

Controllable Hydrothermal Synthesis and Properties of ZnO Hierarchical Micro/Nanostructures

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Abstract: A simple hydrothermal route has been developed for the fabricating ZnO hierarchical micro/nanostructure with excellent reproducibility. SEM and TEM analysis show that the hierarchical rod is a single-crystal, suggesting that many single-crystal micro/nanorods are assembled into ZnO hierarchical micro/nanostructures. The morphologies of the hierarchical rods can be conveniently tailored by changing the reaction parameters. And we also found citric acid plays a crucial role in the formation process of ZnO micro/nanostructures. Room-temperature photoluminescence spectra reveals that the ZnO hierarchical micro/nanostructures have a strong emission peak at 440 nm and several weak emission peaks at 420, 471 and 541 nm, respectively.

Keywords: Hydrothermal route; Micro/nanorod; ZnO

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Introduction

Bottom-up processes which commonly used to manipulate the growth of multi-dimensional nanostructures are very important for understanding advance fundamental nanomaterials and engineering novel functional devices [1,2]. One-dimension (1D) nanostructures or their ordered arrays have attracted considerable interest in recent years because they are expected to improve the performance of various nano-devices [3-7]. Meanwhile, hierarchical or complex architecture built up with well-ordered nanostructures plays a key role in their chemical, optical and electrical properties for functional micro/nanosystems [8]. Different dimension hierarchical ordered nanostructures may induce some novel properties resulting from its unique multi-dimensional shape and a combination of both micrometer-scale and nanometer-scale building blocks [9], such as multi-reflection [10], higher specific surface and porosity [11,12].

A wide range of 1D ZnO nanostructures, including

wires, rods, belts and tubes has been prepared [13]. So far, much attention has been paid to the realization of three-dimensional (3D) ZnO structures based on these 1D structures due to its unique properties for novel applications in advanced catalysts or gas sensors [14]. To date, several techniques have been used for the fabrication of 3D ZnO structures, including chemical vapor deposition (CVD) [15], thermal evaporation [16], sonochemical method [17], hydrothermal route [18] and pyrolysis technique [19]. For example, Umar et al [15] reported flower-shaped ZnO nanostructures obtained on silicon substrates with different orientations by using modified cyclic feeding chemical vapour deposition (CFCVD) technique in which diethyl zinc and high purity oxygen (99.999%) gas were used as raw materials. Zhang et al [18] synthesized prickly sphere- and flower-like ZnO by decomposing $\text{Zn}(\text{OH})_4^{2-}$ precursor in an aqueous solution or $\text{Zn}(\text{NH}_3)_4^{2+}$ precursor in ethanol. Moreover, Choppali et al [19] obtained 3D ZnO structures with hexagonal flower-like morphologies by using a polymeric precursor solution-based pyroly-

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sis technique. Template methods using pre-deposited buffer layers or different surfactants (additives) were also reported by other groups on synthesis of 3D ZnO nanostructures [20]. However, previous efforts usually involved complicated experimental procedures, equipments, expensive substrates or surfactants. Controllable synthesis of hierarchical or complex ZnO structure is still a challenge for researchers.

Herein, we present a one-step hydrothermal route to synthesize ZnO hierarchical micro/nanostructure. The morphology can be simply controlled by changing the reaction parameters. We also investigated the optical properties of flower-like ZnO hierarchical micro/nanostructures using UV-Vis and photoluminescence techniques.

Experimental

All reagents were analytically pure and used without further purification. The precursor solution was prepared by mixing 0.025 mol $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 0.05 mol NaOH and 50 ml $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25-28%) into deionized water with continuous stirring. Firstly white floccules appeared and after a while it dissolved completely. The as-formed solution was transferred into a volumetric flask, diluted to 250 ml with deionized water, and then a precursor solution with 0.1 mol/l Zn^{2+} concentrations was obtained. In a typical procedure, an aqueous solution of precursor and deionized water were mixed in an equal volume. A 0.3 g citric acid was added into the above solution whilst stirring for ~ 10 min. Then 32 ml of this mixture with Zn^{2+} concentration of 0.05 mol/l were transferred into a 50 ml Teflon-lined stainless steel autoclave. After hydrothermal treated at 180°C for 12 h, the autoclave was cooled down to room temperature naturally. The white precipitates were collected and washed with deionized water and ethanol several times to remove impurities. The precipitates were dried in air at 60°C for 5 h.

