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DC-field-induced synthesis of ZnO nanowhiskers in water-in-oil microemulsions

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Abstract

ZnO nanowhiskers were successfully fabricated using DC-field induced water-in-oil microemulsions method. Phase structure, morphology and microstructure of the product were investigated by X-ray diffraction and transmission electron microscopy. Parameters in preparation process such as electric field intensity and surfactant were discussed and the product formation mechanism was studied. XRD and TEM results showed that the obtained ZnO particle was hexagonal wurtzite-type with 1–3 nm in diameter and 20–70 nm in length, and morphology of the particles was shown to be correlated not only with the electric field intensity but also with the surfactant. There was a threshold when the electric field intensity was 80 V/mm. The morphology of the particles was basically spherical before the threshold, while *L*/*D* increased with the raise of electric field intensity. ZnO nanowhiskers were obtained under mixed surfactants but spherical particles were got with a single surfactant.

JEL classification: 61.46.Km; 78.55.Et; 81.10.Dn

Keywords: A2. Microemulsions; A3. Electric field; B1. Whiskers; B2. ZnO

1. Introduction

ZnO is an important semiconductor with wide band gap (3.37 eV) and high exciton binding energy (60 meV) and has been in great interest from wide range of technological field associated with nanotechnology. Nano-ZnO performs a series of special effects, such as small size effect [1], large surface effect [2], volume effect [3]. It also has superior photoelectronic properties. One-dimensional ZnO nanomaterials are widely used in fabricating piezoelectric nanogenerators [4], photodiodes [5], varistors [6], light-emitting diodes [7], displays [8,9], field effect transistors [10–12], solar cells [13], sensors [14–18], etc. ZnO crystal whiskers with high aspect ratio have been used as reinforced composite materials [19] and probing tips in atomic force microscopy and scanning tunneling microscopy [20]. ZnO has been predicted as an alternative to GaN in green, blue, ultraviolet and white light emission materials, since ZnO possesses comparative band gap to GaN (3.4 eV), and larger exciton binding energy than GaN (35 meV). Moreover, ZnO has higher luminous intensity than GaN at room temperature. Meanwhile, high-quality ZnO, such as one-dimensional nano-crystal prepared by directional growth, has a simpler preparation method and a lower cost than GaN. Therefore, ZnO becomes a research hotspot. A lot of studies on ZnO were reported each year, one of which focused on the preparation of ZnO nanomaterials with excellent performances [11,13,14].

Recently, the preparation methods of ZnO nanoparticles with different morphologies have been gradually developed and significant progress has been made. Microemulsion method is an ideal method to prepare ZnO. There are many studies concentration on the preparation of ZnO nanomaterials by microemulsion method [21–23]. But little work has been done on the introduction of external conditions, such as electric field, although Komarneni et al. [24] used microwave field in the

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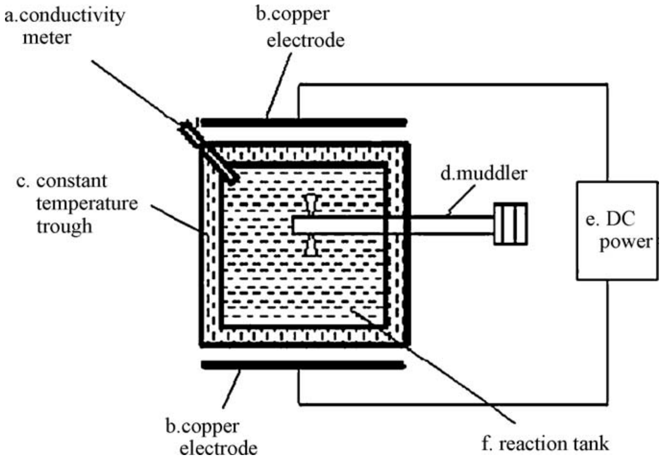

Fig. 1. Schematic diagram of apparatus machine.

synthesis of ZnO. In our work, DC electric field was introduced to investigate the characteristics of ZnO particles prepared by microemulsion method with the anionic/cationic mixed surfactants. Moreover, the condition for acquiring ZnO nanowhiskers was also discussed.

