One-Step Hydrothermal Synthesis of Comb-Like ZnO Nanostructures

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ABSTRACT: Zinc oxide (ZnO) nano-superstructures (NSSs) have attracted intense research interest due to their large surface areas and unique properties. In this work, we report an original approach to synthesize ZnO NSSs in a one-step manner with a hydrothermal method. The crystalline structures and growth mechanism can be understood by surface energy calculations. The reaction kinetics was investigated for the control of the morphology of ZnO NSSs. The critical role of the morphology of Au catalysts in the synthesis of ZnO nanostructures has been demonstrated. Such ZnO NSSs can be fabricated on various rigid and flexible substrates for applications in electronics, solar cells, and piezoelectric devices.

INTRODUCTION

Zinc oxide (ZnO), a wide bandgap semiconductor material, exhibits unique electronic and optical properties when at least one dimension is constrained at the nanoscale.1 These properties have found various applications in optics and energy conversion devices. As a result, the study and fabrication of ZnO nanomaterials, such as nanowires,2 nanodots,3 nanorings,4 and highly branched superstructures5 have been at the forefront of recent research. Among all the ZnO nanostructures, highly branched ZnO nano-superstructures (NSSs) have generated an intense interest for enhanced performance in energy conversion devices, such as polymer–inorganic hybrid solar cells (PIHSCs),6 dye-sensitized solar cells (DSSCs),7−9 and piezoelectric nanogenerators.10

For instance, highly branched ZnO NSSs with multiscale hierarchical configurations can substantially improve the energy conversion efficiency for PIHSCs and DSSCs due to the large surface area and enhanced charge transport properties. It has been demonstrated that ZnO NSSs can improve the energy conversion efficiency (3.74%8,11) by 150% compared with simple one-dimensional (1-D) nanowire arrays (∼1.5%) for DSSCs.7 Highly branched ZnO NSSs also exhibit superior performance in various other devices such as solar-assisted water splitting electrodes,12 nanolasers,13 biosensors,14 optical gratings15,16 or polarizers,16 field emission,17 and microwave absorption.18 However, the applications of ZnO NSSs are still hampered by the difficulty of synthesizing ZnO NSSs in a facile, controllable, and low-cost manner.

Various attempts have been made to synthesize ZnO NSSs, including hydrothermal and thermal evaporation methods. Most thermal evaporation and hydrothermal methods are based on multistep catalyst/seed-assisted reactions.2,8,19−22 For instance, ZnO branches were grown on prefabricated ZnO nanowires via catalysts/seed of gold (Au) or ZnO nanodots dispersed on the surface of the ZnO nanowires. This method requires a complex multistep fabrication process. It also introduces foreign particles, such as Au nanodots, which may impair the performance of nanodevices made of ZnO NSSs. Recently, direct synthesis of ZnO NSSs through a thermal evaporation method without any catalyst was reported.13 The dendritic growth is a result of rapid crystallization with highly supersaturated reactants.23 However, such methods require high temperature and elaborate instrumentation, which are disadvantageous in cost-effective manufacturing. Recently, Li and co-workers reported a metal hydrothermal oxidation approach to prepare ZnO nanofers without catalysts.24 The ZnO nanofers exhibit enhanced visible emission and photocatalysis compared with as-prepared ZnO nanorods.

In this work, we report an innovative approach to synthesize comb-like ZnO NSSs in a one-pot and one-step manner assisted by 1-D catalysts with a hydrothermal method. The 1-D catalysts can be readily removed, leaving the ZnO NSSs intact. By variation of the reactant concentration and reaction time, ZnO NSSs with stems and branches of desirable dimensions can be readily obtained. The critical role of Au catalysts in the synthesis has been discussed and demonstrated. Such ZnO NSSs can be synthesized on both rigid and flexible substrates including silicon, glass, indium titanium oxide (ITO) glass, and kapton tapes, which are suitable for various applications.

EXPERIMENTAL SECTION

To synthesize ZnO NSSs, 14 mL of 10 mM Zn(NO3)2·6H2O (zinc nitrate hexahydrate, Aldrich, 98%) and 14 mL of 10 mM C6H12N4 (hexamethylenetetramine, Aldrich, 99%) were mixed at room temperature and transferred to a 50 mL glass bottle. The Au nanowire...
catalysts with diameters of 300 nm and lengths of 6 μm, prepared by electrodeposition into nanoporous templates, were uniformly dispersed on a 1.5 cm ×1.5 cm Si wafer (with a native oxide layer) and then dried in air. The Si wafer with the Au nanowire catalysts was loaded upside down in the Teflon holder in the glass container and incubated at 90 °C for 16 h. Then we took out the silicon wafer, rinsed it with water, and dried it in air.

