Large-scale synthesis of hierarchical broccoli-like zinc oxide under mild conditions and their catalytic properties

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Large-scale uniform hierarchical broccoli-like zinc oxide (ZnO) superstructures assembled by nanorods were successfully synthesised via a facile solution method under mild conditions by using sodium carboxymethyl cellulose (NaCMC) as crystal growth modifiers. The morphology of the final products was simply tuned by adding different amounts of ammonia in the presence of NaCMC. In addition, the catalytic properties of as-prepared products were investigated. It was found that these ZnO superstructures have good abilities to promote the thermal decomposition of ammonium perchlorate.

1. Introduction: Fabrication of higher ordered inorganic crystals by a self-assembly process has received much attention not only for its importance on crystallisation theories but also for the potential to design new materials used in many fields [1–3]. The hierarchically structured nanomaterials usually show improved physical and chemical properties for applications in catalysts, solar cells, sensors, lithium-ion batteries and so on [3–8]. Although well-organised building blocks have been prepared by using various methods, the controlled organisation from rod-like building blocks has been confirmed to be a difficult task because of their anisotropy [9].

Semiconductor nano and microstructures have attracted more and more attention during the last few decades. Zinc oxide (ZnO) is one of the most promising materials with a large exciton binding energy (60 meV) and a direct band gap (3.37 eV) that have potential applications, such as solar cells, photodetectors and catalysts [10–12]. Since the potential application of nanomaterials depends on the shape of the nanostructure and the controlled morphology can modulate the properties of nanomaterials, extensive efforts have been devoted to control the morphology of ZnO crystals.

Various methodologies have been developed to achieve hierarchical architectures, such as thermal vapour deposition, the hydrothermal method and microwave assistance [13–17]. Large-scale use will require the development of simple low-cost approaches to the synthesis of inorganic functional nanomaterials. Of these methods, the facile solution procedure may be the most simple and effective way to prepare large-scale and well-crystallised materials at a relatively low temperature. Many complex hierarchical nanostructures could be easily obtained by wet chemical routes. For example, Zhou *et al.* [18] synthesised β-Ni(OH)$_2$ sophisticated concave polyhedrons using N_2H_4-coupling self-assembly β-Ni(OH)$_2$ of nanoplates. The template action or the coupling force of small molecules is of key importance for complex three-dimensional hierarchical structures by mild chemical solution methods.

As a key energetic material and main oxidising agent for rocket technologies, ammonium perchlorate (AP) continues to inspire new research efforts to investigate its thermal decomposition process, which is remarkably sensitive to the additives [19]. Many researchers have studied a variety of the additives to enhance their catalytic properties for AP decomposition. Among these additives, metal oxides are used widely as a kind of efficient catalysts accelerating the thermal decomposition of AP [20].

In this work, we developed a simple mild chemical solution method to fabricate novel broccoli-like ZnO superstructures in the presence of sodium carboxymethyl cellulose (NaCMC) as crystal growth modifiers. To our best knowledge, there are few reports on the preparation of broccoli-like ZnO. A possible formation mechanism of the broccoli-like ZnO is proposed. The catalytic properties of the ZnO superstructures were explored. The ZnO superstructures show good abilities to promote the thermal decomposition of AP.

2. Experiment

2.1. Synthesis: In a typical synthesis, 0.22 g of zinc acetate hydrate ($ZnAc_2 \cdot 2H_2O$, analytically pure) was dissolved in 8 ml of deionised water with magnetic stirring and then 1.0 ml ammonia solution ($NH_3 \cdot H_2O$, 25%, analytically pure) was added. After that, 10 ml of 2.8 g/l CMC (300–800 mPa·S, chemically pure) aqueous solution was dropwise added into the solution containing zinc acetate and ammonia. After 5 min stirring, the mixture was transferred to and sealed in a 100 ml flask, kept at 80°C for 2 h and finally cooled to room temperature. The precipitate was collected by centrifugation (4000 rpm, 3 min), washed alternately with deionised water and ethanol and dried in air at ambient condition.

