

Formation mechanism, structural characterization, optical properties and photocatalytic activity of hierarchically arranged sisal-like ZnO architectures

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Abstract

A simple low-temperature solution-based self-construction approach has been demonstrated for fabricating the highly uniform assembly of ZnO nanocones with much higher aspect ratio, in which a highly non-equilibrium chemical environment favors for the large-scale generation of the complex architectures mimicking the sisal-like structures. The formation mechanism has been studied at molecular level. The optical and photocatalytic properties of the as-synthesized product have been correlated with their chemical composition, morphology and structural features. These sisal-like ZnO nanocone assemblies have shown a strong UV emission with a broad blue emission band and a high photocatalytic activity in decomposition of polyaromatics, suggesting their potentials in light and field emission and environmental applications.

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1. Introduction

Synthesis of binary oxide nanostructures has been a research theme owing to their potential applications in constructing nanoscale electric and optoelectronic devices [1,2]. Critical to the properties and behaviour of these potential devices are the crystallinity, stoichiometry, size, shape and structure of these building blocks [3,4]. Different one-dimensional (1D) ZnO nanostructures have been prepared for fundamental studies of the physical properties [1,4,5] as well as for the widespread use in sensors [6], optoelectronics [7], field emission [8], solar cells [9], and surface acoustic waveguides [10]. Nanocones emerge as a new kind of 1D nanostructures that is even superior to nanotubes, nanowires, and nanobelts in some aspects [11,12]. Nanocones are more advantageous candidates for the scanning probes and field emitters due to their sharp point for easy

emission of electrons. However, these interesting properties can be deteriorated during growth. To date, most of the reported methods for the fabrication of ZnO nanocones and their assemblies are restricted to the evaporation and condensation processes (top-down strategy). Although several soft chemical routes have been adopted to obtain aligned ZnO nanotip/nanorod arrays at a relatively low temperature [13], their reaction processes were complicated. Joo et al., reported a non-hydrolytic ester elimination sol-gel reaction for synthesis of aggregated ZnO nanocones with low aspect ratio, which needed the various surfactants and the alcoholic reagent, as well as the relatively high temperature of 200–280 °C [14]. It is still full of promising challenges to develop scalable approaches for fabricating ZnO micro-assemblies with intricate and precisely controlled features.

Herein, we report a simple bottom-up solution-phase route, involving a highly non-equilibrium chemical environment, to generate the programmed assembly of ZnO nanocones into sisal-like hierarchical architectures on the surface of the Zn foil under remarkably mild condition

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(60 °C). The formation mechanism has been studied at molecular level. The synthesized ZnO nanocones owing to the controlled chemical composition, their specific morphology and structural features have shown quite interesting optical and photocatalytic properties in the decomposition of polyaromatics in comparison with conventional nanorods and nanopowders.

2. Experimental

2.1. Synthesis of sisal-like ZnO nanocone assemblies

Zinc sulfate (ZnSO_4), sodium hydroxide (NaOH), and zinc foil were purchased from Aldrich, and ammonium fluoride (NH_4F) from Merck. All chemicals were used as received without further purification. Zn foil (0.25 mm thick) was cleaned by acetone in an ultrasonic bath for 5 min and then washed by deionized water for several times. The synthesis of sisal-like ZnO nanocone assemblies with hierarchical structures was performed in the presence of excessive NH_4F by using ZnSO_4 solution as zinc precursor. Typically, 40 mL of ZnSO_4 aqueous solution (0.075 M) containing NH_4F with $\text{NH}_4^+/\text{Zn}^{2+}$ molar ratio of 30:1 was slowly adjusted to pH \sim 11.70 by a NaOH solution (5 M), and then transferred into a Teflon-lined 60-mL-capacity autoclave. A $1 \times (1-1.5) \text{ cm}^2$ Zn foil was suspended carefully into the solution followed by sealing the autoclave. After 12–15 h of heating at 60 °C, the foil was removed from the solution, rinsed with deionized water and dried in air for further characterization.