The chemical reactions that take place were as follows:

\[
\begin{align*}
\text{C}_6\text{H}_{12}\text{N}_4 + \text{Zn}^{2+} &\leftrightarrow \text{Zn}^{2+} \text{ amino complex} \quad (1) \\
\text{C}_6\text{H}_{12}\text{N}_4 + 4\text{H}_2\text{O} &\leftrightarrow \text{C}_6\text{H}_{12}(\text{NH}_3)^{++} + 4\text{H}_2\text{O} \quad (2) \\
\text{Zn}^{2+} \text{ amino complex} + 2\text{H}_2\text{O} &\rightarrow \text{C}_6\text{H}_{12}(\text{NH}_3)^{++} + \text{Zn(OH)}_2 \\
&\rightarrow \text{ZnO} + 2\text{H}_2\text{O} \quad (3) \\
\text{Zn}^{2+} + 2\text{H}_2\text{O} &\rightarrow \text{Zn(OH)}_2 + 2\text{H}^+ \rightarrow \text{ZnO} + 2\text{H}_2\text{O} \quad (4)
\end{align*}
\]

At room temperature, reaction 1 goes from left to right resulting in the precipitation of a Zn²⁺ amino complex shortly after the mixing of Zn(NO₃)₂·6H₂O and C₆H₁₂N₄. At a temperature of 90 °C, reaction 1 reverses direction and the Zn²⁺ amino complex is dissolved. At the same time, reaction 2 shifts to the right side, which consumes the acid and increases the pH value. This process promotes reactions 3 and 4 to go toward the right. As a result, ZnO nanocrystals are formed. This is a dynamic process, during which the concentration of reagents are changing, as well as the growth speed and morphology of ZnO.

Following the synthesis, the characterization of the as-synthesized ZnO NSSs was conducted by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The SEM images were taken with a Hitachi-S5500 instrument, whereas the TEM images and selected area electron diffraction (SAED) were taken in a JEOL 2010F. For the TEM characterization, in order to eliminate the difficulty of transferring ZnO NSSs from the silicon substrate to the TEM grid and to keep their morphology intact, we prepared ZnO NSSs directly on the SiO₂ film (40 nm thick) supported Si₃N₄ grids (Ted Pella Inc.) coated with Au nanowires under the aforementioned typical synthesis condition.

## RESULTS AND DISCUSSION

### Study of the Morphology and Growth Kinetics

ZnO NSSs are found on the entire surface of the silicon substrate. Typical ZnO NSSs have symmetric comb-like morphologies, with stems (2 μm in width, 10 μm in length) in the middle and branches on both sides of the stems (80 nm in width, 5 μm in length) as shown in the SEM image of Figure 1.

![Figure 1](image.png)

**Figure 1.** SEM images of as-prepared ZnO NSSs. The insets are magnified images of individual ZnO NSSs and branches.

The morphology of the NSSs can be controlled by the reaction kinetics via the reactant concentration and reaction time. In a typical reaction of 10 mM Zn(NO₃)₂·6H₂O and 10 mM C₆H₁₂N₄ at 90 °C, the stems grow and reach their constant length in 6 h before the branches emerge and steadily grow with time as shown in Figure 2a,d. The density of the branches steadily increases and reaches a constant value in 12 h (Figure 2c).

The reaction kinetics can be understood by a reactant-concentration-dependent kinetic process. In the beginning, the concentration of the reactants is relatively high, which favors the growth of stems. With the progress of the reaction, the concentration of the reactants decreases to a threshold value, which no long favors the growth of stems and instead promotes the growth of branches. To confirm this hypothesis, we studied the concentration-dependent kinetic process. In the beginning, ZnO NSSs with desired dimensions in both the stems and the branches could be readily obtained. For instance, if we want to synthesize ZnO NSSs with short stems and long and dense branches, we could design reactions with a low reactant concentration and a long reaction time.

