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Tuned morphologies of DNA-assisted ZnO struggling against pH

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Abstract

In this paper, we utilize DNA as a structure-directing agent to produce a series of novel ZnO structures at pH < 7. With decreasing solution pH values, various three-dimensional ZnO superstructures are formed. Furthermore, all products are well crystalline obtained with DNA, compared with blank samples. At last, a growth process of as-synthesized ZnO is thus proposed.

Keywords: A. Powders: chemical preparation; D. Transition metal oxides; DNA

1. Introduction

Wurtzite ZnO nanostructures, which have a wide and direct band gap of 3.37 eV at room temperature with a large exciton binding energy of 60 meV, are an ideal candidate to use in biological applications such as biosensors [1,2] and antibacterial materials [3]. ZnO is also a biosafe and biocompatible material [4]. These applications largely depend on their dimension, structures and morphologies. It is well known that the morphologies are greatly affected by several reaction conditions including temperature, time and pH value.

Among growth conditions, pH value is a complex condition and has an important influence on morphology of ZnO nanostructures, because of the essential OH^- in the reaction that produces the ZnO crystals. Alkaline solutions, such as NaOH and $NH_3 \cdot H_2O$, were thus usually used to vary the pH value from 7 to 13. To the best of our knowledge, however, there are only limited studies examining the growth of ZnO nanostructures under pH values <7 [5,6]. This is probably because that at this stage ZnO can be slowly dissolved duo to the acid corrosion.

Recently, bimolecule-assisted methods have been successfully used for morphological control of ZnO nanostructures. A great variety of ZnO nanostructures, including nanorods [7,8], flower-like [9], and nacre-like [10], have been obtained. It should be noted that biomolecules such as peptides, RNA and DNA, may have buffer capacity to mediate pH in reaction systems, owing to chemical groups in their side chains and/or backbones. This effect may protect final crystals from possible damage led by acid solution. However, we have not found any reports about morphological control of ZnO nanostructures utilizing this biomolecule-assisted mechanism, particularly, at low solution pH.

In this work, we utilize buffer capacity of DNA molecules to control the ZnO morphology through adjusting the initial pH values. A wide acid range of solution pH value, varying from 1.5 to 5.5, has been used and their effects on ZnO morphology are determined. Multifarious morphologies of ZnO superstructures have thus been obtained. Interestingly, some novel hierarchical ZnO superstructures have appeared at pH < 3.0, but at this stage any three-dimensional ZnO structures have not been found for blank sample grown without DNA, which agrees with our proposal about bimolecule-buffered method.

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2. Experimental

2.1. Preparation

All chemical reagents used in this experiment were of analytical grade. They were all used directly without further purification. Ultrapure grade water was used in all the experiments. In a typical process, 0.06 g DNA (D3150) (sodium salt, from herring sperm, obtained from Sigma) and 4 mmol of $Zn(Ac)_2 \cdot 2H_2O$ were mixed together in 30 ml of ultrapure water under constant stirring. After 5 min, the pH value of the mixture was adjusted by adding HNO_3 to a certain pH value. Then 30 ml of 20 mmol NaOH was added to the above mixture, with stirring for another 10 min. Afterwards, the vessel was sealed and kept inside an oven at 70 °C for 10 h. The product was treated by centrifugation and thoroughly washed with water and absolute alcohol, and finally dried in an oven at 70 °C.

2.2. Characterization

The crystalline phase of products was characterized by X-ray diffraction measurements (XRD, Germany Bruker D8-ADVANCE, Cu-*Kα* radiation). The morphologies of the products were investigated by field emission scanning electron microscopy (FESEM, Hitachi S-4800).