2.2. Characterization

The composition and the phase of these as-prepared products were determined by wide-angle X-ray powder diffraction (XRD) pattern, which was recorded on a Philips PW 1820 diffractometer using Cu $\text{K}\alpha$ radiation. Scanning electron microscopy (SEM) images were carried out with a Philips XL-20 at 20 keV. Transmission electron microscopy (TEM), the selected-area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM) were performed on CM30-FEG, operating at 300 kV (equipped with electron energy loss spectroscopy (EELS)). The photoluminescence (PL) was measured by a PELS55-luminescence spectrophotometer, using 325 nm excitation line of a Xe lamp at room temperature.

2.3. Photocatalytic activity study

The photocatalytic activity experiments on the obtained ZnO nanocones for the decomposition of naphthalene were performed at ambient temperature. The as-prepared ZnO nanocones (removed from the Zn foil, 11 mg) was placed into 66 mL of a saturated naphthalene aqueous solution (30 mg/L, water solubility [15]) in a tubular quartz reactor. The reactor was surrounded with six UV lamps (Osram Eversun, L40/79 K, 40 W). The reaction mixture was stirred

under UV irradiation with the wavelength centered at 350 nm. The analysis of the naphthalene solution concentration in the reactor was performed with a PELS55 luminescence spectrophotometer at $\lambda_{\text{ex}} = 280 \text{ nm}$. As a comparison, the activity of 1D ZnO nanorods [16] and the commercial ZnO powders (Aldrich, size $< 1 \mu\text{m}$, 99.9%) was also tested under the same experimental condition.

3. Results and discussion

3.1. Phase and morphology of the obtained assembly of ZnO nanocones

Fig. 1a shows the X-ray diffraction (XRD) pattern of the products grown on the Zn foil, revealing that the as-prepared samples are hexagonal wurtzite ZnO (space group $\text{p6}_3\text{mc}$; JCPDS card No. 36-1451) with the lattice constants of $a = 0.325 \text{ nm}$ and $c = 0.525 \text{ nm}$. The morphological information of the as-prepared wurtzite-type ZnO materials was derived from the images of scanning electron microscopy (SEM). Fig. 1b is a panoramic SEM image of ZnO structures, which shows that a large quantity of ZnO clusters are randomly dispersed on the surface of the Zn foil. A closer look clearly shows that the clusters are actually sisal-like hierarchical assemblies composed of many ZnO nanocones (Fig. 1c), and the ZnO nanocones with very high aspect ratio have sharp tips (Fig. 1d). All nanosisals are almost identical with the uniform size of 15–20 μm , showing the highly homogeneous growth of nanocone assemblies.

3.2. Structural information of ZnO nanocones

The unique structures of the generated ZnO nanocones were further confirmed by the transmission electron microscopy (TEM). Fig. 2a is a low-magnification TEM image, indicating that a typical ZnO nanocone has a sharp tip of $\sim 90 \text{ nm}$ with a relatively smooth surface. The ripple-like contrast pointed by arrows implies the existence of the strains along the nanocones. The selected-area electron diffraction pattern (the inset of Fig. 2a) reveals single-crystalline nature of the nanocones with $\langle 0001 \rangle$ growth direction, which can be indexed as the $[4\bar{5}10]$ zone axis of ZnO crystals. Fig. 2b is an atomic-resolution high-resolution TEM image of the surface of a nanocone, which clearly shows that the (0001) atomic planes (separation: 0.52 nm) perpendicular to the nanocone axis and thus indicates that $\langle 0001 \rangle$ is the preferred growth direction of these wurtzite-type ZnO nanocones. An outer layer surrounding the nanocone contains some ‘dislocations’ pointed by arrows. The EELS spectrum shows that the nanocones only contain Zn and O elements, without any other impurity.