2. Experimental procedure

2.1. Material and chemicals

Zinc sulphate heptahydrate ($ZnSO_4·7H_2O$, analytically pure), ammonia ($NH_3·H_2O$, analytically pure), hexadecyl trimethyl ammonium bromide (CTAB, >99%), sodium dodecyl sulphate (SDS, analytically pure), octane (C_8H_{18}, >95%), normal butanol ($CH_3CH_2CH_2CH_2OH$, 96%), absolute ethyl alcohol (C_2H_5OH, analytically pure) and redistilled water (homemade) were used as starting materials in present study. All chemicals do not need further purification.

2.2. Synthesis

The sketch map of the experiment is shown in Fig. 1. Two copper electrode plates (the distance between two plates was 5 mm) were fixed outside of the constant temperature reaction tank and the conductivitymeter was put in the tank to measure the conductivity of the system. The size of the reaction tank is 10 cm (length) × 5 mm (width) × 10 cm (height) and the reaction tank is a cuboid. Octane/butanol/SDS + CTAB/$ZnSO_4$ and octane/butanol/SDS + CTAB/ammonia microemulsions were prefabricated. The mass ratio of mixed surfactants, butanol and octane was 2:1:1.3. The molar ratio of water and mixed surfactants (W) was constant in the process ($W = 15.2$). The prepared octane/butanol/SDS + CTAB/$ZnSO_4$ (the mass ratio of SDS and CTAB is 1:1 and the concentration of Zn^{2+} is 0.1 mol/L) microemulsion was poured into the beaker, and the electric field was added. The octane/butanol/SDS + CTAB/ammonia microemulsion (the mass ratio of SDS and CTAB is 1:1 and the concentration of ammonia is 1.0 mol/L) was dropped into the beaker, then stirred for 30 min until the reaction was over (the experiment was carried out at room temperature). After ageing for 30 min, ultrasonic dispersing for 1 h, vacuum filtrating, washing for 4–5 times by redistilled water and absolute ethyl alcohol, the precursor was obtained after drying. The precursor was calcined at different temperatures for 1 h, and ZnO samples were obtained.

2.3. Structure of anionic/cationic mixed surfactants microemulsion under external electric field

SDS is an anionic surfactant and CTAB is a cationic surfactant. Fig. 2a plots the anionic/cationic mixed surfactants microemulsion [25] structure without external electric field. The anionic/cationic mixed surfactants tend to arrange alternately to get the smallest repulsion and the most stable system. In the external electric field, the anionic/cationic mixed surfactants tend to re-arrange along the direction of electric field, as shown in Fig. 2b. With an electric field force of F_N, water nuclear in microemulsion is elongated and its surface area increases, thus the surface tension F_b in the opposite direction of F_N increases too, ignoring the electrostatic attraction of the anionic/cationic mixed surfactants. At last, they achieve a dynamic balance and the water nuclear is

