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# Rapid synthesis of novel flowerlike ZnO structures by thermolysis of zinc acetate

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**Abstract**

Novel flowerlike ZnO structures have been rapidly synthesized on (1 0 0)-Si substrates via thermolysis of zinc acetate in air ambient without any catalyst. The obtained ZnO products exhibit well-defined flowerlike morphologies consisting of multilayer petal crystals with tapering feature. High-resolution transmission electron microscope (HRTEM) and corresponding selected area electron diffraction pattern (SAED) reveal that these petal crystals are single crystal in nature and preferentially oriented in the *c*-axis direction. Room-temperature photoluminescence (PL) spectra show that all the samples exhibit prominent UV emissions around 376.8 nm and very weak visible emission peaks, which demonstrates that there are few deep-level defects in the single crystal petals of the flowerlike ZnO structures. The growth mechanism of the as-synthesized flowerlike ZnO structures was also discussed.


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## 1. Introduction

Since the discovery of oxide semiconducting nanobelts, research into functional oxide-based nano-/microstructures has rapidly expanded due to their importance in basic scientific research and their unique and novel potential applications in electronic and optoelectronic devices [1]. ZnO is one of the most important functional oxides with direct wide band gap (3.37 eV) and large exciton binding energy (60 meV), exhibiting many interesting properties including near-UV emission [2], transparent conductivity [3], and piezoelectricity [4]. In recent years, a variety of ZnO nano-/micromaterials have been synthesized, such as nanowires, nanobelts, nanospring, nanoneedles, walls, tubes, nanobidges, nanonails, sea urchin-like ZnO structures, etc. [5–14]. These nanometer and micrometer ZnO materials with varied geometries have been used for fabricating nanolasers, field effect transistors, gas sensors, nanocantilevers, and nanoresonators [15–19].

Complex ZnO structures have a particular significance in the realization of advanced electronic and optoelectronic devices. Due to the sharp tips with high surface area, the flowerlike structures may find applications in various areas such as the fabrication of field emission devices, sensors, microfluidics, electromechanical coupled devices and transducers [20]. Recently, Gao et al. [21] reported the synthesis of flowerlike ZnO nanostructures via hexamethylenetetramine-assisted thermolysis of zinc–ethylenediamine complex. Hahn et al. [22–24] reported star-shaped and flowerlike ZnO nanostructures were grown on Si substrate by a cyclic feeding chemical vapor deposition method and discussed the growth mechanism in detail. However, despite some progresses in this field, it is inevitable to use toxic, dangerous, and expensive source materials. The simple and rapid synthesis of flowerlike ZnO nanostructures is still very difficult. In this article, we report the catalyst-free preparation of flowerlike ZnO structures by thermolysis of zinc acetate in air atmosphere. These flowerlike ZnO structures exhibit unique geometrical shapes, which are quite different from the morphologies reported previously.

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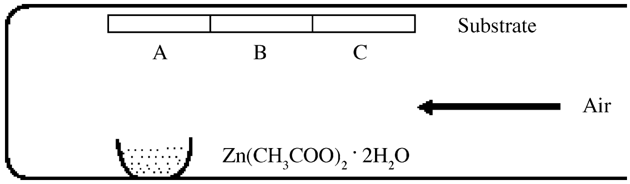


Fig. 1. Schematic illustration of thermolysis system for flowerlike ZnO structures growth.

## 2. Experimental procedure

The synthesis was carried out in a one-side opened horizontal quartz tube furnace (inner diameter: 6 cm, length: 100 cm). Commercially available zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) powders with a high purity of 99.999% were used as the source material, which were placed at the closed end of a slender quartz tube with a dimension of $\Phi 2$ cm × 20 cm. The other end of the quartz tube was open to the air, as schematically illustrated in Fig. 1. Cleaned silicon (1 0 0) wafer pieces for collecting the products were placed above the reactants. When the horizontal tube furnace reached the expected temperature of 700 °C, the small quartz tube was rapidly inserted into the tube furnace. After maintaining this for 15 min, the quartz tube was drawn out from the furnace and cooled down to room temperature. During the experiment, the temperature at different positions of the Si substrate was monitored with a thermocouple. The synthesized products were formed on the surfaces of the Si substrates.

