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Preparation of ZnO Microflowers from a Single Source Reactant

LIWEI MI[1,2], WEIHUA CHEN[3], FENGLING YANG[2], JIANMIN ZHANG[3], CHANGYU SHEN[1,*] and ZHI ZHENG[2,*]

[1]National Engineering and Research Center for Advanced Polymer Processing Technology, Zhengzhou University, 450001 Henan, P.R. China
[2]Institute of Surface Micro and Nano Materials, Xuxhang University, Henan, P.R. China
[3]Department of Chemistry, Zhengzhou University, 450001 Henan, P.R. China

*Corresponding author: Fax: +86 371 63887600; Tel: +86 371 63887600; E-mail: nerczzu@yahoo.cn; zhengzhi9999@yahoo.com.cn

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$[Zn(phen)_2(H_2O)_2]2L\cdot 6H_2O$ (**1**), where HL = 4-methylbenzenesulfonic acid and phen = *o*-phenanthroline was used as a single source reactant to prepare well-crystallized ZnO in aqueous solution of sodium hydroxide at 180 ºC under wide-range pH value for a day without the assistance of a surfactant or microemulsion. The decomposition products from this zinc inclusion complex could keep well-faceted prismatic whiskers in wide range of alkalinity. The ZnO crystal growth mechanism based on the growth units of $[Zn(phen)_4(H_2O)_2]^{2-}$ is employed to explain the formation of the six different ZnO microcrystals because of the strong coordination ability between the central zinc metal ion and *o*-phenanthroline.

Key Words: Inclusion compound, ZnO Microflowers, Hydrothermal.

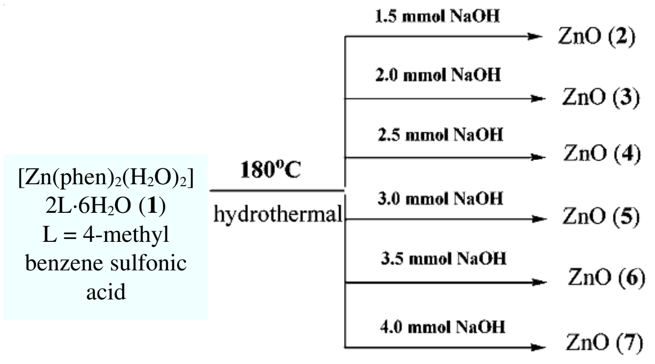
INTRODUCTION

In rencent years, numerous efforts have been employed in the fabrication of nanomaterials with a controllable size and shape because these parameters represent key elements that determine their electrical and optical properties[1-4]. ZnO is a potentially useful semiconductor with a direct band gap of 3.37 eV and it is considered as a strong candidate for solid-state lighting[5,6]. Now nanostructure zinc oxides have shown a wide range of technological applications including transparent conducting electrodes of solar cells, flat panel displays, surface acoustic wave devices and chemical sensors[7-9]. Till now, many methods have been used to prepare this material. Among them, the hydrothermal approach is more favourable to producing well-crystallized ZnO. Herein, ZnO microcrystals with branched spindles and well-faceted prismatic whiskers have been synthesized by hydrothermal treatment of a single source reactant $\{[Zn(phen)_2(H_2O)_2]2L\cdot 6H_2O\}$, where HL = 4-methylbenzenesulfonic acid and phen = *o*-phenanthroline in aqueous solution of sodium hydroxide at 180 ºC under wide-range pH value for a day without the assistance of a surfactant or micro-emulsion. Here it should be noted that previous reports touched on the synthesis of ZnO revealed that the shape of this material should be influence by the adjustment of the basicity[10-12]. However, the decomposition products from this zinc inclusio complex could keep well-faceted prismatic whiskers in very wide range of alkalinity. This might be caused the stability of the precursor's crystal structure in alkali solutions. This search will benefit the preparation of high stale structure materials in rigorous conditions.

EXPERIMENTAL

All chemicals (analytical grade reagents) were purchased from Shanghai Chemical Reagents Co. and used without further purification. $[Zn(phen)_2(H_2O)_2]2L\cdot 6H_2O$ (**1**) was prepared under the direction of previous report[13]. ZnO materials were prepared by one-step hydrothermal decomposition route under moderate condition. Firstly, as-prepared complex **1** was placed into a stainless steel tank with the excess of aqueous solution of 1 mol dm^{-3} NaOH. The tank was held for 8 h after warmed up to 180 ºC at 1 ºC min^{-1}. Then the tank was cooled to room temperature, farinose pink solid powder was obtained. The powder was washed, respectively by distilled water and absolute ethyl-alcohol and then was placed in vacuum desiccator at 60 ºC for 3 h resulting in purified ZnO materials (**Scheme-I**).