The products were characterized with X-ray diffractometer (XRD, Rigaku D/Max-2550 PC, $\text{Cu K}\alpha$ radiation), scanning electron microscope (SEM; JSM-5600LV), transmission electron microscope (TEM; JEOL JEM 200CX 3000F) equipped with an X-ray energy dispersive spectrometer (EDS). The photoluminescence (PL) measurements were performed on a Perkin-Elmer luminescence spectrometer LS55 at room temperature using a Xe lamp with a wavelength of 380 nm as the light source.

Results and Discussion

All as-obtained powders show similar XRD patterns. A representative XRD pattern is shown in Fig. 1, in which products were prepared when the volume ratio

of $\text{Zn}(\text{NH}_3)_4^{2+}$ precursor solution and water is 1:1. It can be indexed to a hexagonal ZnO phase with lattice constants of $a=0.325$ nm and $c=0.521$ nm (JCPDS card: 36-1451). No precursor impurities peaks, such as $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and NaOH were detected within experimental error. The sharp and narrow lines indicate that the products are well crystallized.

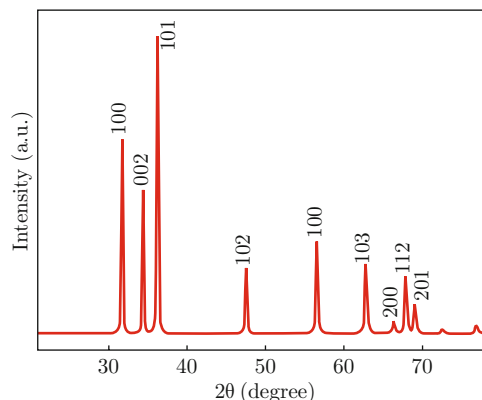


Fig. 1 XRD pattern of the product prepared with the volume ratio of $\text{Zn}(\text{NH}_3)_4^{2+}$ precursor solution and water of 1:1.

A low-magnification SEM image (Fig. 2(a)) reveals that the flower-like products have the average mean diameter of ~ 20 - 40 μm . These flower-like micro/nanostructures consist of hierarchical rod alignments; as further shown in the high magnification SEM image (Fig. 2(b) and 2(c)), the hierarchical rod within the micro/nanostructure is composed of microrods on its lower part and a taper on its upper part. The microrods are regular hexagonal prisms with diameters of ~ 300 nm and lengths of several micrometers, and the taper is consisted of the cone with a width of ~ 300 nm and a cone-like nanorod end with a diameter of ~ 30 nm. The high-resolution TEM image is taken from an

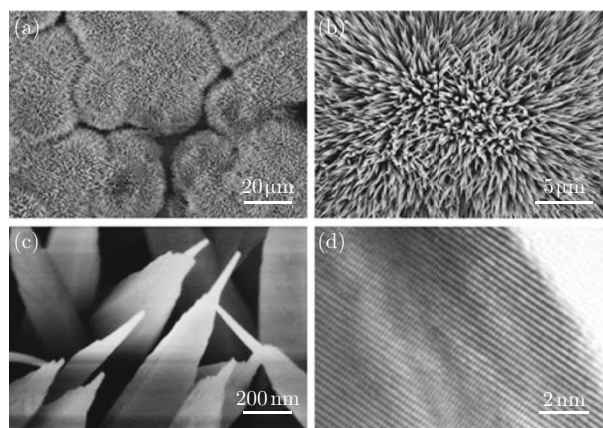


Fig. 2 (a-c) SEM and (d) HRTEM images of the ZnO hierarchical micro/nanostructures synthesized using the volume ratio of $\text{Zn}(\text{NH}_3)_4^{2+}$ precursor solution to water of 1:1.

