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Synthesis of flower-like ZnO thin films by chemical reduction method

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Abstract: Zinc Oxide (ZnO) is a II-VI semiconductor with a wide and direct bandgap of about 3.3 eV which behaves as a transparent conducting oxide. ZnO is a technologically important material exhibiting multifunctional properties for various applications in optoelectronics devices such as solar cells, chemical sensors, piezoelectric transducers, transparent electrodes, photocatalysis, heat mirrors, ultraviolet laser diodes etc. ZnO thin films are prepared on chemically cleaned glass substrates by chemical reduction method. The films are deposited from zinc acetate ($Zn(O_2CCH_3)_2$) and ethylenediamine ($C_2N_2H_8$) of different molarities as source materials at different bath temperatures. Flower-like ZnO nanostructures were synthesized using a low-temperature solution method in the presence of ethylenediaminetetraacetic acid disodium salt (EDTA-2Na). By increasing the EDTA-2Na/Zn^{2+} molar ratio, the morphology transitioned from spherical shaped to flower-shaped architectures. Time-dependent observations revealed a transformation sequence from flat nanosheets to wrinkled nanosheets, eventually forming flower-like structures. The strong chelating ability of EDTA-2Na was identified as a critical factor driving this morphological evolution. Photoluminescence (PL) analysis indicated that the flower-like ZnO structures possess a higher defect density compared to nanowire arrays.

Keywords: Flower-like ZnO;; PL; ethylenediamine; nanocrystalline.

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1. Introduction

In recent years, ZnO nanostructures have attracted considerable interest owing to their exceptional properties and broad range of applications in fields such as dye-sensitized solar cells, light-emitting diodes, nanogenerators, gas sensors, photocatalysis, electron field emission, and room-temperature ultraviolet lasers [1–9]. Considerable efforts have been dedicated to fabricating three-dimensional (3D) hierarchical structures that incorporate one-dimensional (1D) or two-dimensional (2D) ZnO building blocks. These hierarchical ZnO assemblies exhibit distinctive features and promising functional uses. For instance, brush-like architectures demonstrate superior ethanol sensing performance compared to ZnO nanowires [10], while stacked ZnO nanoplate arrays with predominantly exposed (0001) facets display enhanced photocatalytic efficiency relative to nanowire arrays [11].

Various solution-based approaches for producing hierarchical ZnO structures have been developed with the aid of surfactants. Examples include the synthesis of hexagonal bipyramidal, hourglass-shaped, and flower-like morphologies using sodium dodecyl benzene sulfonate, Tween-85, and cetyltrimethylammonium bromide, respectively [12–14]. In the present work, we describe the solution-phase synthesis of flower-like ZnO nanostructures employing EDTA-2Na·2H_2O (EDTA) as a morphology-directing agent. A systematic evolution in particle shape was observed, indicating that EDTA, as a strong complexing agent, plays a pivotal role in controlling the structural transformation of the resulting nanostructures.

2. Experimental

ZnO nanostructures thin films were prepared by a modified low-temperature solution method previously used to prepare ZnO nanowire/nanorod arrays [15]. All chemicals (analytically pure) were purchased from Merk., Ltd and used without further purification. A (100)-Si wafer was used as a substrate, which was cleaned with ethanol and acetone in an ultrasonic bath for half an hour, respectively, followed by etching in a mixed solution consisting of 20 mL of ammonia hydroxide (25%), 20 mL of H_2O_2 (30%) and 100 mL of deionized water.

An alcoholic solution of zinc acetate (2 M) was spin-coated on the cleaned Si substrate (1×1.5 cm2) for 5-7 times, followed by annealing in air at 300 °C for 30 minutes. ZnO seed layers are thus formed on the substrate for the subsequent growth of the flower-like nanostructure. 1.859 g of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 98%) and 0.876 g of ethylenediamine (($C_2N_2H_8$), 98%) were dissolved into 250 mL of deionized water under vigorous magnetic stirring. In order to tune the morphology of ZnO nanostructures, a complexing agent, EDTA-2Na·2H2O (molar ratios of EDTA/Zn2+ = 0.2, 0.5), was added to the solution. The Si substrate covered with ZnO seed layers was immersed upside-down in the solution and heated at 80 °C for 1-9 h. Flower-like nanostructures were thus grown on the substrate. Finally, the substrate was removed from the aqueous solution, rinsed with distilled water for several times, and dried at room temperature.