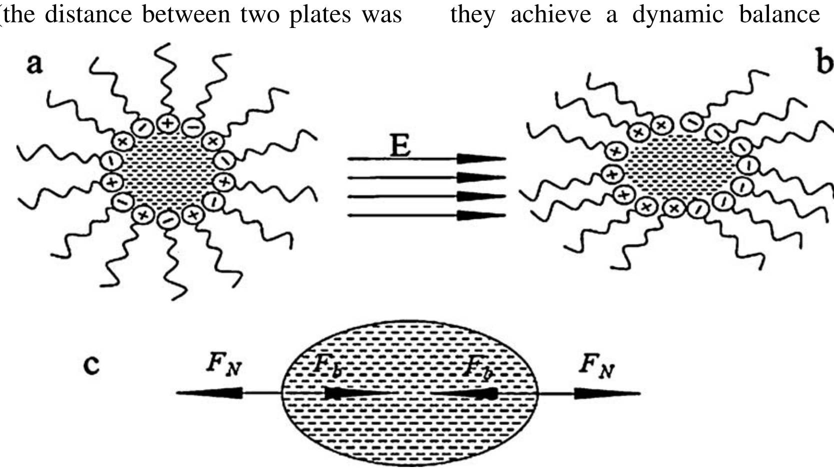

Fig. 2. Schematic diagram of polarization and force balance of mixed surfactants under external electric field. (a) The anionic/cationic mixed surfactants microemulsion structure without external electric field. (b) The anionic/cationic mixed surfactants re-arranged along the direction of electric field. (c) The surface tension F_b and the electric field force of F_N achieved a dynamic balance and the water nuclear was stretched into an ellipse.

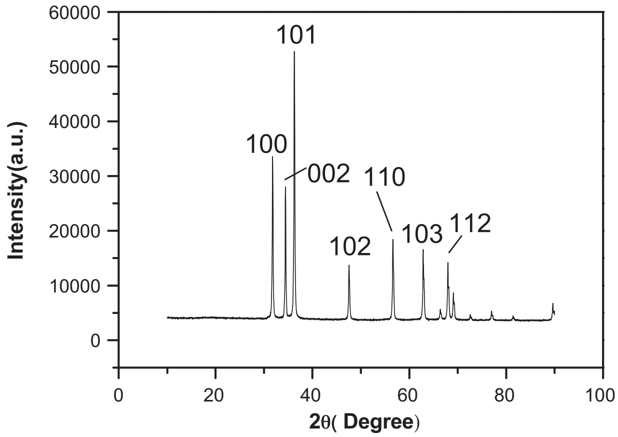

Fig. 3. XRD pattern of ZnO nanocrystal calcined at 300 °C for 1 h when the electric field intensity is 100 V/mm (SDS/CTAB mixed surfactants were used).

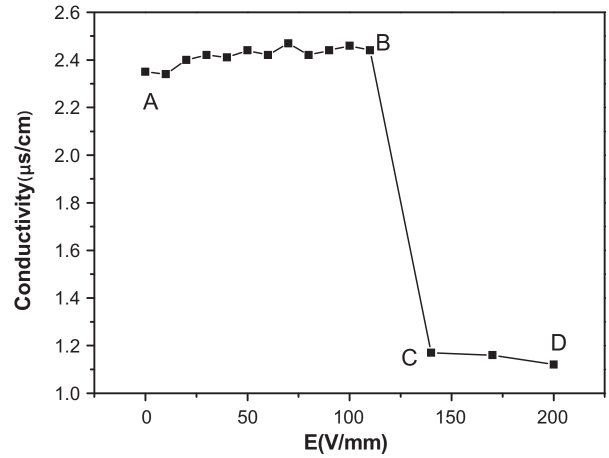

Fig. 5. Electric conductivity curve of microemulsion exposed to electric field.

stretched into a certain length along the direction of the electric field, as we can see in Fig. 2c.

2.4. Characterization

The phase structure of product was characterized by X-ray diffraction (XRD; D/MAX-3B, Rigaku) with Cu Kα radiation (40 kV, 30 mA) at a scan rate of 2°/min. The morphology, microstructure and patterns were observed on a transmission electron microscopy (TEM; TECNA1G2 20S-TWIN, Philips) at an accelerating voltage of 200 kV. The conductivity of microemulsion system was measured by conductivitymeter (DDS-11A, Hong Kong Xingwan Electronic Instrument (Xiamen) Co., Ltd.).