edge of a composed ZnO micro/nanorod within flower-like microstructures (Fig. 2(d)). It reveals that the hierarchical rod is a single-crystal, suggesting that many single-crystal hierarchical rods are self-assembled into ZnO hierarchical micro/nanostructures. Detailed analysis of the lattice fringes give an interplanar spacing of 0.524, which match well the distance of the (001) planes of a ZnO crystal, which may result from lattice orientation perfection among the prismatic rod [21]. The rod axis direction was parallel to the (001) crystallographic orientation of a wurtzite ZnO crystal. This is a frequent growth orientation for the hexagonal close-packed materials, which has been observed in many ZnO nanorods [22].

The morphologies of these ZnO hierarchical micro/nanostructures vary with the volume ratio of $\text{Zn}(\text{NH}_3)_4^{2+}$ precursor solution to water, as shown in Fig. 3. When the volume ratio of $\text{Zn}(\text{NH}_3)_4^{2+}$ precursor solution to water is 32:0 with unchanged other parameters, the ZnO micro/nanostructures are consisted of the cone-like microrod assemblies and many sub-micrometer particles, and the cone-like microrod of the assemblies has a diameter of $\sim 1 \mu\text{m}$ and a length of several micrometers, as shown in Fig. 3(a) and 3(b). When the volume ratio is decreased to 3:1, the ZnO microstructures consisting of several microcones and particles are prepared (Fig. 3(c) and 3(d)). The cone has a diameter of $\sim 3 \mu\text{m}$ and a length of $\sim 6 \mu\text{m}$, and the particle has a diameter of $\sim 1 \mu\text{m}$. With further decreasing the quantity of $\text{Zn}(\text{NH}_3)_4^{2+}$ precursor solution (the volume ratio is 1:3), the flower-like ZnO structures are destroyed (Fig. 3(e) and 3(f)), and it can be seen

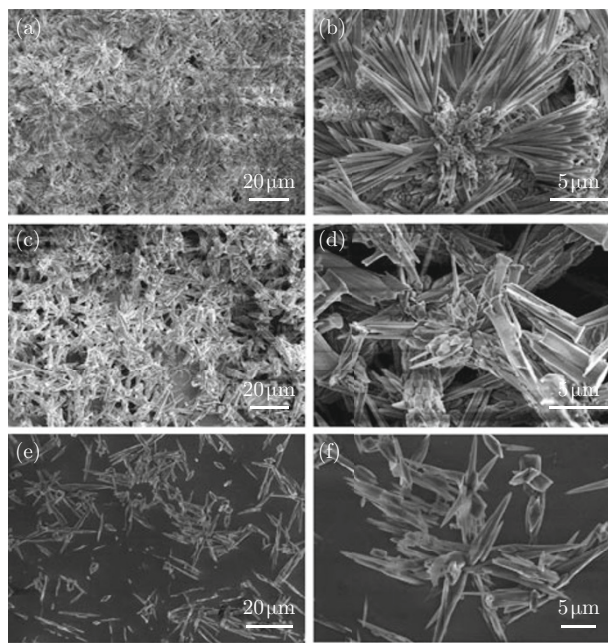


Fig. 3 SEM images of the ZnO micro/nanostructures prepared at different volume ratio of $\text{Zn}(\text{NH}_3)_4^{2+}$ precursor solution to water: (a,b) 32:0; (c,d) 3:1; (e,f) 1:3.

that the products are consisted of many cone-like microrods or particles with $\sim 3 \mu\text{m}$ in diameter and several micrometers in length, which possess the typical tapering feature with the tips. Therefore, ZnO crystals with a series of different morphologies were successfully fabricated only by changing the volume ratio of $\text{Zn}(\text{NH}_3)_4^{2+}$ precursor solution to water; each ZnO micro/nanostructures is composed of the ZnO cones and particles.