The crystal structure of flower-like ZnO nanostructures was analyzed with a D/MAX-2550 diffractometer (Rigaku, Japan) equipped with a rotating anode and a Cu Kα radiation source (λ = 1.54178 Å). A field emission scanning electron microscope (FE-SEM, JEOL JSM-6700F, Japan) was used to examine their morphologies. High-resolution transmission electron microscopy images were taken on a JEOL JEM-2010F microscope (HRTEM; JEOL, Japan) at an acceleration voltage of 200 kV. Photoluminescence (PL) measurements were obtained by exciting the samples with a Xe lamp at 325 nm (Hitachi F-7000, Japan).

3. Results and discussion

Figure 1 shows the typical XRD pattern of the flower-like architecture prepared with a molar ratio of EDTA2Na/Zn^{2+} of 0.5. All of the diffraction peaks can be well indexed to the ZnO wurtzite structure with lattice constants of a = 3.249 Å, c =5.206 Å (JCPDS No. 36-1451). There are three main diffraction peaks (100), (002), and (101) and (002) peak is the strongest.

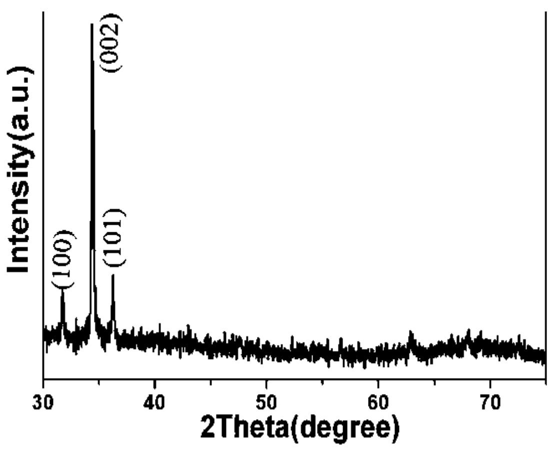

Fig 1. XRD pattern of ZnO flower-like architectures.

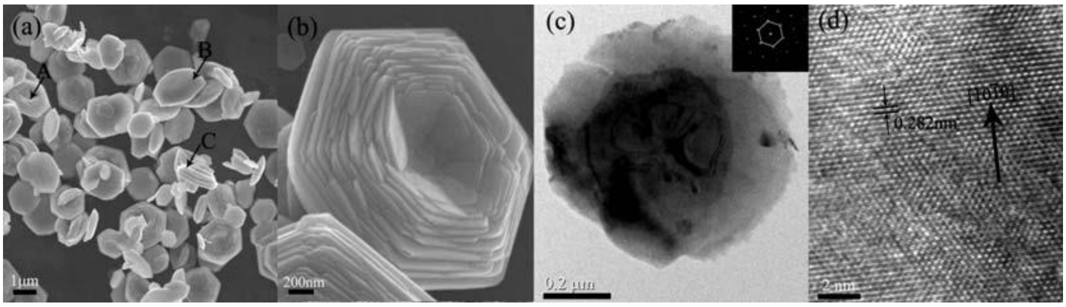

Fig 2. FE-SEM (a, b), TEM (c), and HRTEM (d) images of flower-like ZnO architectures prepared with an EDTA-2Na/Zn2+ molar ratio of 0.5. The inset in (c) is an SAED pattern

