Research Article

Synthesis and Characterization of Flower-Like Bundles of ZnO Nanosheets by a Surfactant-Free Hydrothermal Process

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Flower-like bundles of ZnO nanosheets have been prepared by using preheating hydrothermal process without any surfactants. The flower-like bundles consist of many thin and uniform hexagonal-structured ZnO nanosheets, with a thickness of 50 nm. The selected area electron diffraction (SAED) and high-resolution transmission electron microscope (HRTEM) images indicate that the ZnO nanosheets are single crystal in nature. The growth mechanism of the flower-like bundles of ZnO nanosheets is discussed based on the morphology evolution with growth times and reaction conditions. It is believed that the formation of flower-like bundles of ZnO nanosheets is related to the shielding effect of OH− ions and the self-assembly process, which is dominated by a preheating time. Room temperature photoluminescence spectra results show that the annealing atmosphere strongly affects the visible emission band, which is sensitive to intrinsic and surface defects, especially oxygen interstitials, in flower-like bundles of ZnO nanosheets.

1. Introduction

One of the most important goals of nanoscience and nanotechnology is to develop simpler method for a large-scale synthesis of nanomaterials with full control of size and morphology, because size, shape, and crystal structure are crucial factors in determining the chemical, optical, and electrical properties of nanoscale materials [1–4]. Recently, ZnO nanostructure, with a wide direct band gap and strong excitonic binding energy, has attracted much attention because of its promising characteristics for applications in electronic, photonic, and spintronic nanodevices. So far, various ZnO nanostructures, including nanowires [5], nanorods [6], nanonails [7], nanobridges [7], nanoprisms [8], nanotubes [9], nanobelts [3], nanorings [10], nanowhiskers [11], nanocombs [12, 13], nanohelixes [14], nanopropeller [15], nanobows [16], nanocages [17], nanodisk [18], nanopoins [19], and nanopores [20], have been fabricated by using vapor-phase process and solution phase route. Vapor-phase process such as molecular beam epitaxy (MBE) [21], metal-organic chemical vapor deposition (MOCVD) [22], sputtering method [23], pulsed laser deposition (PLD) [24], infrared irradiation [25], thermal decomposition [26], and thermal evaporation and condensation [27] is favored for its simplicity and high quality products. However these methods generally require high temperatures, high vacuums, rigorous procedures, and expensive pieces of equipment, which may limit potential applications, particularly requiring large-scale production. In contrast to the high-temperature vapor-phase process, the solution phase routes, which are based on a wet chemical and a bottom-up process, have been proved to be effective and convenient in
preparing various ZnO nanostructures due to their low growth temperature, low cost, and potential for scale-up. So far hydrothermal decomposition [28, 29], electrochemical reaction [30], and template-assisted sol-gel process have been employed to synthesize ZnO nanowires and nanorods. Additionally, more complex and aesthetic ZnO nanostructures, for example, flower-like nanostructures [31–34], hierarchically branched 2D nanostructures [35–38], 3D hollow micro- and nanospheres [39–43], also have been successfully synthesized by introducing organic surfactants during solution phase synthesis. From a thermodynamic point of view, surfactants, such as trisodium citrate, ethylenediamine, poly (ethylene glycol), and cetyltrimethylammonium bromide, can change the surface free energy of different ZnO crystal faces and control the rates of nucleation and growth, leading to their preferential growth or elimination. Although flower-like surfactant-free hydrothermal synthesis of ZnO architectures, which are made of thin nanosheets, by using organic solvent at high temperature (180°C) [48], it is also a challenge to fabricate flower-like bundles of ZnO nanosheets by surfactant-free aqueous solution phase method at low growth temperature.

The main goal of our research is to synthesize complex ZnO nanostructures using a surfactant-free hydrothermal method and to study their optical properties and applications. In this paper, we report the fabrication of flower-like ZnO architectures, which are made of thin nanosheets, by using a surfactant-free hydrothermal process. The growth mechanism for surfactant-free hydrothermal synthesis of flower-like ZnO architectures was discussed based on the morphology evolution with reaction time and the effect of the preheating time of precursor solution on their morphologies. The morphology, composition, and crystalline and optical properties of the as-grown flower-like ZnO architectures were investigated by X-ray diffraction (XRD), field-emission scan electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), and photoluminescence (PL) spectroscopy.