The effect of the surfactant quantity on the morphology of the ZnO hierarchical micro/nanostructures was also investigated. SEM images of the products prepared using the different amounts of citric acid are shown in Fig. 4. Without using citric acid as the surfactant, the flower-like ZnO hierarchical superstructures are composed of sub-micrometer rod, and individual rods gradually tapered and tipped in the form of cone with a diameter of about $\sim 1 \mu\text{m}$ (Fig. 4(a)). When the amount of citric acid was increased to 0.025 g or 0.05 g, the formation of the flower-like ZnO hierarchical structures consisted mainly of these micro-sized prisms, Fig. 4(b) and 4(c). When the amount of citric acid was increased to 0.1 g, the ZnO hierarchical structures are composed of sub-micrometer hierarchical rod or single hierarchical rod, and individual rod is prism-like and gradually tipped in the form of several nanocones with a diameter of about $\sim 100 \text{nm}$ (see Fig. 4(d)). Besides, when the amount of citric acid was increased to 0.3 g, the hierarchical microrod with a taper on its upper part began to aggregate into flower-like micro/nanostructures (see Fig. 2).

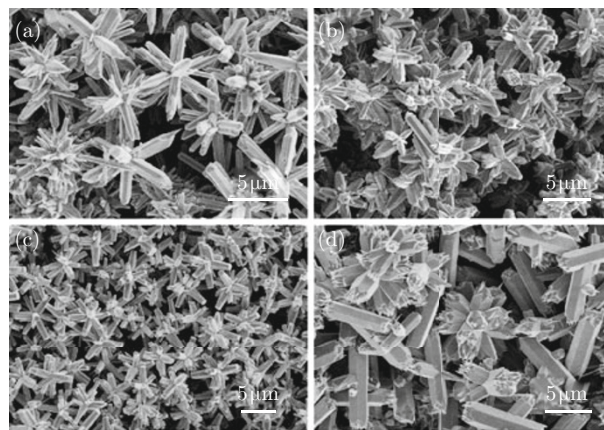


Fig. 4 SEM images of the ZnO micro/nanostructures prepared at different amounts of citric acid: (a) without citric acid; (b) 0.025 g; (c) 0.05 g; (d) 0.1 g.

ZnO particles by the direct decomposition of soluble $\text{Zn}(\text{NH}_3)_4^{2+}$ precursor under hydrothermal conditions were fabricated, which follows the growth habit of ZnO crystals [23]. The crystal growth process involves two stages of nucleation and crystal growth [24]. External conditions may stress tremendous effects on the morphology and size of a given crystal by participating

in the nucleation and growth [25]. In the present case, with the amounts of surfactant increasing gradually, the surfactant affects the overall size and the morphology by participating in the nucleation and growth. So, the surfactant plays a crucial role on the formation process of the ZnO micro/nanostructures.

We investigate the optical properties of ZnO hierarchical micro/nanostructures using a combination of UV-Vis and PL technologies. Figure 5(a) shows the UV-Vis spectra of ZnO hierarchical micro/nanostructures. The band gap energies (E_g) calculated on the basis of the corresponding absorption edges are 3.27 eV, which are comparable to the values of bulk ZnO. The PL properties of the as-prepared hierarchical micro/nanostructures were measured using 380 nm as an excitation wavelength at room temperature (Fig. 5(b)). It is clear that the spectra consist of a strong emission peak located at 440 nm and several weak emission peaks at 420, 471 and 541 nm, respectively. The near-UV emission at 420 nm agrees with the band gap of bulk ZnO (Gaussian peaks from 365 to 420 nm) [26], which comes from the recombination of free excitons. One possible reason for the variations in the position of the band-edge emission in ZnO nanostructures with relatively large dimensions are different concentrations of native defects [27]. The weak broad peaks at 440 and 471 nm are attributed to the exciton transitions [28] and the present of various point defects, either extrinsic or intrinsic, respectively. The green

emissions at 541 nm are related to the singly ionized oxygen vacancy [29], and these emissions result from the recombination of photogenerated hole with a singly ionized charge state of the specific defect.

