$ (JCPDS 72-0922) [11-13].
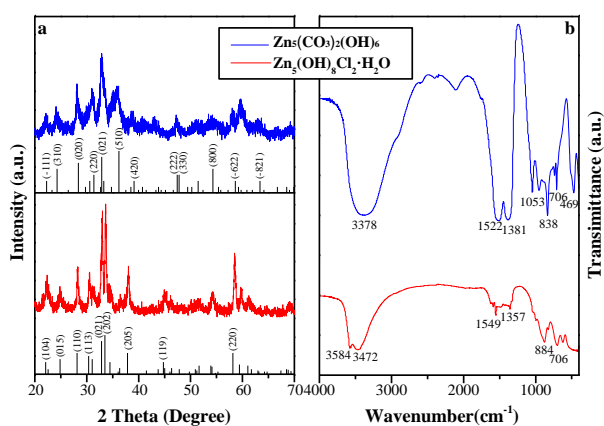


*Fig. 1. (a) XRD patterns and (b) FTIR spectra of the pre-synthesized precursors precipitated by $Na_2CO_3$ and NaOH, respectively*

These observations from XRD were further corroborated by FTIR measurements. Fig. 1b shows the FTIR spectra of both precursors. In the spectrum of $Zn_5(CO_3)_2(OH)_6$ precursor, the band around 3378 and 1053 $cm^{-1}$ could be attributed to the vibration of hydroxyl group, 1522, 1381, 838 and 706 $cm^{-1}$ were corresponding to the bending vibration of carbonate group, and 469 $cm^{-1}$ was originated from the vibration of Zn-O [14-16]. In the spectrum of $Zn_5(OH)_8Cl_2 \cdot H_2O$ precursor, the band around 3584 and 3472 $cm^{-1}$ were assigned to the vibration of hydroxyl group and water molecules [16,17]. The bands around 1549, 1357 and 706 $cm^{-1}$ indicated that the precursor was doped with carbonate group, which should be brought into through small amount of carbonate anion impurity existed in NaOH solution. The carbonate group was so few that it was difficult to be characterized by XRD. Obviously, the main phase of precursor precipitated by NaOH should be still considered as $Zn_5(OH)_8Cl_2 \cdot H_2O$, although Zn-Cl vibration occurred below 400 $cm^{-1}$ could not be detected by FTIR [16,18].

Fig. 2 shows the SEM images of the pre-synthesized

precursors. It could be seen that the $Zn_5(CO_3)_2(OH)_6$ precursor displayed irregular plate-like structure with a size of around 30-100 nm, and $Zn_5(OH)_8Cl_2 \cdot H_2O$ precursor presented large aggregates consisted of small irregular particles of 20-50 nm.
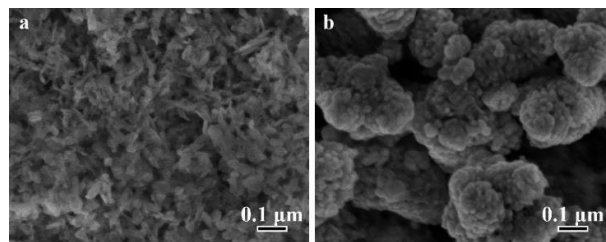


*Fig. 2. SEM images of the pre-synthesized precursors (a) $Zn_5(CO_3)_2(OH)_6$ and (b) $Zn_5(OH)_8Cl_2 \cdot H_2O$.*

In the subsequent hydrothermal treatment, each precursor was immersed in NaOH or $NH_3 \cdot OH$ alkaline solution with pH value of 13.5 and treated at 160 $^oC$ for 4 h in a reaction kettle. Alkaline solution hydrolysed zinc ions of the precursors to result in the formation of ZnO structures, which were confirmed by the XRD patterns in Fig. 3. All peaks could be identified as hexagonal wurtzite structure of ZnO (JCPDS 36-1451).
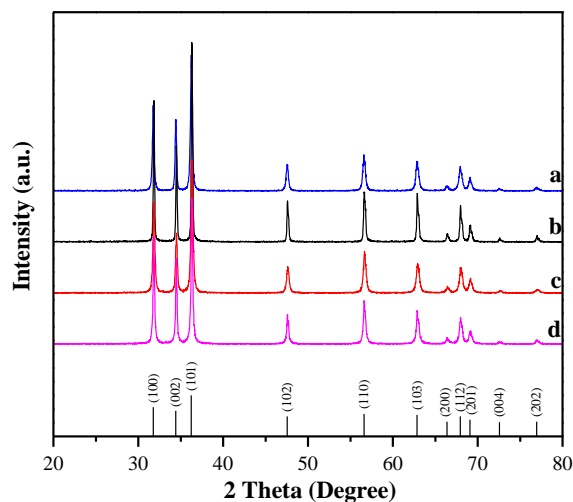


*Fig. 3. XRD patterns of the as-obtained ZnO crystals through hydrothermally treating $Zn_5(CO_3)_2(OH)_6$ in (a) NaOH or (b) $NH_3 \cdot H_2O$ solutions, and $Zn_5(OH)_8Cl_2 \cdot H_2O$ in (c) NaOH or (d) $NH_3 \cdot H_2O$ solutions*