### Growth Mechanism of the ZnO NSSs

Next, we investigated the growth mechanism of the ZnO NSSs with TEM/SEM imaging and surface energy calculations. The bright-field TEM image of as-prepared ZnO NSSs showed the comb-like morphology [Figure 3a]. SAED was conducted on both the stems [Figure 3b] and branches [Figure 3c]. The fast growth directions of the stems and branches were determined to be [0001] and [1120], respectively. The top surface plane of ZnO NSSs (includes both the stems and branches) was calculated to be ⟨1100⟩. To further confirm this hypothesis, we studied the growth in the direction of the branches, high-resolution (HR) TEM imaging was conducted, as shown in Figure 4a–c. The results show that the branches indeed grew along the [1120] direction and perpendicular to [0001]. This can be confirmed by rotating the sample 30° about the [0001] axis. We found that the [1120] direction changed to the [1010] direction along the branches, while the [0001] orientation remains unchanged as shown in Figure 4d–f. Here we note that the [0001] spots shown in the diffraction pattern in Figure 4f can be attributed to the double diffraction effect that is often observed in ZnO. The 30° tilted angle matches the calculated angle between the [1120] and [1010] directions in ZnO crystals. Therefore, the combination of SAED and HRTEM imaging confirm that the branches grew along the [1120] direction.

The {0001}, {1120}, and {1100} planes are frequently reported surface planes of wurtzite ZnO nanostructures, and the {0001}, {1120}, and {1100} are the corresponding fast growth directions. It is commonly believed that under thermodynamic equilibrium conditions, the surface areas of high-energy facets are smaller than those of low-energy facets. The crystal orientations of the ZnO NSSs can be understood by surface energy calculations that have been reported previously. We did surface energy calculations based on density functional theory and obtained a similar trend (Supporting Information, S2). As shown in Table 1, the values of as-

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calculated surface energy follow the order of \( E_{\{0001\}} > E_{\{1 \bar{1} 20\}} > E_{\{1 \bar{1} 00\}} \). Therefore, it can be readily understood that the \( \{1 \bar{1} 00\} \) surfaces with the lowest energy have the lowest growth rate along \( \langle \bar{1} \bar{1} 00 \rangle \) and are prone to be the most stable surfaces with a large area; by the same token, \( \{0001\} \) surfaces with the highest energy have the highest growth rate along \( \langle 0001 \rangle \).

Combined with the previously discussed kinetic study, this result helps us further understand the growth mechanism of the ZnO NSSs synthesized in our work. In the initial stage of the reaction, the concentration of \( \text{Zn}^{2+} \) in solution is sufficient; ZnO NSSs grow fastest along the \( \{0001\} \) direction and form the \( \{\bar{1}100\} \) plane as the largest top surface, which result in the stems of the NSSs. With continuing consumption of the reactants, the concentration of \( \text{Zn}^{2+} \) become insufficient for further growth of the stems of ZnO NSSs. Instead, small crystallite units in the form of nanobranches become preferable to support the further growth of the ZnO crystal. Thus, most branches grow on both sides of the stems in the second fastest growth direction, which is the \( \{1 \bar{1} 20\} \) direction, perpendicular to \( \{0001\} \). Also, some branches grow on the tips of the stems along the fastest growth direction of \( \{0001\} \) [Figure 5a]. Moreover, secondary nanobranches can develop on existing branches along the two fastest \( \{0001\} \) and \( \{1 \bar{1} 20\} \) directions.

Table 1. Surface Energy Calculation Results

<table>
<thead>
<tr>
<th>surface</th>
<th>energy (eV/Å²)</th>
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<tr>
<td>{0001}</td>
<td>0.162833</td>
</tr>
<tr>
<td>{1 \bar{1} 20}</td>
<td>0.114417</td>
</tr>
<tr>
<td>{1 \bar{1} 00}</td>
<td>0.109241</td>
</tr>
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Figure 2. Morphology control of ZnO NSSs by adjusting reaction time and reactant concentration. (a) The morphology evolution of ZnO NSSs with time (6, 16, and 36 h) for the conditions of 10 mM Zn(NO₃)₂·6H₂O, 10 mM C₆H₁₂N₄, and 90 °C. (b) The morphology dependence on the reactant concentration (1, 5, and 20 mM, respectively, at 6 h and 90 °C). (c) The length of the branches steadily increases with time, while the length of the stems remains constant. (d) The density of the branches reaches a constant value at 12 h. (e) The length of the stems and branches increase and decrease, respectively, with the reactant concentration.

Figure 3. (a) Bright-field TEM image of a ZnO NSS. SAED of the ZnO NSS in panel a shows that (b) the branches grow in \( [1 \bar{1} 20] \) direction and (c) the stem grows in \([0001]\) direction.