Figure 2a is the typical FE-SEM image of the rose-like ZnO nanostructures grown on a Si substrate. Most of the "petals" lie on the substrate with the front up (indicated by "A") or the back up (indicated by "B"). There are also some "flowers" standing up, as shown by "C". Their sizes are typically 1-2 µm. The amplified view of an individual "rose" (Fig. 2b) clearly reveals that the flowers consist of multilayer stacking nanosheets of tens of nanometres in thickness. Figure 2c shows the TEM image of a single flower. The selected-area electron diffraction (SAED) pattern taken along a direction perpendicular to one of the nanosheets in the flower shows a hexagonal symmetry, corresponding to the {1010} crystal planes perpendicular to the [0001] zone axis. The HRTEM image of the nanosheet exhibits clear lattice fringes about 0.282 nm between adjacent lattice planes, consistent with the interplanar spacing of (1010) planes of the ZnO wurtzite hexagonal phase. These observations indicate that the flower-like flowers are composed of nanosheets whose top/bottom surfaces are ± (0001) planes. This structure can account for the strongest (002) peak in the XRD pattern.

Figure 3 shows the FE-SEM images of ZnO nanostructures prepared under different molar ratios of EDTA2Na/Zn^{2+}. In the absence of EDTA-2Na in the reaction system, ZnO nanowire arrays with a length of ~ 1.3 µm and a diameter of ~ 80 nm (aspect ratio of ~ 16) vertically grown on the substrate were produced, which agrees with the previous report [15]. However, in the presence of EDTA-2Na, for the ratio of EDTA-2Na/Zn^{2+} of 0.2, ZnO nanostructures formed. But there are still short arrays grown on ZnO nanostructures (see the insert in figure 3b). With increasing the ratio to 0.5, all formed nanostructures are flower-like (Fig. 3c and its insert). With doubling the concentrations of the precursors and EDTA-2Na while keeping EDTA-2Na/Zn^{2+} unchanged (0.5), the "petals" will evolve into more complex and more interesting architectures containing many "flowers" (Fig. 3d and its inset).

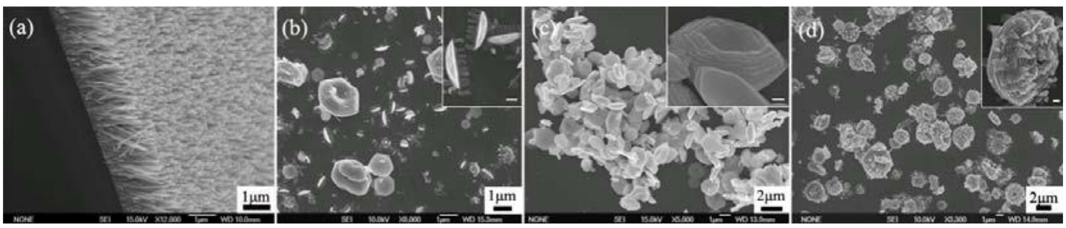

Fig. 3 FE-SEM images of flower-like ZnO nanostructures prepared under different EDTA-2Na/Zn2+ molar ratios: (a) 0, (b) 0.2, (c) 0.5, and (d) 0.5 but doubling the concentrations of the precursors and EDTA-2Na.

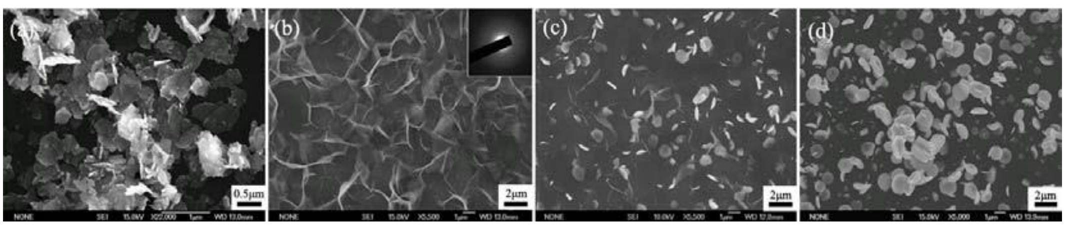

Fig. 4 FE-SEM photographs showing the growth process of the flower-like structures for given reaction times: (a) 1 h, (b) 2h, (c) 3 h, and (d) 4 h. The insert in (b) is an SAED pattern.