3. Results and discussion

Fig. 1 shows field emission scanning electron micrographs (FESEM) and XRD patterns of the final products grown at different pH values. In is noted that the solution is pH 3.3 when the solution was not adjusted with acid. Seen from the images of the products, various ZnO morphologies are formed. At pH 5.5, dominant bead-like ZnO crystals are produced, consisting of ZnO nanoparticles with sizes of usually several hundred of nanometers (Fig. 1a). Some disk-like ZnO crystals are also shown and they have edged hexagonal faces and elongated parallel to the c-axis direction, overlapping with each other. When pH is decreased to 4.0, the products are still mostly composed of a large quantity of bead-like ZnO (Fig. 1b). With decrease of pH value to 3.3, the ZnO disks vanish, and the sphere-like ZnO structures are formed (Fig. 1c). At pH 2.0 and 1.5, the morphologies of products have changed greatly (Fig. 1d–g). Beside ZnO microspheres (Fig. 1d), many hierarchical ZnO superstructures begin to appear, including overlapped ZnO plates (Fig. 1e), rose-like ZnO superstructures (Fig. 1f and g). At pH 1.5, in particularly, ZnO superstructures become more diversiform, as shown in(Supporting Information Fig. SI-1). It is interesting to note that the amount of such ZnO superstructures is increased with continuous decrease of pH values. As we know, these ZnO morphologies have not been reported for biomolecule-templated inorganic materials.

Fig. 1h shows that all the products formed in the presence of DNA exhibited almost the same XRD characteristics as the standard data of ZnO crystals ($a = 0.325$, $c = 0.522$, JCPDS file no. 89-0510). Only the strength of the peaks of the products weakens with the decreasing pH.

The experiments without DNA are also performed, and the FESEM images and XRD patterns of products are shown in Fig. 2. When $pH > 3$, only hexagonal-faceted ZnO nanorods are obtained, and their amount is decreased with decreasing pH (Fig. 2a–c). It is noted that when $pH < 3$, only sheet-like precipitates are obtained and they become smaller with decreasing pH (Fig.2d–e). The results are because that the acid etching is dominating over the growth of ZnO nuclei at lower solution pH.

Fig. 2f shows the corresponding XRD patterns of the blank products. When $pH > 3$, all the diffraction peaks of each product can be indexed to the standard hexagonal structure of ZnO with calculated lattice constants $a = 0.325$, $c = 0.522$ (JCPDS file no. 89-0510); when $pH < 3$, however, the characteristic peaks of ZnO become very weak and those of $Zn(OH)_2$ are observed, which is never exhibited for the products synthesized in the presence of DNA.

The hexagonal ZnO crystal is expressed with both polar and nonpolar facets stacked along the *c*-axis direction. The polar surface of the crystal is usually either Zn^{2+} terminated (0001) face or O^{2-} terminated (000-1) face. The polar surface with potentially high activity is often relatively diminished as crystal grows. Because of faster growth rate along the [0001] direction than along the other directions, the rod shapes are often shown for hexagonal ZnO crystal. Therefore, in our system, it is expected that ZnO rods are formed at $> pH$ 3 in the absence of DNA.

It is well known that biomolecules can retard the anisotropic growth rate through the selective adsorption on the facets of inorganic crystals, so that the spherical or quasi-spherical products are sometimes obtained [11,12]. This theory also applies to our results. In the presence of DNA, the products display a coexistence of the minor disk-like and the major bead-like morphology. Sporadically distributed overlapped ZnO disks can be evolved from the rod-like structures, because of the adsorption effect of DNA on the crystals. When spherical or quasi-spherical ZnO nanoparticles are connected with each other, the bead-like morphology is formed. The result is attributed to the property of DNA molecules. DNA has double helix chain structure, which is affected by various conditions such as ions, temperature and pH. When DNA acts as structure-directing agent for inorganic materials, its structures can be usually copied. So it is common that chain-like inorganic products are synthesized by utilizing this property of DNA molecules [13–15]. In addition, with decrease of pH values, the connection between the ZnO spheres gradually become slighter, which may be resulted from the change of DNA conformation made by pH.