2. Experimental Details

All the chemicals were analytic grade reagents and used without further purification. Thin-ZnO film coated glass slides (75 × 25 × 1 mm) were used as substrates for subsequent growth of flower-like ZnO. ZnO thin films were grown by pulsed laser ablation of a ZnO hot pressed disk target (Ceramic, 99.999%) for 30 min, using the focused output of a KrF laser (Lambda-Physik COMPex 201, 248 nm, 5 Hz repetition rate). Energy used was 250 mJ · pulses⁻¹. The target was rotated in order to prevent repeated ablation of the same area. All depositions were conducted in a low background pressure of oxygen (P,O₂ = 10⁻² Torr, 99.99% stated purity, flowing at 10 standard cm³ min⁻¹ (sccm)).

0.1M precursor solutions of zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and hexamethylenetetramine (HMT) in distilled water (H₂O) were prepared, then 100 mL aliquots of each solution were mixed together in another glass bottle of maximum volume 250 mL, and the bottle was then sealed and heated to 95°C and was kept with this temperature 5–24 h, namely, the preheating process. At the end of preheating process, the ZnO seed layer-coated glass substrates were immersed in the preheated aqueous solution and tilted against the wall of bottle with ZnO thin films facing down. Subsequently, the bottle was sealed and heated to 95°C again for 10 h without any stirring. The as-grown samples were rinsed in deionized water and then dried in air. Then the as-grown ZnO samples were annealed at 550°C in air and in vacuum atmospheres for 2 h.

The morphology and structure of the samples were characterized by using XRD (Bruker D8 ADVANCE system with Cu Ka of 1.5406 Å), field-emission scanning electron microscopy Philips XL30FEF FESEM, and JEOL JEM-2100F HRTEM. The photoluminescence (PL) spectra were recorded at room temperature by He-Cd (325.0 nm) laser excitation.

3. Results and Discussion

3.1. Morphology and Structure. Figure 1 shows the FESEM images of ZnO sample obtained after preheating for 12 h. It can be seen from the low magnification top view FESEM image shown in Figure 1(a) that high density flower-like ZnO architectures uniformly grow and highly disperse in the substrates without any aggregation, indicating high yield and good uniformity achieved with this fabrication condition. The middle magnification FESEM image in Figure 1(b) shows that each flower has a diameter of about 40–50 μm and consists of hundreds of thin curved nanosheets, which are spokewise, projected from a common central zone. As shown in Figures 1(c) and 1(d), high magnification FESEM image reveals that these ZnO nanosheets are about 10–15 μm in length, 3–6 μm in width, and about 50 nm in thickness, which are assembled to form the flower-like architectures. Additionally, low density ZnO nanorods, as shown in Figure 1(e), can be observed on the space without flower-like ZnO architectures indicated by the white square in Figure 1(b). Magnified FESEM image clearly reveals that the shape of nanorods is hexagonal prism with a pyramidal top and smooth side surface, as shown in Figure 1(f). The diameter of the ZnO nanorods is about 100–150 nm; their length is about 1 μm, and most of the nanorods are perpendicular to the ZnO coated substrates.

Figure 2(a) shows a typical low resolution TEM image of an individual flower-like ZnO architecture scraped off from the substrate, which clearly demonstrates that it is made up of projected thin nanosheets. Middle resolution TEM image of an individual ZnO nanosheet in Figure 2(b) shows that the nanosheets are of good transparency to the electron beam and are homogenous, which indicates that the nanosheets are very thin and their surfaces are very flat, respectively. Two sets of well resolved parallel lattice fringes are observed in high resolution TEM, as shown in Figure 2(c). The interplanar spacing is measured to be 0.52 nm and 0.28 nm, respectively, corresponding to that of {0002} and {01-10} planes of ZnO crystals. Figure 2(d) is its SAED pattern and exhibits visible bright spots corresponding to all the crystal planes of the
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Figure 1: FESEM images of flower-like ZnO architectures grown on ZnO thin film coated glass substrates. (a) Low magnification, (b) middle magnification, (c) and (d) high magnification of FESEM images of ZnO flowers, and (e) and (f) middle magnification of FESEM images from the space without ZnO flower, as indicated by the white square in (b).