Figure 4 illustrates the morphological evolution of ZnO nanostructures when the EDTA-2Na/Zn^{2+} ratio is 0.5. After 1 hour of reaction, flat nanosheets were produced (Fig. 4a). By the second hour, these nanosheets transformed into wrinkled amorphous structures, as confirmed by the characteristic SAED ring pattern (inset of Fig. 4b). At the 3-hour mark, a mixture of amorphous nanosheets and rose-like structures was observed, suggesting that the flower-shaped formations likely emerged through the folding and subsequent crystallization of the amorphous nanosheets. After 4 hours, the nanosheets had completely converted into rose-like architectures (Fig. 4d).

The low-temperature solution reaction [16] proceeds as follows:

$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO\ (g) + 4NH_3\ (g)$ (1)

$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$ (2)

$2OH^- + Zn^{2+} \leftrightarrow Zn(OH)_2\ (s) \leftrightarrow ZnO(s) + H_2O$ (3)

Without EDTA-2Na, ZnO crystals typically form nanorod or nanowire arrays due to their anisotropic growth pattern. The relative growth rates of different crystal planes follow the order: V(0001) > V(101¯\bar{1}1¯0) > V(101¯\bar{1}1¯1) > V(0001¯\bar{1}1¯), leading to preferential growth along the [0001] axis [16]. In contrast, when EDTA-2Na is present, the one-dimensional growth is inhibited, favoring the formation of two-dimensional nanosheets that assemble into rose-like hierarchical structures. This significant morphological shift indicates that EDTA has a decisive role in directing the shape transformation. We propose that EDTA ions strongly chelate with Zn^{2+} ions on the (0001) plane, thereby suppressing crystal growth along [0001] while enhancing growth along the [101¯\bar{1}1¯0] direction. Consequently, nanosheet formation becomes more favorable than nanowire formation. Over time, these nanosheets stack and overlap through self-assembly, creating multilayer flower-like structures. A comparable transformation from nanowire arrays to stacked nanoplates has been reported in the presence of citrate [11], another complexing agent that, like EDTA-2Na, plays a critical role in shaping ZnO architectures.

Figure 5 presents the room-temperature photoluminescence (PL) spectra of flower-like structures and spherical shaped samples excited with 325 nm UV light. In the case of the flower-like sample, the PL response spans a broad wavelength range starting from approximately 370 nm extending up to 500 nm. The ultraviolet emission centered around ~398 nm is associated with band-edge exciton recombination [17,18], while the blue–green emissions, with peaks near 450, 468, 483, and 493 nm, are primarily linked to surface defect states arising from zinc interstitials and oxygen vacancies [17–22]. In contrast, the nanowire sample exhibits a sharp and intense band-edge emission at 381 nm, accompanied by only weak defect-related luminescence. This comparison suggests that the flower-like structures possess a higher density of defects than the nanowire counterparts.

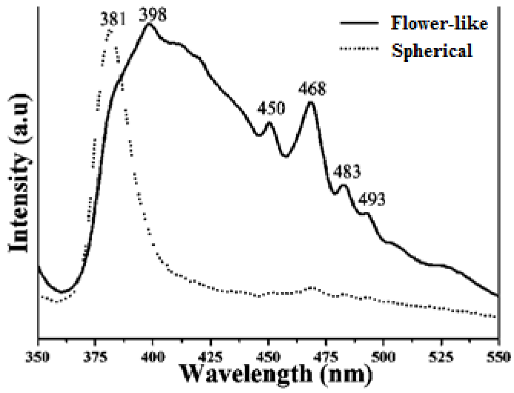

Fig. 5 PL spectra of flower-like and spherical ZnO structures measured at room temperature

4. Conclusion

Flower-like ZnO nanostructures were synthesized via a low-temperature solution method in the presence of EDTA-2Na. By adjusting the EDTA-2Na/Zn^{2+} molar ratio and the reaction duration, various morphologies were achieved. EDTA-2Na acts as a crucial structure-directing agent; its strong chelation with Zn^{2+} ions suppress one-dimensional growth while promoting the formation of two-dimensional ZnO nanosheets, which subsequently assemble into flower-like hierarchical architectures. Photoluminescence analysis reveals that these flower-like ZnO structures contain a higher concentration of defects compared to spherical shaped ZnO.

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