3. Results and discussion

Fig. 3 shows the XRD pattern of the product under the optimum parameters (the electric field intensity was 100 V/mm. The precursor was calcined at 300 °C for 1 h and SDS/CTAB mixed surfactants were used). It indicates that the product was hexagonal wurtzite-type ZnO (JCPDS 89-1397) and no impurity peaks were detected (Fig. 3). The sharp and narrow diffraction peaks reveal that the synthesized nanowhiskers are highly crystalline materials. Corresponding TEM images are given in Fig. 4. The whisker-like ZnO with 1–3 nm in diameter and 20–70 nm in length were observed. Furthermore, the ZnO nanowhiskers were relatively uniform in diameter and well dispersed.

In order to determine the range of electric field intensity in which the microemulsion system can stably exist, we measured the electric conductivity and observed the apparent condition of the system via changing the voltage of two electrode plates, and got the critical electric field intensity when the microemulsion system was destroyed.

As indicated in Fig. 5, mutations of conductivity and turbidity were observed when the electric field intensity was 110 V/mm (the point of B in Fig. 5). The conductivity remained basically unchanged and the overall solution maintained transparent when the electric field intensity was below 110 V/mm (from A to B in Fig. 5). The conductivity decreased and the solution turned to turbid and precipitation was formed, when the electric field intensity was above 110 V/mm (from C to D in Fig. 5). Therefore, it can be judged that the microemulsion region only existed within the intensity of 0–110 V/mm. As no obvious increase stage of electrical conductivity was observed in the curve, it can be inferred that bicontinuous microemulsion [26] was not formed in this

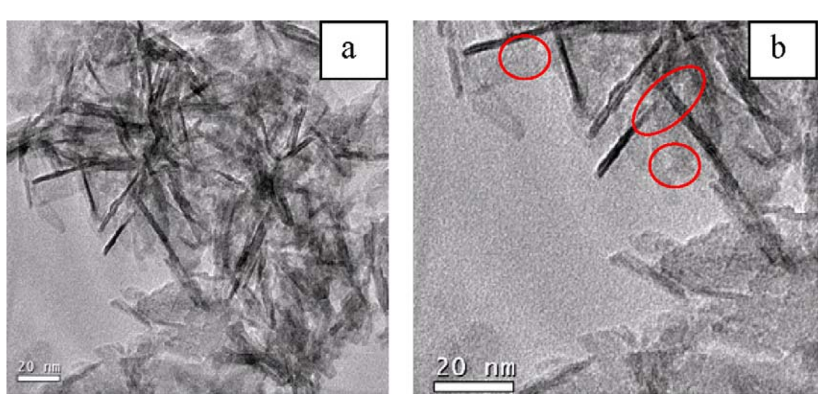

Fig. 4. Corresponding TEM images of ZnO nanowhiskers; (a) entirety and (b) region zoomed.