wurtzite ZnO, indicating a single crystalline with a good crystal quality. Based on HRTEM and SAED results, we can thus suggest that the single crystal wurtzite ZnO nanosheet grows along [0001] and [01-10] crystallographic directions within the (2-1-10) plane.

Figure 3 shows the XRD pattern of the ZnO sample scraped from the substrates to eliminate the influence of ZnO seed layer. Three diffraction peaks in the pattern can be indexed as the hexagonal ZnO with lattice constants \( a = 3.249 \) Å and \( c = 5.206 \) Å, consistent with the values in the standard card (JCPDS 36-1451). An energy dispersive spectroscopy (EDS) of flower-like ZnO, as shown in Figure 4, contains only elements of Zn and O, without any other impurity contamination in the sample.

3.2. Morphology Evolution with Growth Time. To understand how the flower-like ZnO architectures are formed, the growth time dependent morphological evolution process was examined by FESEM. Figures 5(a)–5(d) show the morphologies of the flower-like ZnO architectures with different growth times after the growth solution was preheated for 12 h. Figure 5(a) reveals that only ZnO nanorods are observed after 2 h. A careful examination shows that these ZnO nanorods are 80 nm in diameter and 500 nm in length. When the reaction time increased up to 4 h, a quasisphere nanostructure with a diameter of 4-5 \( \mu \)m emerged over the top of ZnO nanorods, which is aggregated from numerous small-size nanosheets with 20 nm in thickness, as shown in Figure 5(b). When the reaction time was prolonged to 6 h, some nanosheets with large length and width extend from the quasisphere center to outside, assembling into flower-like structures as a whole, as displayed in Figure 5(c). After 9 h, the nanosheets became bigger and longer and began to connect to each other, forming a complete flower-like structure, as shown in Figure 1(b). All the nanosheets are joined to each other through basic quasisphere center in such a manner that the flower exhibits a spherical shape. When the growth time was prolonged further to 24 h, the flower-like ZnO
Figure 2: TEM images of flower-like ZnO architectures. Typical TEM images of (a) an individual ZnO flower and (b) a piece of ZnO nanosheet. (c) HRTEM image and (d) SAED image of a piece of ZnO nanosheet.

Figure 3: XRD pattern of flower-like ZnO architectures.

Figure 4: The EDS spectrum corresponds to the flower-like ZnO nanostructures.

3.3. Morphology Evolution with Preheating Time. Further experiments indicate that the preheating time is crucial for the formation of such complex ZnO architectures. Figure 6 exhibits the morphologies of the products with different preheating times when other experimental conditions keep unchanged. Without preheating process, only nearly vertically arranged nanorod arrays are formed on the ZnO seed layer-coated substrates, as shown in Figure 6(a), which are 120 nm in the diameter and 2 μm in the length after growing for 10 h. The same results have been extensively reported [28, 29]. After preheating for 7 h, ultralong ZnO nanowires with honeycomb-like micropatterns (indicated by dotted line) could be observed from the overview image as shown in Figure 6(b). Such honeycomb-like micropatterns consisting of ultralong ZnO nanowires are similar to the one described by Lu et al. [49–51]. A magnified FESEM image shown in Figure 5(c) shows that the nanowires are of high aspect ratio (>200), with the diameter of 50 nm and the length of up to 10 μm. A higher magnification FESEM image of the ZnO nanowire roots reveals that ZnO nanowires also selectively grow from ZnO nanorod arrays, as shown in the inset of Figure 6(c). A further increase in preheating time to 12 h gives rise to a flower-like ZnO architecture, as shown in Figure 1(b). However, if preheating time is too long, for example, more than 24 h, nothing can be observed from the substrates. These results indicate that flower-like ZnO architectures can only be synthesized in a suitable preheating time of about 12 h.
Figure 5: The morphology evolution of flower-like ZnO architectures depends on the growth time: (a) 2 h, (b) 4 h, (c) 6 h, and (d) 24 h.