The phase purity of the as-synthesized products was examined by X-ray diffraction (XRD) using a Philips X'Pert PRO SUPER X-ray diffractometer equipped with graphite monochromatized Cu K_α radiation (λ = 1.541874 Å). The morphology and size of the obtained ZnO products were further observed by a field-emission microscope (Jeol-JSM-6700F 20 KV).



Scheme-I

RESULTS AND DISCUSSION

Crystal structure of [Zn(phen)$_2$(H$_2$O)$_2$]2L·6H$_2$O (**1**) (L = 4-methyl benzene sulfonic acid) was shown in Fig. 1. As reported by Ma and his co-worker, zinc ion lies on a crystallographic twofold axis. Similar to the other inclusion complexes, complex **1** also consists of two parts: cationic parts [Zn(phen)$_2$(H$_2$O)]$^{2+}$, in which Zn(II) ion is six-coordinated by four nitrogen atoms from two phenanthroline molecules and two water oxygen atoms. The sulfonate anions are non-coordinating owing to the weak coordination strength of sulfonate ion toward transition metal ions[14,15]. Two oxygen atoms of the sulfonate ion are hydrogen-bonded to one water molecule, respectively and the remaining oxygen atom forms hydrogen bonds with two water molecules. The coordinating water molecule is hydrogen-bonded to one lattice water molecule and one sulfonate oxygen atom. [Zn(phen)$_2$(H$_2$O)]$^{2+}$ ions, sulfonate ions and lattice water molecules are linked by hydrogen bonds to form infinite zigzag chains (Fig. 1b).

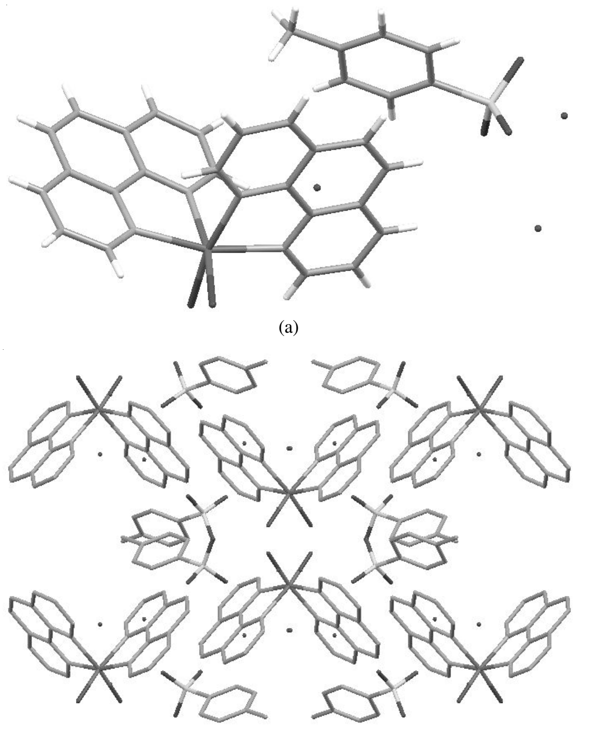


Fig. 1. (a) Building block of [Zn(phen)$_2$(H$_2$O)$_2$]2L·6H$_2$O (**1**) and (b) solid state packing view of this zinc inclusion complex (hydrogen atoms were deleted for clarity)

Herein, it should be noted that this precursor has two merits: one is that the starting materials for the preparation of this reactant is very cheap and it could be easily synthesized in high yield under moderate conditions; the other is that the negative part, 4-methylbenzenesulfonate, could be served as surfactant or dispersant agent.