3.3. Influence of growth conditions on ZnO crystallite structures

The programmed one-step growth of the unique sisal-like ZnO nanocone assemblies by this simple solution-

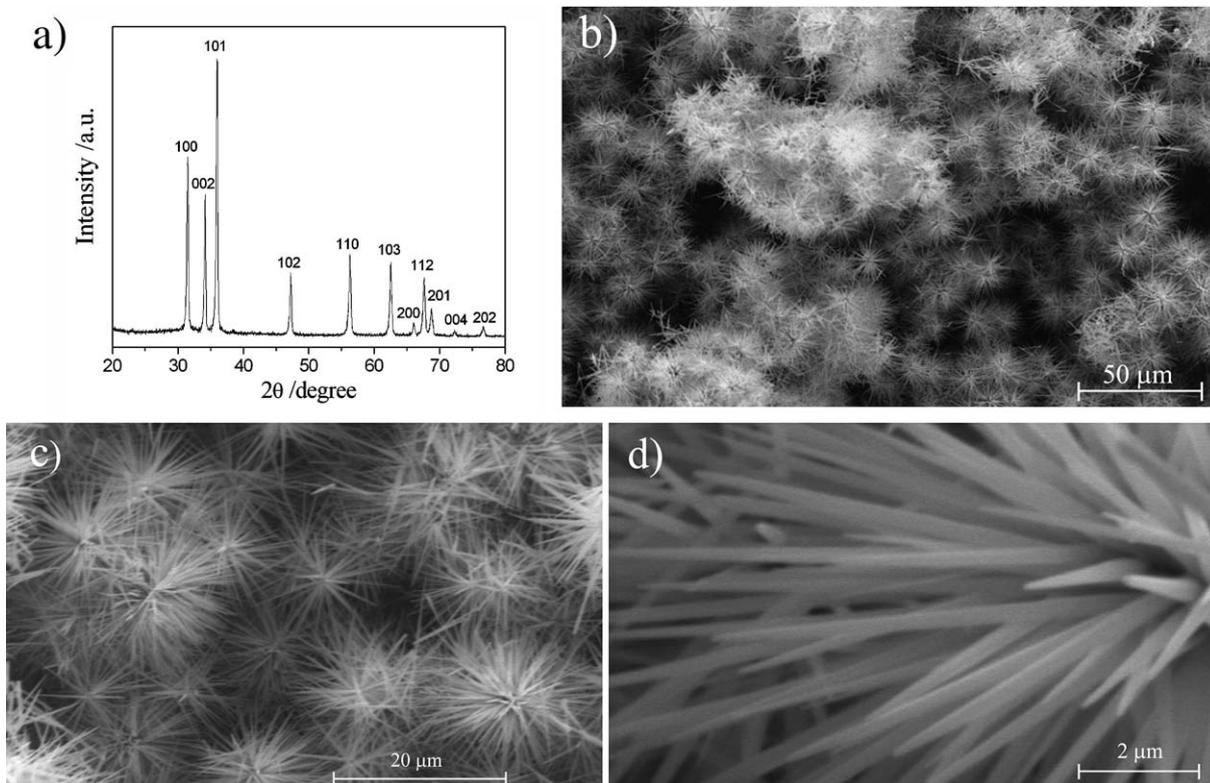


Fig. 1. (a) XRD pattern of the obtained products, indexed to a pure wurtzite ZnO. (b) Overview SEM image, showing a large quantity of ZnO clusters. (c,d) Enlarged SEM images, indicating that the clusters are the nanocone assemblies with the sisal-like hierarchical structures.

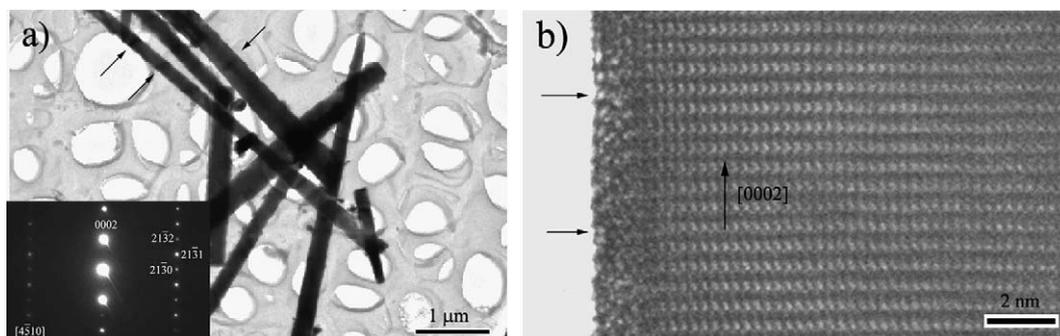


Fig. 2. (a) Low-magnification TEM image of several ZnO nanocones and the corresponding SAED pattern (inset). (b) High resolution TEM image of a nanocone.