Figure 6: FESEM images of samples after different preheating time at 95°C: (a) without preheating, (b) and (c) 7 h, and (d) 24 h.

In addition, nothing can be synthesized on the bare glass substrate without a ZnO seed layer on its surface, indicating ZnO seed layer is also favorable for the formation of nanosheet flower-like architecture.

3.4. Formation Mechanism. The flower-like ZnO growth process is summarized in Figure 7. In our study, Zn$^{2+}$ and OH$^-$ are provided by hydration of Zn(NO$_3$)$_2$ and HMT, respectively. Therefore, the key chemical reactions can be formulated as follows:

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\begin{align*}
(CH_2)_6 N_4 + H_2O & \xrightarrow{\Delta} 4NH_3(g) + 6HCHO(g) \\
NH_3 + H_2O & \rightarrow NH_4^+ + OH^- \\
Zn^{2+} + 2OH^- & \rightarrow Zn(OH)_2(s) \\
Zn(OH)_2 & \xrightarrow{\Delta} ZnO(s) + H_2O
\end{align*}
\]
Generally, the typical growth direction of ZnO crystal is along the [0001] direction due to the higher growth rate compared to other growth facets [50, 52–54]; thus, nanorod or nanowires type morphologies are obtained often. Considering the crystal growth in liquid medium, although the crystal growth habit is mainly determined by the intrinsic structure, it is also affected by the external conditions such as organic surfactants, pH of solution, saturation, and temperature. For example, the organic surfactants can change the surface free energy of different ZnO crystal faces, adjust the growth rates of various crystal planes, and control their preferential growth or elimination, leading to various crystal structures and morphologies.

In this work, three factors are considered to play a key role in the formation of nanosheet based flower-like ZnO architectures, the concentration of zinc, pH value of growth solution, and ZnO seed layer. In the whole hydrothermal process, the Zn\(^{2+}\) concentration linearly decreases with preheating and growth time due to the formation of ZnO crystal precipitates. However, pH of the solution nearly keeps constant because HMT acts as not only a source of OH\(^-\) to drive the precipitation reaction, but also a pH buffer to slow release of OH\(^-\) by reactions 1 and 2 [55–57]. Without preheating, high zinc ion concentration benefits the formation of ZnO nanorods with small aspect ratio. This can be further demonstrated from the fact that the diameter of ZnO nanorod increases with increasing the zinc concentration. After preheating process for 7 h, the ZnO nanorods or nanowires with small diameter and high aspect ratio can be obtained due to the dissolution-regrowth and transport limiting in the solution and the shielding effect of HMT [58–61]. With increasing preheating time, partial ZnO nanorods will be decomposed into zinc ions again because of the consumption of the zinc ions in solution. In our case, the dissolution of six crystallographic nonpolar {01-10} planes was accelerated due to small diameter and high contact interface with precursor solution. At the same time, the decomposed zinc ions directly transfer to the vicinal polar Zn-terminated (0001) planes with high chemical-active. Then it results in the decreasing of the diameter and the quick increase of length and aspect ratio. Additionally, residual hexamine after preheating process, being a nonpolar chelating agent, would preferentially attach to the nonpolar facets of the ZnO nanorods/wires, thereby exposing only the polar Zn-terminated (0001) plane for epitaxial growth, which also promotes the growth along [0001] direction and drives the formation of small-size ZnO nanowires. After preheating was further increased to 12 h, zinc concentration further decreases into a suitable value; the growth rates of nonpolar (2-1-10) and nonpolar (01-10) planes are largely enhanced due to lower surface energy compared to that of polar (0001) plane. Simultaneously, the consumption of HMT weakens the shielding effect of HMT. On the contrary, the superfluous OH\(^-\) ions are easily adsorbed on the positively charged (0001) Zn-terminated surface and the growth rates along [01-10] and [2-1-10] directions are enhanced to a certain extent due to the shielding effect of OH\(^-\) ions on the (0001) surface [62]. As a result, the highest growth rate along the [0001] direction and the larger growth facets of (2-1-10) and (01-10) result in the formation of ZnO nanosheets.