However, as-obtained ZnO crystals presented very different morphologies in the SEM images as shown in Fig 4. When $Zn_5(CO_3)_2(OH)_6$ was used as precursor and NaOH as alkaline solution in hydrothermal treatment, it is exhibited urchin-like ZnO structure consisted of aggregated sharp-tip hexagonal rods. The diameter and length of the ZnO rods were about 0.2-0.3 μm and 2-3 μm. While NaOH was replaced by $NH_3 \cdot H_2O$, one end

connected aggregations also could be obtained, which consisted of flat-end hexagonal column with a much larger diameter of 2-3 μm. When $Zn_5(OH)_8Cl_2 \cdot H_2O$ was used as precursor and treated in NaOH or $NH_3 \cdot H_2O$ solution, the obtained ZnO crystals both were irregular particles, no well-defined morphologies could be observed. Based on the above observations, it was demonstrated that carbonate ions of the precursor promoted the formation of ZnO crystals with well-defined morphologies.

Gao group's work [19] proposed that transformation from the precursor into ZnO in hydrothermal condition goes through a dissolution-recrystallization-decomposition-growth process. Firstly, the as-synthesized precursor dissolved and was hydroxylated into $ZnO \cdot nH_2O$, then decomposed into ZnO nanoparticles; finally, oriented attachment of these nanoparticles formed 1D ZnO structure. According the literature study, it was deduced that the both $Zn_5(CO_3)_2(OH)_6$ and $Zn_5(OH)_8Cl_2 \cdot H_2O$ precursor transformed into ZnO nanoparticle, however, ZnO nanoparticle attached into well-defined ZnO structure only in the system containing carbonate. Carbonate anion might promote anisotropic growth of ZnO crystals through some kind of interaction with ZnO nucleus, which presented structure-directing effect. Moreover, it should be noted that our synthesized ZnO rods grown along [0001] direction, not consistent with the previously reported ZnO wires grown along [1-10] direction [19].
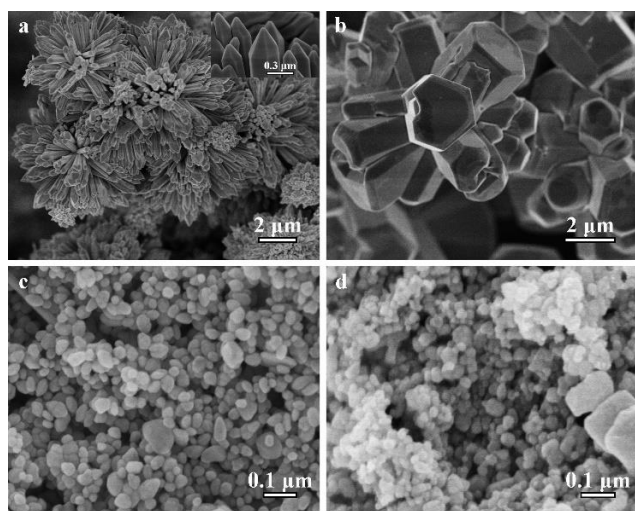


*Fig. 4. SEM images of the as-obtained ZnO crystals through hydrothermally treating $Zn_5(CO_3)_2(OH)_6$ in (a) NaOH or (b) $NH_3 \cdot H_2O$ solutions, and $Zn_5(OH)_8Cl_2 \cdot H_2O$ in (c) NaOH or (d) $NH_3 \cdot H_2O$ solutions*

Treating the precursors containing carbonate ions by NaOH or $NH_3 \cdot H_2O$ solutions also resulted in different morphologies. This suggested that the alkaline solutions used in hydrothermal treatment also played the key role in anisotropic growth towards 1D ZnO through controlling the growth rate. Using $NH_3 \cdot H_2O$ in hydrothermal treatment, $Zn^{2+}$ and $NH_3$ could combine to form $Zn(NH_3)_4^{2+}$, which is a reversible reaction. With the reaction proceeded, $Zn(NH_3)_4^{2+}$ gradually decomposed to

maintain a stable amount of $Zn^{2+}$ in the solution and compensate for $Zn^{2+}$ reacted with $OH^-$. The ZnO nucleation and growth considerably slowed down. Thus fewer nuclei formed and grown into larger crystals, flat-end hexagonal columns with a low aspect ratio, indicating that too low growth rate lead to almost no preferential growth along [0001] direction. Although NaOH and $NH_3 \cdot H_2O$ solutions with the same pH value were used, more ZnO nuclei formed in NaOH solution, and higher growth rate favoured preferential growth along [0001] direction, so sharp-tip hexagonal rods with a high aspect ratio could be obtained. Actually, too high growth rate was not favourable to preferential growth along c axis. When the pH value was lowered in the presence of carbonate ions, i.e., a more appropriate growth rate was provided together with structure-directing effect, significantly preferential growth along [0001] direction and wire-like ZnO crystals with much higher aspect ratio could be easily achieved.

## 4. Conclusions

In summary, four ZnO crystals with different morphologies, sharp-tip hexagonal rod, flat-end hexagonal column and two irregular particles were synthesized using a two steps route including precursor precipitation and hydrothermal post-treatment. It was proved that carbonate ions of the precursor promoted the formation of ZnO crystals with well-defined morphologies, and the alkaline solutions used in hydrothermal treatment also played the key role in anisotropic growth towards one-dimensional ZnO crystals through controlling the growth rate.

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