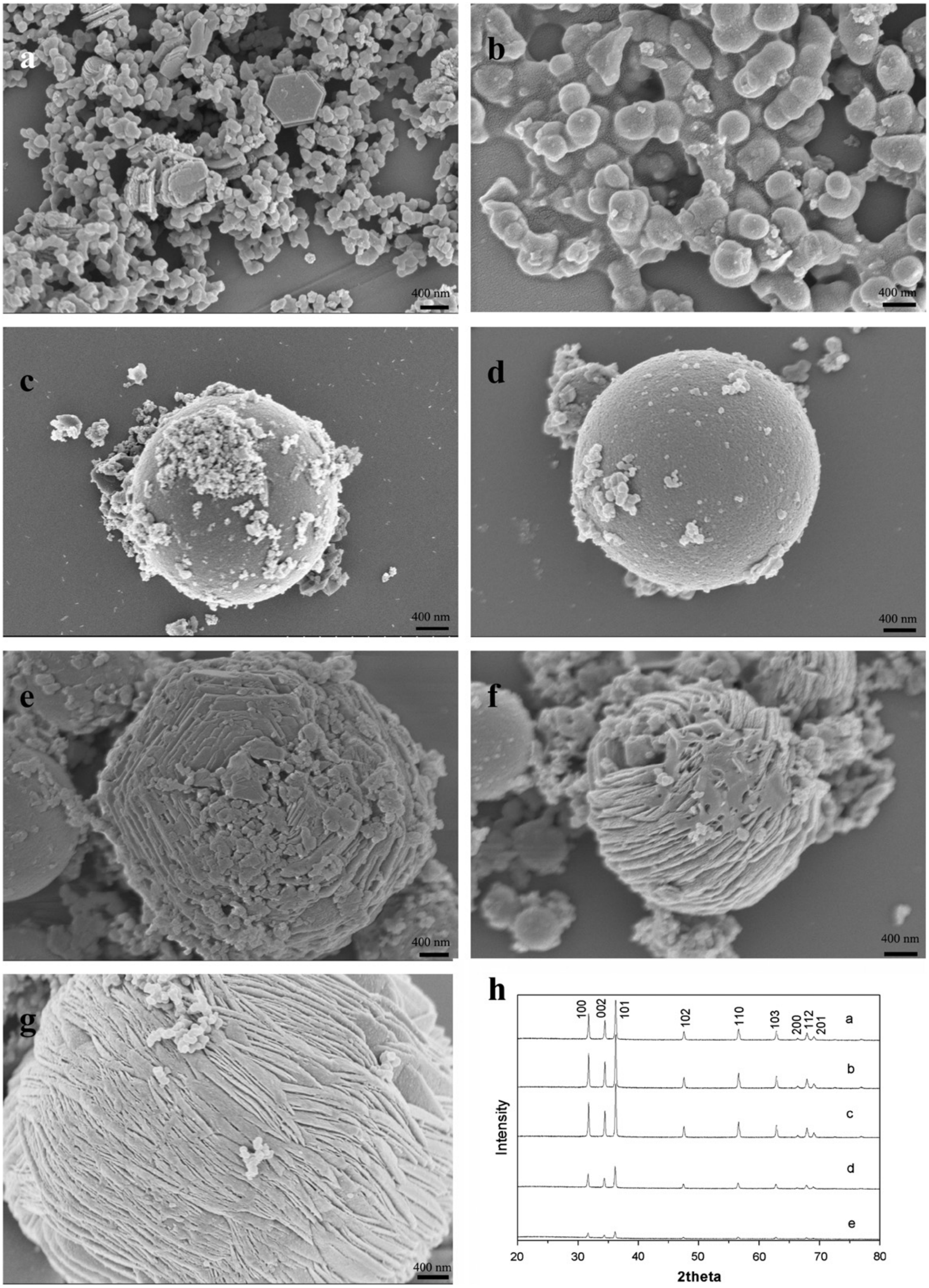

Fig. 1. FESEM images of the products synthesized with DNA at (a) pH 5.5, (b) pH 4.0, (c) pH 3.3, (d–f) pH 2.0 and (g) pH 1.5, respectively, and (h) corresponding XRD patterns of the products without DNA.

When pH $<$ 3.0, the various hierarchical ZnO superstructures appear, which is never shown for blank samples obtained in the absence of DNA. However, we have failed to further increase the amount of ZnO superstructures through the adjustment of two reaction parameters, *i.e.* the DNA concentration and time. The mechanism is currently being underway.