Figure 4. (a, b) Bright-field TEM images of ZnO NSS branches. (c) HRTEM shows the branch growth direction to be along the \( [1 \bar{1} 20] \). (d, e) Bright-field TEM images tilted 30° about the \( [0001] \) direction. (f) HRTEM shows the direction \( [1 \bar{1} 20] \) becomes \( [1 \bar{1} 00] \) after tilting 30°. [Insets of c and f are fast Fourier transform (FFT) images; \( [\bar{1}100] \) and \( [\bar{1}210] \) are directions of the electron beam. The ratio \((1/L_2)/(1/L_1) = 0.64; (1/L_1)/(1/L_2) = 0.911\).]
substrate. The morphology of the Au catalysts determines the morphology of the ZnO NSSs. Without Au, ZnO nanostructures cannot be obtained. (a) 2-D Au thin films catalyze the growth of ZnO NSSs parallel to the substrate. (b) 0-D Au nanodots catalyze the grown of 1-D ZnO nanowires vertical to the substrate.

(2) 1-D Au nanowire catalysts of controlled dimensions (diameter 50–300 nm, length 3–12 μm): ZnO NSSs were successfully synthesized (See Figure S3, Supporting Information). Both ZnO NSSs attached to and not attached to Au nanowires were obtained. The majority of ZnO NSSs do not have attached Au nanowires. We observed a very small amount (<5%) of Au nanowires embedded in ZnO NSSs, most of which were transversely inserted through the middle of ZnO stems as shown in Figure S3b, Supporting Information. Overall, there is no significant correlation between the distribution (location, orientation, shape) of the Au nanowires and ZnO NSSs for the majority ZnO NSSs as discussed in S3, Supporting Information. The morphology of ZnO NSSs essentially remains the same for Au nanowire catalysts with different dimensions under the same reaction conditions (See Supporting Information, S3).

(3) 0-D Au nanodot catalysts (10 nm in diameter) dispersed on the Si wafer: ZnO nanorods were grown vertically to the substrate [Figure 6b].

(4) No Au on Si wafer: no ZnO NSSs.

(5) An increase of the coating density of Au nanowires will lead to an increase of ZnO NSSs density, for example, an increase in the density of Au nanowires from ~3000 to ~9000 mm−2 leads to an increase in the density of ZnO NSSs from ~2200 to ~5100 mm−2 (90 °C, 10 mM, 16 h).

The above experiments indicate that Au plays an important role in the synthesis of ZnO NSSs. The dimension and morphology of Au determine the morphology of ZnO nanostructures: zero-dimensional (0-D) Au nanodots catalyze the growth of vertical ZnO nanorod arrays; on the other hand, 1-D Au nanowires and 2-D thin films result in comb-like ZnO NSSs. Further investigation is ongoing to understand the specific role of the catalyst morphology in the synthesis of ZnO NSSs. The Au nanowires are advantageous as catalysts for the ZnO NSSs synthesis owing to the simplicity of the experimental procedure and the ease of removal of the Au nanowire catalysts with the ZnO NSSs intact, which eliminates the problem of device impairment as found in other ZnO devices.

In summary, the growth of ZnO NSSs can be described as follows: in the beginning of the reaction, when the reactant concentration is high, the stems preferentially grow along the [0001] direction. As the reaction proceeds, the reactant concentration decreases to a threshold value, which promotes the growth of branches, which grow along the [1120] and [0001] directions on the sides and tips of the stems, respectively.

By use of this method, the ZnO NSSs can be synthesized on various substrates, either rigid substrates, such as Si, glass, or ITO substrate, or soft substrates such as kapton tapes. The morphology of the ZnO NSSs is similar to that in Figure 6a.

CONCLUSION

We report the synthesis of comb-like ZnO NSSs by hydrothermal method. The fast growth directions of the stems and branches of the ZnO NSSs were determined to be [0001] and [1120], respectively, which is different from most reported high-temperature synthesized ZnO NSSs. The growth of our ZnO NSSs can be understood from the theoretical surface energy calculations. By varying the reactant concentration and reaction time, ZnO NSSs with desirable dimensions in both the stems and the branches can be readily obtained. Au plays a critical role in the synthesis of ZnO nanostructures. The ZnO NSSs can be grown on both rigid and soft substrates, such as Si wafer, glass, and kapton tapes, which enable them to find applications in electronics, solar cells, and piezoelectric devices.

ASSOCIATED CONTENT

Supporting Information

EDS of ZnO NSSs, method of surface energy calculation, and relationship between dimension and distribution of Au nanowires and the morphology of the ZnO NSSs. This
material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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