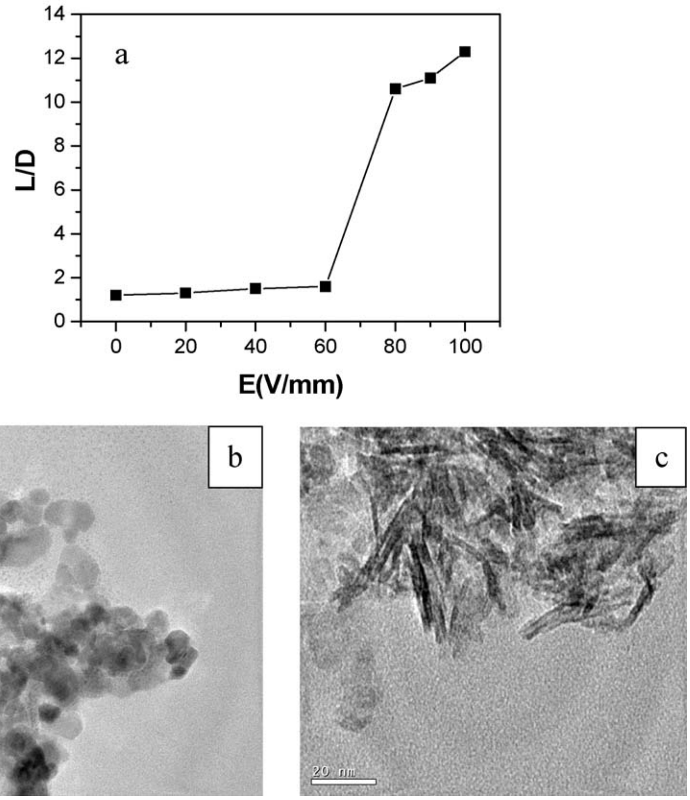

Fig. 6. Length–diameter ratio (*L*/*D*)–electrical field intensity curve (a) and TEM images of product before (b) (the electric field intensity is 20 V/mm) and in (c) (the electric field intensity is 80 V/mm) threshold field intensity (SDS/CTAB mixed surfactants were used and the precursor was calcined at 300 °C for 1 h).

process and the microemulsion was destroyed directly when the electric field intensity was above 110 V/mm. Thus, nanomaterials can be prepared using this microemulsion system only when the electric field intensity is below 110 V/mm.

Fig. 6a describes the relationship between the electric field intensity and the length–diameter ratio (*L*/*D*) of ZnO with the existence of SDS/CTAB mixed surfactants. When the electric field intensity is less than 80 V/mm, *L*/*D* is small and the morphology of the product is basically spherical (Fig. 6b). When the electric field intensity is 80 V/mm, *L*/*D* suddenly turns to 10.6 (Fig. 6c), and then the *L*/*D* increases with the raise of electric field intensity. It can be interpreted that there is an electric field intensity threshold when the mixed surfactants are re-arranged at the oil–water interface. Only when the external electric field intensity is greater than the threshold intensity, the mixed surfactants will be re-arranged and polarized, and the water nuclear is elongated then, and the ZnO with large length to diameter ratio can be obtained finally.

Fig. 7 is the TEM images of nano-ZnO prepared with SDS (Fig. 7a) and CTAB (Fig. 7b) respectively (the electric field intensity is 100 V/mm and the precursor was calcined at 300 °C for 1 h) instead of using SDS/CTAB mixed surfactants. The nano-ZnO prepared by microemulsion method with a single surfactant, either SDS or CTAB, is mostly spherical, square and the length–diameter ratio is much smaller than the one prepared with mixed surfactants, which is because single surfactant

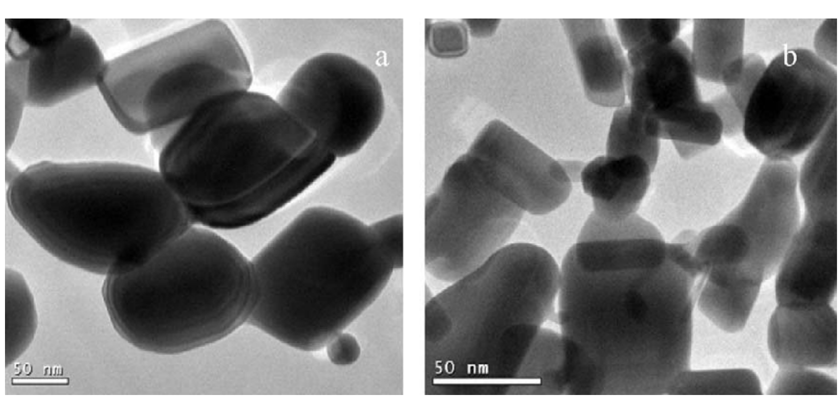

Fig. 7. TEM images of ZnO nanocrystal prepared with single surfactant (the electric field intensity is 100 V/mm and the precursor was calcined at 300 °C for 1 h).