2.2. Characterisations: Powder X-ray diffraction (XRD) measurements were performed with a SHIMADZU XRD-6000 X-ray diffractometer at Cu Kα radiation with 40 kV beam voltage and 30 mA beam current. The data were collected in the 25°–80° range (2θ) with steps of 0.02. Scanning electron microscopy (SEM) images were obtained with a Hitachi S-4800 field-emission microscope. The catalytic roles of broccoli-like ZnO in the thermal decomposition of AP were studied by a differential scanning calorimeter (DSC) using a STA 449C thermal analyser at a heating rate of 20°C·min^{-1} in N_2 atmosphere over the temperature range of 20–500°C. The mass percentage of ZnO to AP in the mixture is fixed at 2%.

3. Results and discussion: XRD is a rapid analytical technique primarily used for phase identification of crystalline material and the intensity of XRD peaks. Fig. 1 shows the XRD patterns of the typical as-prepared products. All the diffraction peaks index to a hexagonal wurtzite structure of ZnO (JCPDS 36-1451). No

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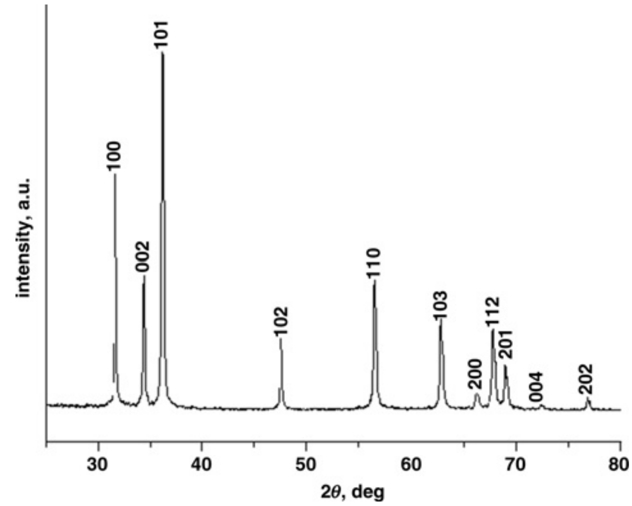

Figure 1 *XRD patterns of as-prepared ZnO with the amount of ammonia 1.0 ml at 80°C for 2 h*

impurity peaks were detected. The sharpness of the peaks implies the high crystallinity of these as-prepared samples.

The morphologies of the ZnO products were illuminated by SEM images. A panoramic SEM image of broccoli-like ZnO is shown in Fig. 2*a*, from which broccoli-like nanostructures with high uniformity were clearly observed and no other morphologies could be detected. The SEM images (Fig. 2*b*) with high magnification reveal that the broccoli-like nanostructures are assembled by many short nanorods from centre to tops. The length of these nanorods is in the range of 100–500 nm and the diameter is around 20 nm based on a top-view of the end of the nanorods.

The morphology and the size of the products could be tuned by changing the amount of ammonia. Figs. 3*a* and *b* show the SEM images of the sample prepared with 0.6 ml of 25% ammonia solution. The morphology of the products keeps the broccoli-like structure. As the amount of ammonia decreases, more branches are obtained in the broccoli-like superstructure. Figs. 3*c* and *d* show the SEM images of the sample prepared with 1.2 ml of 25% ammonia solution. The dumbbell-like ZnO can be obtained as the amount of ammonia increases. The diameter of the assembled units is about 50 nm. As the amount of ammonia increases, the size of products is also increasing.

$$Zn^{2+} + 4NH_3H_2O \rightleftharpoons [Zn(NH_3)_4]^{2+} + 4H_2O \qquad (1)$$

$$[Zn(NH_3)_4]^{2+} + 3H_2O \rightleftharpoons ZnO + 2NH_4^+ + 2NH_3\,H_2O \qquad (2)$$

In the preparation, the amount of ammonia is excess and $[Zn(NH_3)_4]^{2+}$ complexes are formed (1). Thermal treatment of the $[Zn(NH_3)_4]^{2+}$ solution leads to the formation of broccoli-like ZnO (2). As the amount of ammonia is increasing, the nucleation rate of ZnO crystal is decreasing to form the dumbbell-like ZnO.

