Tomato-Like ZnO Clusters with Complex Crystallization

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We report a new structure self-assembled by ZnO nanolayers, nanoplatelets and microparticles under one-pot condition without surfactants. The structure shows tomato-like morphology with hexagonal symmetry. Selected area electron diffraction (SAED) analysis indicates that the assembly is highly oriented. However, considering the nonuniformity of the subunits, the structure is much different from the commonly observed ZnO mesocrystals. The growth of the complex structure in the solution is proposed to relate to the evolution of the supersaturations and segregation of the intrinsic defects.

Keywords: ZnO, Clusters, Mesocrystals, Solution Method.

1. INTRODUCTION

ZnO is one of the most important inorganic materials. The properties of ZnO are affected by their sizes and morphologies, thus much effort has been devoted to fabricate ZnO nano- or microstructures with different morphologies and microstructures.1-4 Vapor-phase and solution-phase methods are two widely adopted approaches, but considering the cost and the simplicity, the latter may be more promising. Through solution routes, various ZnO crystals have been synthesized.5-6 In particular, several three-dimensional (3D) structures have been fabricated in recent years.5-12 These structures are usually self-assembled or aligned by uniform subunits, for example, hollow ZnO dandelions with nanorods or nanoplatelets,5 ZnO microspheres with multipods,12 and ZnO doughnuts with nanoplates.8,9 Moreover, surfactants or templates are often used to assist the crystal growth.9-12 These additives change the growth behavior of ZnO, resulting in the production of hierarchical structures. In general, the growth velocity of ZnO is \( V_{001} > V_{01-10} > V_{000-1} \) in solution without additives, thus the obtained morphologies of ZnO are usually 1D nanostructures. Here we report a new ZnO 3D structure with nonuniform subunits and complex crystallization. The structure exhibits tomato-like morphology with hexagonal symmetry. The ZnO tomatoes were synthesized in water-ethanol mixed solvent under one-pot condition. No surfactant was used, and they showed special formation and destruction processes. We suggest that the growth of the structure is caused by the evolution of the supersaturations and segregation of the intrinsic defects.

Optical properties of the nanostructured ZnO tomatoes were also studied.

2. EXPERIMENTAL DETAILS

In a typical synthesis, zinc acetate (Zn(Ac)\(_2\) \( \cdot \) 2H\(_2\)O) and hexomethylenetetramine (HMT) with equal molar ratio were dissolved into ethanol to form a 0.025 M solution. 2 mL of distilled water was then added to 38 mL of the solution and maintained at 70°C for 24 h. The white precipitate was centrifuged, washed and finally dried at 70°C in air. The products were characterized with field-emission scanning electron microscopy (SEM, SIRION), energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM, Tecnai G2 20) equipped with selected area electron diffraction (SAED). The photoluminescence (PL) spectrum was measured using an F-4500 spectrofluorometer (\( \lambda_{ex} = 325 \) nm) at room temperature.

3. RESULTS AND DISCUSSION

Figure 1(a) shows the SEM image of the products obtained from the solution at 24 h. The particles exhibit a unique morphology, one side is flat (the bottom) and the other side (the top) is retuse, like tomatoes to some extent. The tomatoes are \( \sim 8 \) \( \mu \)m in diameter and \( \sim 5 \) \( \mu \)m in height. The lateral faces of them are rather rough (Fig. 1(b)). Figure 1(c) shows the bottom of a tomato, which exhibits well-defined
hexagonal geometry with six symmetrical edges. No primary nanoparticles or pores can be recognized as shown in the enlarged image in Figure 1(d). Layered structures can be clearly seen above the bottom, but they are different in size and stagger in the corners, resulting in the ellipsoidal faces of the tomatoes. Figure 1(e) shows the top of a tomato, which exhibits distinctively different morphology from the bottom. A hexagonal prism is in the center of the retuse top and the brim is divided into six arciform parts. Figure 1(f) is the enlarged image of the brim consisting of nanoplatelets, and Figure 1(g) is the enlarged image of the central hexagonal prism with well-faceted sides and a raised top. The surface of the prism is much smoother than that of the brim. To further reveal the difference of the hexagonal prism and the brim, micro-area EDS analysis was performed. As shown in Figure 1(h), the prism has more zinc (Zn/O = 1.15) and the brim has more oxygen (Zn/O = 0.42). Si peaks arise from the Si substrate used to place the particles. The extra zinc in the hexagonal prism may come from oxygen vacancies and zinc interstitials, and the high content of O in the brim possibly originates from the surface adsorption due to the rough and porous surface.