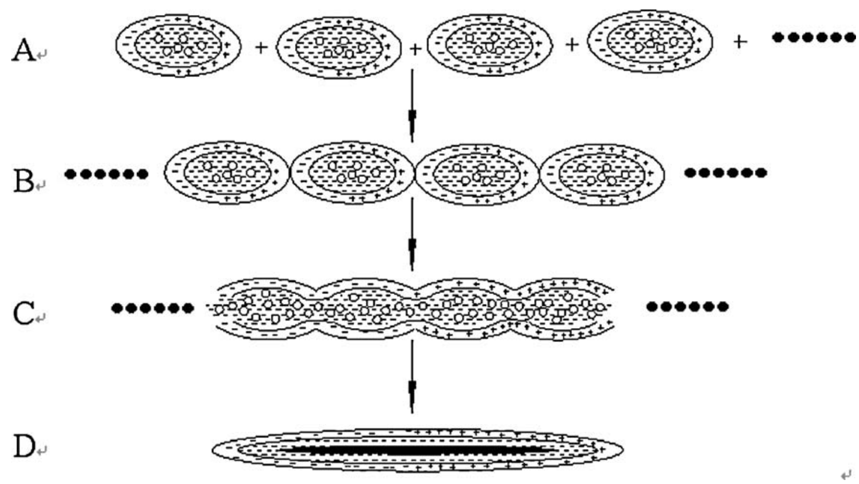

Fig. 8. Formation schematic diagram of precursor. (A) The microreactors are stretched into ellipses with a certain length under the action of the electric field. (B) Elliptical microreactors tend to align directionally end to end. (C) The two adjacent microreactors linked into a longer elliptical microreactor. (D) Aggregations in multiple microreactors at last connected into a rod-like reaction vessel, and the precursor was prepared.

cannot be polarized and re-arranged in electric field. However, the products are not perfectly spherical because the ions and surfactants in the microemulsion can be charged by themselves and have dispersion, and also the double electric layer in the water nuclear cause a certain polarization effect in the electric field. But the polarization effect is less important than that caused by mixed surfactants.

Based on our experiment results, we believe that the formation of ZnO nanowhiskers is divided into two phases: in the first phase, whisker-like ZnO precursor is generated after anionic/cationic mixed surfactants re-arrangement and polarization in the microemulsion interface in the electric field. When the external electric field is large enough (up to the electric field threshold), mixed surfactants can be re-arranged and polarized in the electric field and a higher concentration of SDS/CTAB mixed surfactants in solvent can result in microreactors [27]. The microreactors are stretched into ellipses with a certain length under the action of the electric field. Due to the different polarity of charge at both ends, elliptical microreactors tend to align directionally end to end. Reactant ions within two microreactors in contact with each other pass through the interfacial films to the other, and then promote water layers in the microreactors to aggregate at both ends and form a ''water bridge'', so that the two microreactors link into a longer elliptical microreactor. Aggregations in multiple microreactors at last connect into a reaction vessel, thus the whisker-like precursor was prepared. Fig. 8 reflects the process. In the second phase, nano-ZnO self-assembles into whisker-like morphology. Nano-ZnO tends to assemble into larger whisker-like nano-structures during the calcination process, owing to the interaction force (such as electrostatic force) and the very small particle size (even smaller than 1 nm). Such speculation could be supported by the Fig. 4b, in the circle area of which we can see whisker-like nano-ZnO present bifurcation in the head or layer stripe-shaped, resulted from that nanowhiskers self-assembly have not yet completed.

4. Conclusion

ZnO nanowhiskers with diameter of 1–3 nm and length of 20–70 nm were prepared by introducing direct current electric field into anionic/cationic mixed surfactants microemulsion. Studies show that, there was an electric field threshold between the length–diameter ratio of ZnO nanowhiskers and the external electric field intensity. The length–diameter ratio kept no change before the threshold, and then increased with the raise of electric field intensity. Single surfactant cannot produce ZnO nanowhiskers as it's hard to be polarized. Further study suggests that the formation of ZnO nanowhiskers by electric field induced microemulsion method is divided into two phases: Firstly, whisker-like ZnO precursor is generated after anionic/cationic mixed surfactants re-arrangement and polarization in the microemulsion interface in the electric field. In the second phase, nano-ZnO self-assembles into whisker-like morphology because of the interaction force and the very small particle size.

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