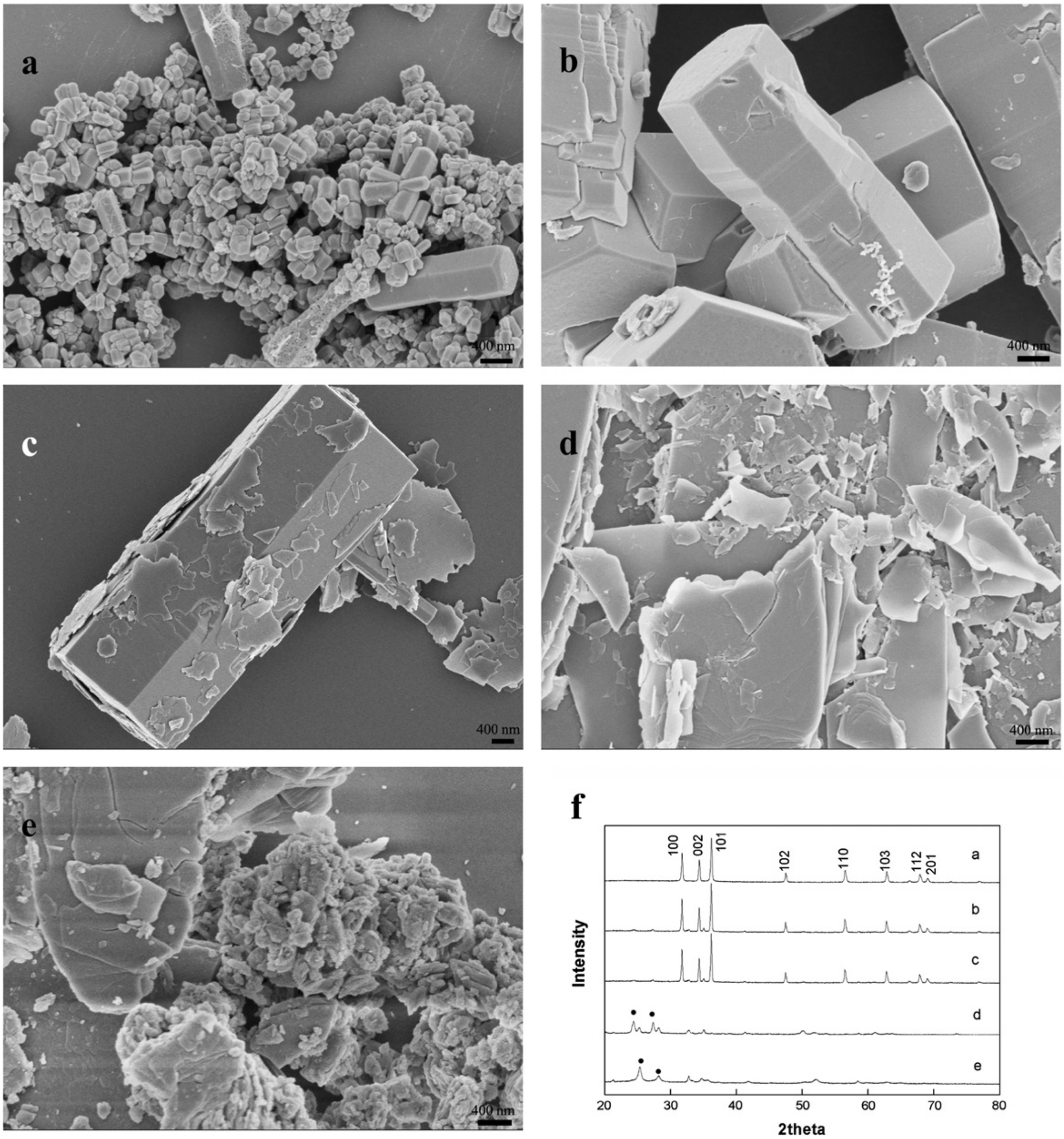

Fig. 2. (a–e) FESEM images of the blank products in absence of DNA at pH 5.5, 4.0, 3.3, 2.0 and 1.5, respectively, and (f) corresponding XRD patterns of the products without DNA. The label (●) points to the diffraction peaks from $Zn(OH)_2$ (JCPDS file no. 089–0138).

4. Conclusions

In summary, buffer effect of DNA molecules is applied to the morphological control of ZnO structures. Various complex ZnO morphologies are formed with decreasing solution pH values, though it is believed that low acidic solution usually damages the structures of ZnO crystals. On the basis of the property of DNA molecules, we have proposed a growth process of the as-synthesized ZnO crystals.

Acknowledgments

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Appendix A. Supplementary Information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.ceramint.2012.06.071.

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