Conclusion

ZnO hierarchical micro/nanostructures with the different morphology are fabricated by a simple hydrothermal method with excellent reproducibility. These morphologies can be conveniently tailored only by selecting the reactant concentration and the quantity of citric acid. SEM and TEM analysis reveal that the hierarchical rod is a single-crystal, suggesting that many single-crystal micro/nanorod are assembled into ZnO hierarchical micro/nanostructures. The surfactant plays a crucial role on the formation process of the ZnO micro/nanostructures. Room-temperature PL spectra reveal that the ZnO hierarchical micro/nanostructures have a strong emission peak at 440 nm and several weak emission peaks at 420, 471 and 541 nm, respectively.

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References

- [1] Z. L. Wang, *Mater. Today*, 7, 26 (2004). [http://dx.doi.org/10.1016/S1369-7021\(04\)00286-X](http://dx.doi.org/10.1016/S1369-7021(04)00286-X)
- [2] J. S. Na, B. Gong, G. Scarel and G. N. Parsons, *ACS Nano*, 3, 319 (2009). <http://dx.doi.org/10.1021/nm900702e>
- [3] M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo and P. Yang, *Science* 292, 1897 (2009). <http://dx.doi.org/10.1126/science.1060367>
- [4] G. Boschloo, T. Edvinsson and A. Hagfeldt, in *Nanostructured Materials for Solar Energy Conversion*, (Ed. T. Soga), Elsevier, 227 (2009).
- [5] W. I. Park and G. C. Yi, *Adv. Mater.* 16, 87 (2004). <http://dx.doi.org/10.1002/adma.200305729>
- [6] Y. K. Tseng, C. J. Huang, H. M. Cheng, I. N. Lin, K. S. Liu and I. C. Chen, *Adv. Funct. Mater.* 13, 811 (2003). <http://dx.doi.org/10.1002/adfm.200304434>
- [7] M. Law, L. Greene, J. C. Johnson, R. Saykally, and P. Yang, *Nat. Mater.* 4, 455 (2005). <http://dx.doi.org/10.1038/nmat1387>
- [8] X. F. Gao and L. Jiang, *Nature*. 432, 36 (2004). <http://dx.doi.org/10.1038/432036a>
- [9] L. Shi, Y. M. Xu, S. K. Hark, Y. Liu, S. Wang, L. M. Peng, K. W. Wong and Q. Li, *Nano Lett.* 7, 3559 (2007). <http://dx.doi.org/10.1021/nl0707959>

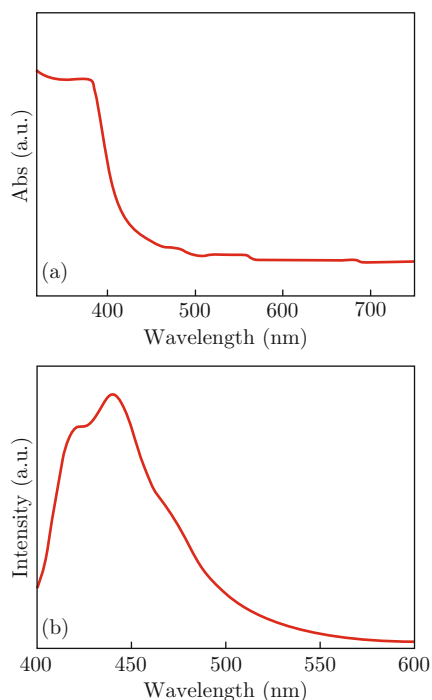


Fig. 5 (a) UV-vis absorption spectra, (b) Room temperature PL spectra of the ZnO hierarchical micro/nanostructures.