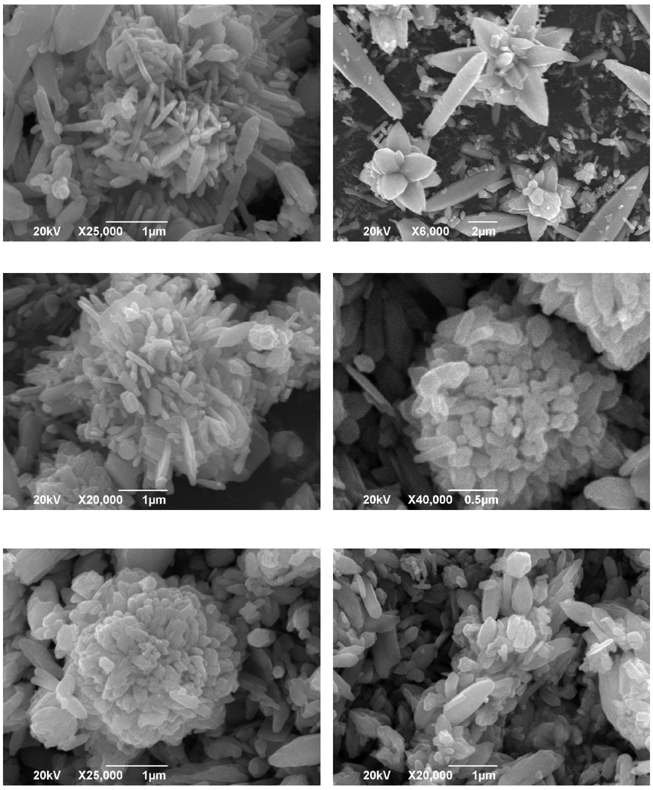


Fig. 2. SEM images of as-prepared ZnO (**2-7**) through the hydrothermal decomposition of **1** (a for **2** NaOH: **1** = 3:1; b for **3** NaOH: **1** = 4:1; c for **4** NaOH: **1** = 5:1; d for **5** NaOH: **1** = 6: 1; e for **6** NaOH: **1** = 7: 1; f for **7** NaOH: **1** = 8: 1)

In this paper, we adopt single source reactant by one-step hydrothermal decomposition route under moderate condition and successfully obtain well-shaped ZnO crystals in high purity. Fig. 2 shows the typical SEM images of the ZnO microstructures at low and medium magnifications. From these images, we can see that the morphology of ZnO is flower-like rod clusters. The initial crystal size calculated by Scherrer's equation and normal to [101] diffraction plane is equal to 12.6 nm. The grain size by SEM is larger than that calculated from XRD, which results from the conglobation of the ZnO particles for SEM test. The XRD patterns of the ZnO particles were illustrated in Fig. 3. The patterns are well consistent with each other and contain multiple peaks that can be clearly distinguishable. The entire peaks match well with the characteristic reflections of ZnO. The main peaks with 2θ values of 31.79, 34.45, 36.32, 47.61, 56.71, 62.86, 66.45, 68.03 and 69.12 correspond to 100, 002, 101, 102, 110, 103, 200, 112 and 201 crystal planes of cubic phase. All the reflections can be indexed to wurtzite structure of ZnO with lattice parameters, which is in agreement with the reported data for ZnO (JCPDS 36-1451). No characteristic peaks were observed for other impurities such as Zn and/or Zn(OH)$_2$.

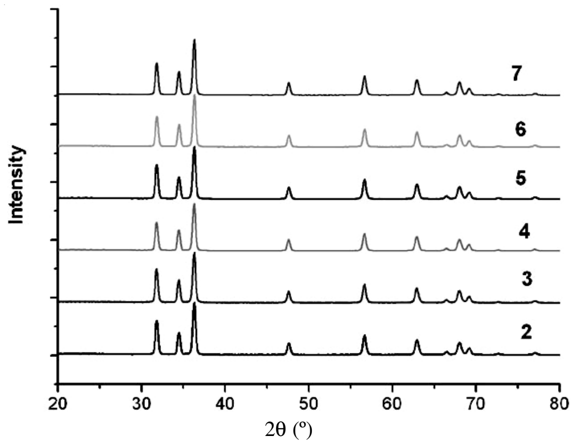


Fig. 3. XRD patterns of as-obtained ZnO **2-7**

Conclusion

In summary, ZnO microcrystals in various flower-like morphology have been controllably synthesized by the hydrothermal process using zinc clusion complex as a single source reactant without the assistance of the adscititious dispersant. The flowerlike ZnO microcrystals are hexagonal and single crystalline in nature. The ZnO crystal growth mechanism based on the growth units of $[Zn(phen)_4(H_2O)_2]^{2-}$ is employed to explain the formation of the three different ZnO microcrystals. Because of the strong coordination ability between the central zinc metal ion and *o*-phenanthroline, the morphology of its decomposition complex could keep flower-like in wide range of alkalinity. It is anticipated that method presented in this work offers a solution to controlling the morphology of crystal under rigorous conditions.

ACKNOWLEDGEMENTS

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