phase route is a spontaneous and self-organized process in the absence of organic agents and/or hard templates (such as Al_2O_3 membrane). To understand the self-formation of these novel sisal-like ZnO nanocone assemblies on the zinc foil surface, a series of reactions were carried out under the different conditions, and it has found that the appearance of sisal-like ZnO nanocones assemblies is some experimental factors dependent, such as the substrate, the temperature and ammonium fluoride (NH_4F). In the controlled experiments, no ZnO nanocones assembly was obtained when substituting Zn foil with Zn powder or processing in the absence of Zn foil, which illuminates that the geometry of a Zn foil obviously favours a more or less unidirectional diffusion of metal ions resulting in the observed

vertical growth of ZnO nanocones [17]. And the structures of the final products have a good relevancy with the reaction temperature. If the synthesis was performed at a temperature as low as 40 °C, little sisal-like ZnO nanocone assemblies could be obtained, due to the lack of introduction of foreign seed particles onto the substrate at too low temperature. While at an optimized temperature of 60 °C, sisal-like ZnO nanocone assemblies with hierarchical structures can be produced in a large scale by this simple approach. However, the increase of the temperature to 80 °C or higher would result in only the uneven ZnO rods with their diameters changed from ~ 1.2 to ~ 1.5 μm (Fig. 3). This clearly indicates that the supply rate of zinc precursors can be turned from low to high level by increas-

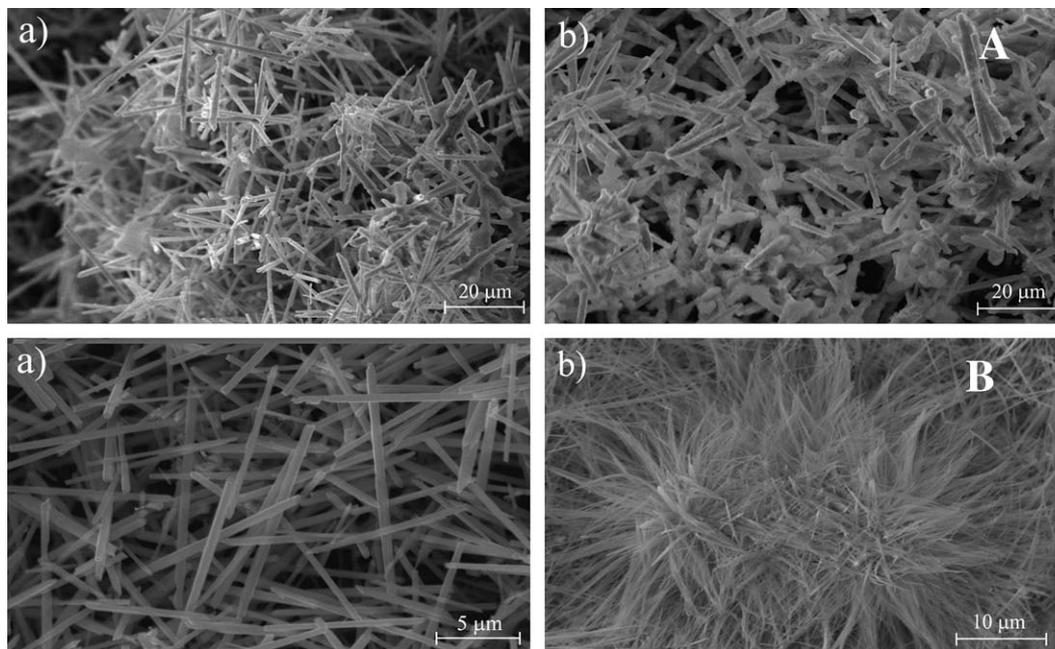


Fig. 3. SEM images: (A) ZnO structures synthesized at (a) 80 and (b) 100 °C. (B) ZnO nanorods (c) obtained in the presence of NH_4NO_3 and (d) flower-like ZnO nanowires with twin architectures prepared when using NaF.

ing the reaction temperature, which results in the growth of ZnO nanorods occurring under the kinetically controlled condition, suggesting that the rapid supply of ZnO precursor favours the formation of nanorod aggregation rather than nanocone assemblies.