- [10] M. Shang, W. Z. Wang, W. Z. Yin, J. Ren, S. M. Sun and L. Zhang, *Chem. Eur. J.* 16, 11412 (2010). <http://dx.doi.org/10.1002/chem.201000639>
- [11] X. W. Lou, L. A. Archer and Z. Yang, *Adv. Mater.* 20, 3987 (2008). <http://dx.doi.org/10.1002/adma.200800854>
- [12] J. Elias, C. Lévy-Clément, M. Bechelany, J. Michler, G. Y. Wang, Z. Wang and L. Philippe, *Adv. Mater.* 22, 1607 (2010). <http://dx.doi.org/10.1002/adma.200903098>
- [13] Y. G. Sun, J. Q. Hu, N. Wang, R. J. Zou, J. H. Wu, Y. L. Song, H. H. Chen, H. H. Chen and Z. G. Chen, *New J. Chem.* 34, 732 (2010). <http://dx.doi.org/10.1039/b9nj00708c>
- [14] L. P. Xu, Y. L. Hu, C. Pelligra, C. H. Chen, L. Jin, H. Huang, S. Sithambaram, M. Aindow, R. Joesten and S. L. Suib, *Chem. Mater.* 21, 2875 (2009). <http://dx.doi.org/10.1021/cm900608d>
- [15] A. Umar, S. Lee, Y. H. Im and Y. B. Hahn, *Nanotechnology.* 16, 2462 (2005). <http://dx.doi.org/10.1088/0957-4484/16/10/079>
- [16] N. S. Ramgir, I. S. Mulla and V. K. Pillai, *J. Phys. Chem. B.* 110, 3995 (2006). <http://dx.doi.org/10.1021/jp056629b>
- [17] S. Jung, E. Oh, K. Lee, Y. Yang, C. G. Park, W. Park and S. Jeong, *Crystal Growth & Design.* 8, 265 (2008). <http://dx.doi.org/10.1021/cg0702961>
- [18] J. Zhang, L. Sun, J. Yin, H. Su, C. Liao and C. Yan, *Chem. Mater.* 14, 4172 (2002). <http://dx.doi.org/10.1021/cm020077h>
- [19] U. Choppali and B. P. Gorman, *J. Am. Ceram. Soc.* 90, 433 (2007). <http://dx.doi.org/10.1111/j.1551-2916.2006.01437.x>
- [20] Y. J. Kim, J. Y. Yoo, B. H. Kwon, Y. J. Hong, C. H. Lee and G. C. Yi, *Nanotechnology.* 19, 315202 (2008). <http://dx.doi.org/10.1088/0957-4484/19/31/315202>
- [21] J. F. Banfield, S. A. Welch, H. Z. Zhang, T. T. Ebert and R. L. Penn, *Science* 289, 751 (2000). <http://dx.doi.org/10.1126/science.289.5480.751>
- [22] X. Liao and X. Zhang, *J. Phys. Chem. C.* 111, 9081 (2007). <http://dx.doi.org/10.1021/jp0663208>
- [23] Z. Wang, X. F. Qian, J. Yin and Z. K. Zhu, *Langmuir.* 20, 3441 (2004). <http://dx.doi.org/10.1021/la036098n>
- [24] J. Zhang, L. Sun, J. Yin, H. Su, C. Liao and C. Yan, *Chem. Mater.* 14, 4172 (2002). <http://dx.doi.org/10.1021/cm020077h>
- [25] B. M. Wen, Y. Z. Huang and J. J. Boland, *J. Phys. Chem. C.* 112, 106 (2008). <http://dx.doi.org/10.1021/jp076789i>
- [26] E. M. Wong and P. C. Searson, *Appl. Phys. Lett.* 74, 2939 (1999). <http://dx.doi.org/10.1063/1.123972>
- [27] A. B. Djurišić and Y. H. Leung, *Small.* 2, 944 (2006). <http://dx.doi.org/10.1002/sml.200600134>
- [28] B. J. Jin, S. H. Bae, S. Y. Lee and S. Im, *Mater. Sci. Eng. B.* 71, 301 (2000). [http://dx.doi.org/10.1016/S0921-5107\(99\)00395-5](http://dx.doi.org/10.1016/S0921-5107(99)00395-5)
- [29] Y. Li, G. S. Cheng and L. D. Zhang, *J. Mater. Res.* 15, 2305 (2000). <http://dx.doi.org/10.1557/JMR.2000.0331>