The formation of flower-like ZnO architectures was achieved via a self-assembly process. From the thermodynamics point of view, the surface energy of an individual nanosheet is quite high with two main exposed planes, and thus they tend to aggregate to decrease the surface energy by reducing exposed areas. The surface energy is substantially reduced after the neighboring nanosheets are self-assembled. Additionally, the long range electrostatic interactions among the polar charges of [0001] planes also can induce self-assembly process. As a result, flower-like ZnO architectures assembled from nanosheets building blocks are constructed by this self-assembly process.

After preheating for 12 h, the degree of supersaturation of growth precursor is too low to heterogeneously nucleate on the substrates due to lattice mismatch. However, the presence of the ZnO seed layer can effectively lower the nucleation energy barrier, and homogeneous nucleation easily occurs on the seed layer, are benefit to the growth of nanorods and nanosheets.

3.5. Optical Properties. Figure 8 shows the room temperature PL spectra of flower-like ZnO architectures. The PL spectrum is featured by a peak near the ultraviolet region (UV) and a peak related to defects in the visible region (VIS). Through Gaussian fitting, the UV PL centered at 400 nm can be fitted well by two peaks centered at 383 and 410 nm, as shown by the dash dot line in Figure 8. The emission at 383 nm originated from the free excitonic recombination, which can be observed at room temperature due to the large exciton binding energy of ZnO (about 60 meV). It has been reported that thermal energy at room temperature may be enough to release bound excitons because the binding energy of bound excitons is only a few millielectron volts [62, 63]. The violet emission at 410 nm, which has been frequently observed in glass substrates, is commonly attributed to the oxygen dangling
bonds on the glass surface or the interface between glass substrate and ZnO nanostructures [64, 65]. Additionally, a large number of irradiative defects related to the traps existing at the nanosheet boundaries possibly contribute to the violet emission due to the transition between this level and the valence band [66, 67]. Although the presence of cubic ZnO, which might exist near the glass substrate interface, can be considered as a possible origin for this emission in the light of Sekiguchi’s report [68], this cannot explain the emission in our case, because there is no evidence for the existence of cubic ZnO from the XRD analysis.

The strong VIS-PL is fitted well by three Gaussians with a weak blue peak located at 450 nm, a strong orange peak centered at 603 nm, and a red shoulder at 715 nm, as shown by the dash lines in Figure 8. The blue emission was reported in tetrapodal nanocrystals [69, 70] and is often attributed to oxygen vacancies [69–74] or zinc vacancies [75]. Fu et al. [76] and Janotti and van de Walle [67] thought that the oxygen vacancy is a shallow intrinsic donor in ZnO and zinc vacancies form the deep acceptor level. They deduced that the blue emission included two transitions of electrons: from the shallow donor of oxygen vacancies to the valence band or to the acceptor of zinc vacancies. Other hypotheses include zinc interstitials, which were proposed by Zhang et al. [74], based on the band structure calculations. They deemed that the blue emission may correspond to the electron transition from the shallow donor level of zinc interstitials to the valence band or to the acceptor energy level of zinc vacancies.

The orange emission is also reported in ZnO nanostructures, and it represents a common feature in samples prepared by electrochemically [77], hydrothermally [68], and spray pyrolysis methods [78]. The orange emission is commonly attributed to oxygen interstitials, which is supported by the reports of decreasing or vanishing of orange peak after annealing under vacuum or in a H₂/Ar mixture [79, 80]. In addition to this common hypothesis, the possible presence of Zn(OH)₂ or hydroxyl groups (OH⁻) at the surface was identified as a possible origin of the orange emission at 600 nm [81–83].