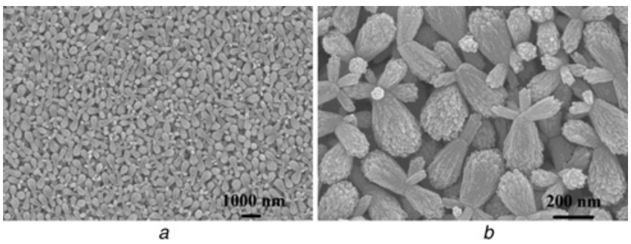

Figure 2 *SEM images of as-prepared ZnO with 1.0 ml $NH_3{\cdot}H_2O$ at 80°C for 2 h*

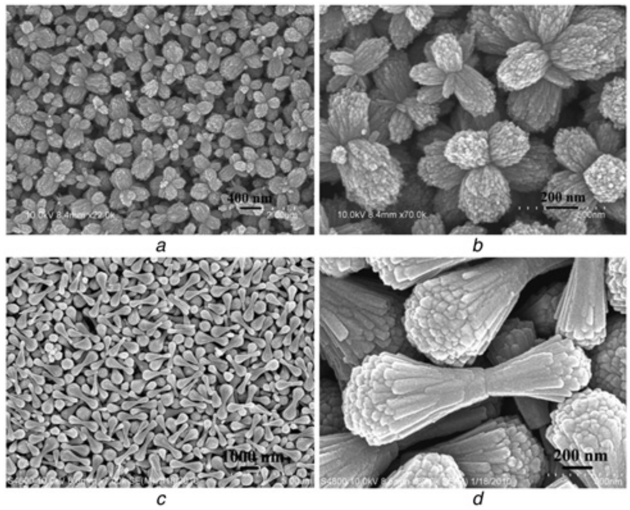

Figure 3 *SEM images of as-prepared ZnO with the amount of ammonia 0.6 ml (a, b) and 1.2 ml (c, d) at 80°C for 2 h*

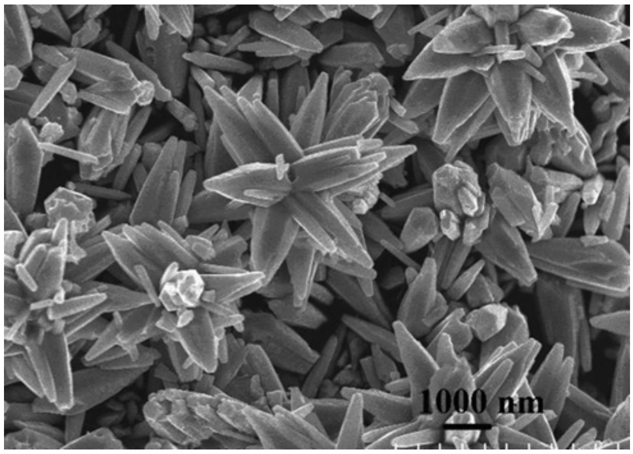

Figure 4 *SEM images of as-prepared ZnO with the amount of ammonia 1.0 ml without the addition of NaCMC*

The presence of an appropriate amount of water-soluble NaCMC is crucial for the formation of these unique broccoli-like ZnO architectures. Without the addition of the NaCMC in the reaction system, only ZnO microrods were obtained, as the SEM image in Fig. 4. The NaCMC molecules contain a large number of carboxymethyl groups, such that the hydroxyl groups of the backbone cannot get close enough to hydrogen bond to each other. The result is that water can slip in between the NaCMC molecules and hydrate them. Hence, the solvent such as water can be divided into numerous 'channels' formed in the reaction system by the CMC molecules. NaCMC not only serves as a soft template to confine the growth of ZnO to form the ZnO nanorod, but also serves as an assembling agent to construct the nanorods into the broccoli-like ZnO architectures. In the reaction system, the numerous nanorods formed from small particles at first in the 'channels', then to lower the surface energy the nanorods arrayed together like 'broccoli'. On the basis of the results, a possible growth mechanism of the double-cage superstructure is proposed, as shown in Fig. 5.

The catalytic properties of broccoli-like ZnO as a potential additive for the decomposition of AP were evaluated using the simultaneous thermal analysis system. AP is a widely used common oxidiser in composite solid propellants [19], where AP plays an important role in the burning process. Fig. 6 shows the DSC curves of both pure AP and the mixture of AP with ZnO at a 2% mass basis.