Furthermore, the excessive quantity of NH_4F is indispensable for the formation of sisal-like ZnO nanocone assemblies. The deposition rate on the substrate can be reduced because of the strong coordination of the most electronegative F^- anions to Zn^{2+} cations, which would be accompanied by the heterogeneous nucleation [11,18] and thus prefer to the oriented complex architectures, such as sisal-like and flower-like nanostructures. Our controlled experiments also indicate that the cooperation of NH_4^+ and F^- would play a crucial role in the appearance of the sisal-like structures. Other nanostructures rather than nanocones would be obtained if substituting NH_4F with NH_4NO_3 or NaF at the same molar ratios to Zn^{2+} ions. Typically, the straight ZnO nanorods would be achieved when NH_4NO_3 was used instead of NH_4F , whilst another interesting flower-like nanowire assembly was prepared in the substitution of NH_4F with NaF (Fig. 4). It appears to be the synergy of NH_4^+ and F^- ions that orients the growth direction of nanocrystals. Additionally, there is a progressive decrease in the amount of ZnO species along the [0001] direction of the growing nanostructures, leading to the formation of nanocones [19]. The growth of ZnO nanocones, similar to the reported TGC [20], may be decomposed into axial and radial directions, respectively, where the root-based radial growth is a process of continuous formation of additional outside layers while the axial growth simultaneously elongated the formed layers along the axial growth.

Although this synthetic procedure is very simple, the formation mechanism and the self-assembly process seem to be quite complex. The multiple and dynamical interactions strongly control the formation of highly ordered structures. Difference in kinetics (growth rates, adsorption of counter-ions on the growing crystal faces, etc.) are the likely origin [19,21]. Both the internal crystal structures and the interaction between NH_4F and Zn^{2+} come into play to engender the formation of sisal-like nanocone assemblies with hierarchical structures in the mineralization process. ZnO crystals, directed by the coordination of many factors, grow in the direction where the crystalli-

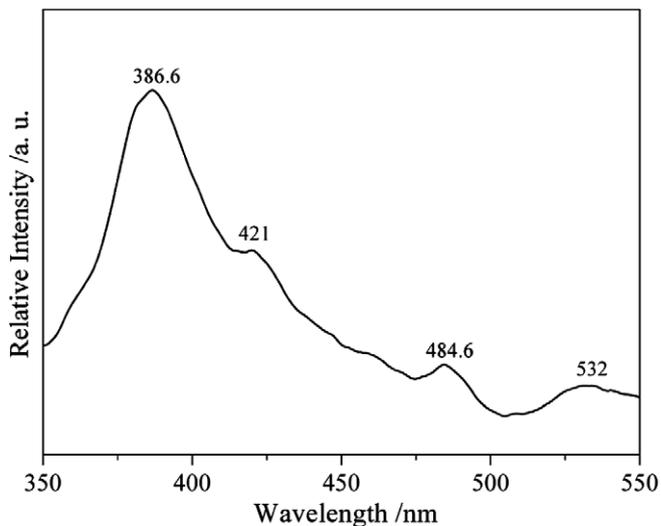


Fig. 4. Photoluminescence spectrum of sisal-like ZnO nanocone assemblies at room temperature ($\lambda_{\text{ex}} = 325 \text{ nm}$).

zation hindrance is weakest. This evidences that in the well-programmed highly non-equilibrium environment, the self-organisation of ions in relation to crystal growth can occur just like in a biomineralization process. The interactions between these chemical species would ultimately determine the geometry and distances where they come to equilibrium in a self-assembled system and thus attain the most stable form [22]. However, further investigation is needed to better understand this pseudo biomineralization mechanism of the morphology evolution.