Although most of the studies attribute the origin of red emission to excess oxygen interstitials [84, 85], recently zinc-related defects were also proposed as an original of a red emission [82, 84, 86]. Further studies are needed to clarify the origin of the red emission.

In order to investigate the nature of the VLS-PL in the as-grown sample, a series of annealing experiments were undertaken involving both ambient and vacuum environment, and the results were shown in Figure 9.

The PL spectrum of the sample after annealing in air at 550 °C for 2 h is shown in Figure 9. The position of the orange emission has changed a little and its intensity slightly increased, indicating that orange emission is not due to Zn(OH)₂ or hydroxyl groups (OH⁻) at the surface, because their concentrations obviously decrease after annealing at rich oxygen atmosphere due to desorption [82, 83], resulting in reduction in orange emission intensity. However, a strong green emission is observed after annealing in vacuum at 550 °C for 2 h. The green emission centered at 540 nm, commonly seen in ZnO structures synthesized from oxygen-deficient conditions, is often attributed to the recombination of electrons and holes in singly ionized oxygen vacancies [86–91] and could be quenched or red-shifted after annealing in oxygen-rich atmosphere. These results suggest that the orange emission in as-grown sample is mainly attributed to oxygen-related defects. However, no evidence of a green emission and no apparent red-shift make a possibility of existing oxygen vacancies in as-grown flower-like ZnO structures nearly zero. Therefore, it could be concluded that the as-grown flower-like ZnO nanostructures are oxygen-rich, and the orange emission centered at 600 nm can be attributed to only oxygen interstitials, in agreement with a previous study on ZnO films [92] and ZnO nanorod arrays [77].

Due to absence of oxygen vacancies in oxygen-rich as-grown flower-like ZnO nanostructures, only zinc related defects can be used to explain the origin of the blue emission.
at 440 nm. Based on the defect energy levels calculated by Sun and others [93–95] using full-potential linear muffin-tin orbital method, the energy interval from the donor level of zinc interstitial (Zn$_i$) to the top of the valence band (2.9 eV) and to the acceptor level of zinc vacancies (2.6 eV) is close to the energy of the blue emission (2.8 eV) observed in our case. But the possibility of forming zinc vacancies is little because the enthalpy of defect (ΔH) is 7 eV. Therefore, we believe that the transition of electrons from zinc interstitials to the valence band dominates the blue emission. After annealing, the intensity of blue emission decreases because the concentration of zinc interstitials decreases due to the diffusion [79, 96] and evaporation [70] of zinc interstitials resulted from a relatively high mobility.

Both oxygen interstitial and zinc interstitial defects in the as-grown flower-like ZnO architectures can be related to the red emission. The enhancement of red emission after annealing in air and its disappearance after annealing in vacuum apparently indicate that mechanism of the red emission is related to defects associated with excess oxygen. On the other hand, if the red emission was caused by zinc interstitials, the violet emission derived from zinc interstitial defects will be quenched or vanished with the disappearance of the red emission after annealing in vacuum, which disagreed with the result shown in Figure 9, indicating that zinc interstitial defects are not dominated origin for red emission in our case.

4. Conclusions

The flower-like ZnO architectures with a diameter of 40–50 μm, which consist of large numbers of thin and uniform hexagonal-structured ZnO nanosheets with a thickness of 40–50 nm, have been synthesized by using preheating hydrothermal method without any additives. The morphology of ZnO transforms from nanorod to nanosheets with increasing the preheating time and a low concentration of zinc ions in precursor solution after preheating for 12 h was proved to be a crucial factor in the formation of ZnO nanosheets blocks and flower-like architectures. Room temperature PL spectra results show that strong visible emission in the orange-red range in as-grown sample is replaced by green emission peak with a lower intensity after annealing in vacuum at 550°C for 2 h. The blue-shift of visible emission peak indicates that the position and intensity of orange-red peak can be strongly affected by annealing atmosphere and likely originates from intrinsic and surface defects, especially oxygen interstitials.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References