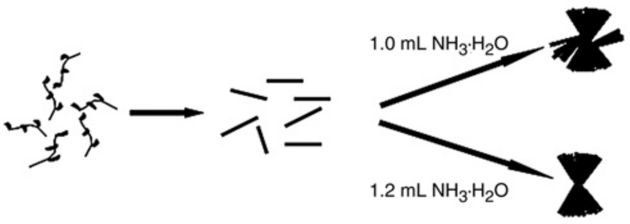

Figure 5 *Possible growth mechanism of ZnO superstructures*

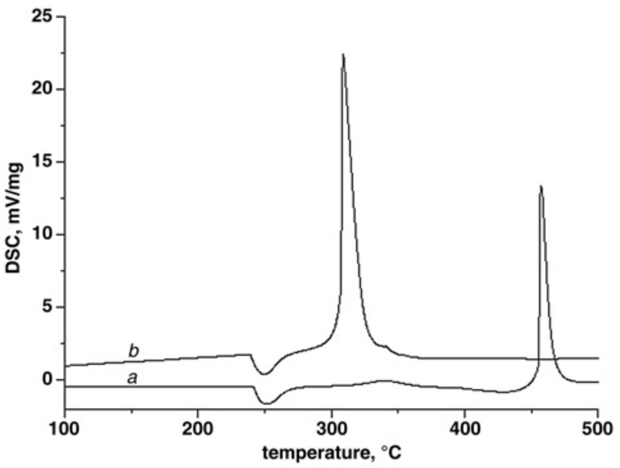

Figure 6 *DSC curves of pure AP (a) and the mixture of AP with as-prepared ZnO with 1.0 ml $NH_3{\cdot}H_2O$ (b)*

For pure AP, the first endothermic peak appeared at about 245°C, which is associated with a phase transition of AP from orthorhombic to cubic because no mass changes appeared in the corresponding temperature range. The second peak centred at about 350°C is exothermic, which exactly corresponds to the low-temperature decomposition process. The third peak centred at about 460°C is referred to as high-temperature decomposition process [21]. Only two thermal signals were observed for the mixture of AP with ZnO, which compares with the three obvious peaks for pure AP. The first endothermic peak at 245°C is because of the crystal transformation of AP from orthorhombic to cubic phase, while the second exothermic peaks that occurred at 303°C are attributed to the AP decomposition. This decomposition temperature is lower than the decomposition temperature catalysed with ZnO cones reported by Sun *et al.* [16] under the same conditions. These broccoli-like ZnO have good abilities to promote the thermal decomposition of AP.

4. Conclusions: In summary, we report a facile solution method for the construction of uniform hierarchical broccoli-like ZnO superstructures assembled by nanorods under mild conditions by using NaCMC as crystal growth modifiers. The morphology of the final products was simply tuned by adding different amounts of ammonia in the presence of NaCMC. The broccoli-like ZnO superstructures have good abilities to promote the thermal decomposition of AP.

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6 References

[1] Dick K., Depper K., Larsson M., ET AL.: 'Synthesis of branched 'nanotrees' by controlled seeding of multiple branching events', *Nat. Mater.*, 2004, **3**, pp. 380–384

[2] Manna L., Milliron D.J., Meisel A., Scher E.C., Alivisatos A.P.: 'Controlled growth of tetrapod-branched inorganic nanocrystals', *Nat. Mater.*, 2003, **2**, pp. 382–385

[3] Gu J.M., Li S.H., Wang E.B., ET AL.: 'Single-crystalline α-Fe_2O_3 with hierarchical structures: controllable synthesis, formation mechanism and photocatalytic properties', *J. Solid State Chem.*, 2009, **182**, pp. 1265–1272

[4] Li X., Zhao F., Fu J., ET AL.: 'Double-sided comb-like ZnO nanostructures and their derivative nanofern arrays grown by a facile metal hydrothermal oxidation route', *Cryst. Growth Des.*, 2009, **9**, pp. 409–413

[5] Pan Q.T., Huang K., Ni S., Yang F., Lin S.M., He D.Y.: 'Synthesis of sheaf-like CuO from aqueous solution and their application in lithium-ion batteries', *J. Alloys Compd.*, 2009, **484**, pp. 322–326