3.4. Optical properties

Photoluminescence (PL) spectroscopy is an effective technique to evaluate both ZnO defects and its optical property available as a photonic material. Fig. 4 shows a typical room temperature PL spectrum of sisal-like ZnO nanocone assemblies, where a strong UV emission at ~ 386.6 nm dominates with several weak emission peaks at ~ 421 nm, 484.6 nm and 532 nm, respectively. The strong emission at ~ 386.6 nm (3.22 eV) is resulted from the annihilation of free-exciton, and the deep level emission at ~ 532 nm (2.38 eV) is generally attributed to the recombination of electron in singly occupied oxygen vacancies with photoexcited holes [23]. The emissions at ~ 421 nm (2.95 eV) and ~ 484.6 nm (2.56 eV) originate from the electron transition from the level of the ionized oxygen vacancies to the valance band [24]. The sharp excitonic emission and the weak deep level emission peaks indicate that the ZnO nanocones have high optical property [16], which suggests that the as-prepared ZnO nanocone assemblies may have potential light and field emission applications.

3.5. Photocatalytic activity in the decomposition of naphthalene

The photocatalytic testing has revealed a very high photocatalytic activity of naphthalene degradation (Fig. 5). During the degradation of naphthalene over the as-obtained sisal-like ZnO nanocone assemblies, the concentration of the naphthalene could quickly decrease to 1.8% after 30-min UV irradiation, and continue down to $<0.3\%$ when prolonging the irradiation time to 60 min, respectively. In comparison, the concentration of the naphthalene could decrease to 2.1% after 30-min UV irradiation on the conventional 1D ZnO nanorods, which further decrease to 0.36% after 60-min irradiation and down to $<0.3\%$ after 75-min irradiation. Whereas the commercial ZnO powders need at least 120 min to decompose the naphthalene to $<0.3\%$ of the saturated concentration. Additionally, compared to previously synthesized ZnO nanowires [25], the photocatalytic activity of the as-obtained ZnO nanocone assemblies is also improved. It is thus obvious that ZnO nanocones have better photocatalytic properties than ZnO powders. This enhanced catalytic property could be attributed to the unique surface nanofeatures [26]. These valuable results indicate that the sisal-

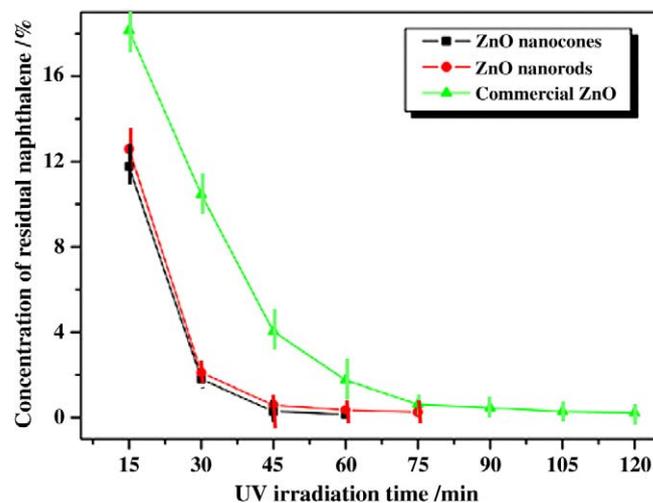


Fig. 5. The concentration of residual naphthalene after UV irradiation at different times over the as-prepared ZnO nanocones and the pre-obtained 1D ZnO nanorods, as well as the commercial ZnO powders.

like ZnO nanocone assemblies could have valuable activity in air and waste-water purification.

4. Conclusions

A facile solution-phase route has been employed to fabricate the sisal-like hierarchical architected ZnO nanocone assemblies on the surface of Zn foil at 60°C , involving a highly non-equilibrium chemical environment rather than other extend driving force. The formation and assemblies of nanocones on the surface of zinc foil could be controlled by carefully tuning the reaction parameters. The sharp excitonic emission observed with these ZnO nanocone assemblies indicate that the ZnO nanocones have a low defects concentration and high optical properties, which may find great potential in nanoscale devices and systems. And the enhanced photocatalytic properties suggest that these sisal-like ZnO nanocone assemblies are more compelling for the environmental applications.

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