The morphologies and structures of the as-grown products were characterized and analyzed by X-ray diffraction (XRD), field-emission scanning electron microscope (FE-SEM) and by high-resolution transmission electron microscope (HRTEM) at an accelerating voltage of 300 kV. Photoluminescence (PL) measurements were performed at room temperature using a He–Cd laser operating at 325 nm as the excitation source.

## 3. Results and discussion

Typical morphologies of the ZnO products grown on Si(1 0 0) substrates are shown in Figs. 2 and 3, which were collected from regions A–C, as shown schematically in Fig. 1. To our great interest, the particles are beautiful flowerlike microstructures, which were first observed.

Fig. 2(a) shows a representative low-magnification SEM image obtained in region A. It can be seen that the particles with diameters in the range 10–30 μm disperse uniformly on Si substrate, showing controllability of the process. Actually, this process has very high repeatability following the procedures given in the experimental section. A closer examination of the particles indicates that they are flowerlike structures consisting of multilayer petals and centric buds growing homocentrically, as presented in Fig. 2(b). Both the petals and the buds exhibit the hexagonal tapering feature with the root size of 2–3 μm in average. It is interesting that the tops of the petals and buds dehisce and consist of several small tips. Moreover, some flowerlike structures are composed of two halves, such as the one displayed in Fig. 2(c).

A typical low-magnification SEM image obtained in region B is given in Fig. 2(d). As can be seen, the particles also disperse uniformly on Si(1 0 0) substrate, suggesting that they were formed by individual nucleation and growth. Two sizes of the particles were found, i.e., ~20 and ~10 μm in diameters, as unambiguously shown in Fig. 2(e) and (f), respectively. All the particles also exhibit flowerlike structures similar to that obtained in region A. However, compared with the flowerlike structures in region A, they have more but smaller petals with the root size of ~1 μm in average.

Fig. 3 exhibits the representative SEM images obtained in region C. From Fig. 3(a), we can see that the sizes of the particles are 4–6 μm in average and obviously smaller than that in Fig. 2. In addition, the morphologies of the particles are also flowerlike structures but very different from that observed in regions A and B. Some flowers have corollas paralleling to the substrate, such as the one displayed in Fig. 3(b), while in some other cases, the flower is just composed of multilayer hexagonal petals, as exhibited in Fig. 3(c). Moreover, it is very interesting that some flower clusters consist of two flowers (Fig. 3(d)), three flowers (Fig. 3(e)) or four flowers (Fig. 3(f)). These unique structures further demonstrate that ZnO is probably the richest family of nano-/microstructures among all materials [25].

XRD results show that the different flowerlike ZnO morphologies possess the same phase structure. Fig. 4 shows the typical XRD pattern of the as-grown materials. It can be seen that all the diffraction peaks can be indexed to the known hexagonal wurtzite structure of ZnO with cell parameters of $a = 3.242$ Å, and $c = 5.205$ Å. No other diffraction peaks of impurities were observed. The preferential orientation is [0 0 0 1].

To obtain more structural information, TEM measurements of the flowerlike ZnO structures formed in region C were made. The bright-field TEM image in Fig. 5(a) confirms that the flowerlike ZnO structure is composed of tapering feature ZnO petal crystals. From Fig. 5(b), it can be seen that the HRTEM image shows a clear lattice fringes indicating a single crystalline textured orientation. No dislocations or stacking faults are observed in the areas measured. The spacing between two adjacent lattice planes was about 0.26 nm corresponding to the lattice constant of the (0 0 0 2) plane of wurtzite structured ZnO, which implies that the preferred growth orientation is along the [0 0 0 1] direction. Corresponding selected area electron diffraction pattern (SAED) along the axis direction of the petal crystal, as given in Fig. 5(c), confirms the growth direction and also indicates that the petal crystal is of high crystallinity and hexagonal phase.

On the basis of the results described above, we attribute the possible growth mechanism of flowerlike ZnO structures in our experiments to the symmetrical nucleation and growth model. Zinc acetate dihydrate powders were used as the source material in our experiments. As temperature increases, the