A mystery exists that a hexagonal prism can be clearly seen from the top, which seems to grow from the inside, but it leaves no marks on the bottom. To understand this phenomenon, time-dependent shape evolution study was conducted. The SEM images of products obtained at 8–15 h show that plates were formed in the initial stage (Fig. 2(a)), then hexagonal prisms nucleated and started to grow on the center of the plates (Figs. 2(b and c)), finally resulted in the clusters (Fig. 2(d)). We also found that the ZnO tomatoes were kinetically metastable. Figure 3(a) shows the SEM images of products obtained at 36 h. The ZnO particles still show tomato-like morphologies, but some of them have holes in the center of the hexagonal prisms. The hole can be clearly seen in Figure 3(b). Further extending the ripening time will lead to the disaggregation of the tomatoes. As shown in Figure 4(a), most of the tomatoes have broken into fan-shaped pieces, and some have cracked as depicted in Figures 4(b) and (c). However, through these cracked tomatoes we can investigate the inside structures of the tomatoes. Layered structures can be seen in Figure 4(b), which is consistent with the morphology of the lateral faces shown in Figure 1(b). More importantly, no hexagonal structures can be identified in the center of the cracked tomatoes as shown in Figure 4(b), indicating the inside hexagonal prisms and the layered structure have fused together during the growth. However, in the final stage the hexagonal prism grew into a bulge on the center of the top and nanoplatelets aggregated on the brim forming a concave. The hexagonal prism can be seen in the center of the cracked tomatoes as shown in Figure 4(b), which is like a hollow ZnO tomato removing the hexagonal prism. We suppose that the rings are the products of the eroded tomatoes as shown in Figure 3(b).
Fig. 4. SEM images of samples obtained at 48 h. (a) A general-view image, (b) and (c) cracked ZnO tomatoes, (d) a ZnO ring.

The cracked ZnO tomatoes also benefit the TEM analysis. An intact ZnO tomato was too thick to get through for the electrons. The intrinsic structures can only be investigated using the cracked pieces. Figure 5(a) is the TEM image of a hexagonal prism and Figure 5(b) is the enlarged image of its edge. No primary particles can be identified and the corresponding SEAD pattern can be indexed as the [01-11] zone axis of single-crystal ZnO. Figure 5(c) shows the TEM image of a fan-shaped piece. It is aggregated from nanoparticles as shown in the enlarged image in Figure 5(d). However, it also shows perfect single-crystal scattering behavior which can be indexed by the diffraction of the [01-11] zone axis. This indicts that the whole ZnO tomato may have mutual orientation.

The formation process of the complex ZnO clusters is proposed to be a process controlled by the supersaturations. During the solution process, HMT is used as the precipitation reagent which provides OH\(^-\) ions by hydrolysis according to the following reactions:

\[
(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \quad (1)
\]
\[
NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (2)
\]

The hydrolysis is slow since the solution is mainly ethanol, thus the solution is from low supersaturations to higher supersaturations. Single crystals would form at low supersaturations, and higher supersaturations would enable oriented aggregation yielding mesocrystals. Noting that the ZnO tomato grows from the smooth bottom to the complex top and the hexagonal prism forms before the stacked nanoplatelets, the crystallization of the structure transforms from single crystals to mesocrystals, which is just synchronous with the supersaturations change of the solution. When the HMT is further hydrolyzed which provides excess hydroxide ions, the structures become unstable, the surface of the hexagonal prism may be etched and the nanolayers are broken down. We also suggest that the hexagonal prism and the center of the bottom layers contain more intrinsic defects, for example, oxygen vacancies and zinc interstitials as indicated by the EDS analysis. These defects facilitate the nucleation and preferential growth of the hexagonal prisms in the initial stage, but also cause the erosion of them in the aging stage.

The existence of intrinsic defects can be further confirmed by the PL analysis. As depicted in Figure 6, the PL spectrum shows sharp UV emission centered at 400 nm, blue emission at 452 nm and 469 nm, and a broad green emission around 520 nm. The UV emission is a near-band-edge transition. It is generally accepted that the origin of
the blue emission at 452 nm corresponds to interstitial zinc, and the green emission is the electron-hole radiative recombination at oxygen vacancy, while the origin of 469 nm emission is not still very clear.13,14

4. CONCLUSION

We have reported an unusual tomato-like ZnO structure with complex crystallization. The clusters are constructed by ZnO nanolayers, nanoplatelets and microparticles. These subunits are highly oriented as indicated by the SAED analysis. Moreover, the clusters are kinetically metastable. Upon extended ripening, they will be disaggregated into fan-shaped pieces, hexagonal particles and even rings. The special formation and destruction processes may be caused by the evolution of the supersaturations and segregation of the intrinsic defects. The tomato-like ZnO clusters provide an unique model for crystallographic research, and the blue emission of them may have application in optoelectronics.

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References and Notes


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