[6] Zhang Y., Xu J., Xiang Q., Li H., Pan Q., Xu P.: 'Brush-like hierarchical ZnO nanostructures: synthesis, photoluminescence and gas sensor properties', *J. Phys. Chem. C*, 2009, **113**, pp. 3430–3435

[7] Bierman M.J., Jin S.: 'Potential applications of hierarchical branching nanowires in solar energy conversion', *Energy Environ. Sci.*, 2009, **2**, pp. 1050–1059

[8] Wang H., Pan Q., Cheng Y., Zhao J., Yin G.: 'Evaluation of ZnO nanorod arrays with dandelion-like morphology as negative electrodes for lithium-ion batteries', *Electrochim. Acta*, 2009, **54**, pp. 2851–2855

[9] Gao X.P., Zheng Z.F., Zhu H.Y., ET AL.: 'Rotor-like ZnO by epitaxial growth under hydrothermal conditions', *Chem. Commun.*, 2004, **12**, pp. 1428–1429

[10] Hara K., Horiguchi T., Kinoshita T., Sayama K., Sugihara H., Arakawa H.: 'Highly efficient photon-to-electron conversion with mercurochrome-sensitized nanoporous oxide semiconductor solar cells', *Sol. Energy Mater. Sol. Cells*, 2000, **64**, pp. 115–134

[11] Rodriguez J.A., Jirsak T., Dvorak J., Sambasivan S., Fischer D.J.: 'Reaction of NO_2 with Zn and ZnO: photoemission, XANES, and density functional studies on the formation of NO_3', *J. Phys. Chem. B*, 2000, **104**, pp. 319–328

[12] Lu J.G., Chang P., Fan Z.: 'Quasi-one-dimensional metal oxide materials – synthesis, properties and applications', *Mater. Sci. Eng., R. Rep:*, 2006, **52**, pp. 49–52

[13] Hu J., Bando Y., Zhan J., Yuan X., Sekiguchi T., Golberg D.: 'Self-assembly of SiO_2 nanowires and Si microwires into hierarchical heterostructures on a large scale', *Adv. Mater.*, 2005, **17**, pp. 971–975

[14] Wang Q., Xu G., Han G.: 'Synthesis and characterization of large-scale hierarchical dendrites of single-crystal CdS', *Cryst. Growth Des.*, 2006, **6**, pp. 1776–1780

[15] Cao H., Gong Q., Qian X., Wang H., Zai J., Zhu Z.: 'Synthesis of 3-D hierarchical dendrites of lead chalcogenides in large scale via microwave-assistant method', *Cryst. Growth Des.*, 2007, **7**, pp. 425–429

[16] Sun X., Qiu X., Li L., Li G.: 'ZnO twin-cones: synthesis, photoluminescence, and catalytic decomposition of ammonium perchlorate', *Inorg. Chem.*, 2008, **47**, pp. 4146–4152

[17] Huang P., Zhang X., Wei J., Feng B.: 'ZnO hierarchical structures synthesized via hydrothermal method and their photoluminescence properties', *J. Alloys Compd.*, 2010, **489**, pp. 614–619

[18] Zhou W., Yao M., Guo L., Li Y., Li J., Yang S.: 'Hydrazine-linked convergent self-assembly of sophisticated concave polyhedrons of β-$Ni(OH)_2$ and NiO from nanoplate building blocks', *J. Am. Chem. Soc.*, 2009, **131**, pp. 2959–2964

[19] Boldyrev V.V.: 'Thermal decomposition of ammonium perchlorate', *Thermochim. Acta*, 2006, **443**, pp. 1–36

[20] Zhou Z., Tian S., Zeng D., Tang G., Xie C.: 'MOX (M=Zn, Co, Fe)/AP shell–core nanocomposites for self-catalytical decomposition of ammonium perchlorate', *J. Alloys Compd.*, 2013, **513**, pp. 213–219

[21] Yang S., Wang C., Chen L., Chen S.: 'Facile dicyandiamide-mediated fabrication of well-defined CuO hollow microspheres and their catalytic application', *Mater. Chem. Phys.*, 2010, **120**, pp. 296–301

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