Straight and Thin ZnO Nanorods: Hectogram-Scale Synthesis at Low Temperature and Cathodoluminescence

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A novel seed-assisted chemical reaction at 95 °C has been employed to synthesize uniform, straight, thin, and single-crystalline ZnO nanorods on a hectogram scale. The molar ratio of ZnO seed and zinc source plays a critical role in the preparation of thin ZnO nanorods. At a low molar ratio of ZnO seed and zinc source, javelin-like ZnO nanorods consisting of thin ZnO nanorods with a diameter of 100 nm and thick ZnO nanorods with a diameter of 200 nm have been obtained. In contrast, straight ZnO nanorods with a diameter of about 20 nm have been prepared. Dispersants such as poly(vinyl alcohol) act spatial obstructors to control the length of ZnO nanorods. The morphology, structure, and optical property of the ZnO nanostructures prepared under different conditions have been characterized by transmission electron microscopy, field emission scanning electron microscopy, X-ray powder diffraction, high-resolution transmission electron microscopy, and cathodoluminescence. The formation mechanisms for the synthesized nanostructures with different morphologies have been phenomenologically presented.

As an important II−VI semiconductor, ZnO possesses unique optical, acoustic, and electronic properties, thus being of immense research interest.[1] In recent years, ZnO nanostructures have become one family of the most extensively studied nanomaterials due to their potential applications in field emission, nanolasers, waveguides, nanosensors, ultraviolet detectors, optical switches, and so on.[2] Quite a few interesting nanostructures of ZnO including nanowires, nanorods, nanobelts, nanobridges, nanonails, and nanoribbons have been fabricated by thermal evaporation, chemical vapor deposition (CVD), chemical reaction, the hydrothermal/solvothermal process, and the template-assisted method, which can be generally classified into vapor-phase processes and solution routes.[3] Recently, several reports have focused on the topic of controllable growth of large-scale straight ZnO nanorods with a small diameter by the template- or catalyst-free approach.[4] However, most of the studies focused on the synthesis of ZnO nanostructures on the substrate via inhomogeneous nucleation; unfortunately, the yield of nanostructures is limited. Therefore, a big problem for a large-scale process such as hectogram-scale controllable growth of straight ZnO nanorods with a small diameter by the template-, catalyst-, or substrate-free approach is still not substantially solved. It seems that solution routes such as hydrothermal and solvothermal processes can overcome the issue of low yield by homogeneous nucleation.[5] However, dendrite-like growth is always inevitable in the solution routes. Furthermore, the simple, large-scale, cost-effective synthesis of straight ZnO nanorods can exploit novel industrial applications such as organic sewage purification and sun block and promote practical applications in the optical, acoustic, and electronic fields. Very recently, Hyeon et al. synthesized straight ZnO nanorods without dendrite-like growth free from substrate in the solvent.[6] Overall, obtaining straight ZnO nanorods with a very small diameter on a hectogram scale and at low temperature still remains a tremendous challenge.

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Recently, two reports appeared to give inspiration to solve the above-mentioned challenge. First, Weller and co-workers reported a very effective route to synthesize small-sized ZnO nanorods by self-assembly of ZnO nanoparticles via the oriented attachment mechanism, which provides the possibility of formation of ZnO nanorods by chemical reaction at a temperature lower than 100 °C without the assistance of a template or catalyst.[7] However, it is difficult for this route to obtain uniform ZnO nanorods on a hectogram scale in a relatively short period of time. Second, Yang and co-workers reported a simple solution approach to synthesize wafer-scale ZnO nanorod arrays on a silicon substrate, which indicates that the ZnO particles on the substrate can control the one-dimensional growth of ZnO nanostructures.[8] Enlightened by these two reports, we believe that, with the addition of a large amount of ZnO seeds to the precursor solution, hectogram-scale growth of straight, thin ZnO nanorods can be realized at low temperature under the appropriate conditions. Although Zhou and co-workers have reported the synthesis of ZnO nanostructures by a similar approach, the problem of yield, diameter, and straightness has not been solved.[9]

Herein, we report a simple approach to hectogram-scale growth of straight and thin ZnO nanorods at low temperature by a seed-assisted chemical reaction. Our route features the following three key points: (a) the molar ratio of ZnO seed and zinc source controls the growth of ZnO nanorods; (2) nearly neutral reactants including zinc nitrate hydrate and diethylenetriamine do not dissolve the ZnO seeds before the chemical reaction; (3) a dispersant such as poly(vinyl alcohol) (PVA) acts as a spatial obstructor to control the length of ZnO nanorods.

ZnO seeds were prepared according to the method described in ref 7. Briefly, 270 mg of zinc acetate dihydrate was dissolved in 60 mL of methanol at 60 °C under stirring. Then, a solution of 210 mg of potassium hydroxide in 65 mL of methanol was slowly added for 3 h.

The experimental procedures for preparing ZnO nanorods are simply described as follows: 2.67 g of zinc nitrate hydrate and

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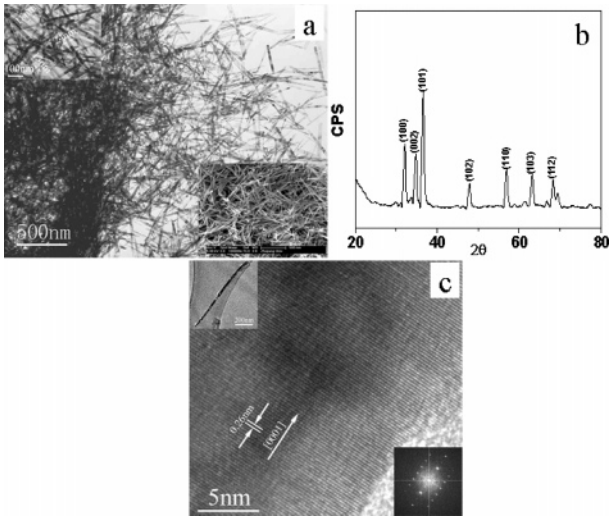

Figure 1. Morphological and structural characterizations of thin ZnO nanorods prepared by seed-assisted chemical reaction at 95 °C with a molar ratio of 0.03 of ZnO seed and zinc source using PVA as a dispersant: TEM image (a); XRD pattern (b); HRTEM image (c). The upper left and lower right inset images of (a) are the magnified TEM and FESEM images, respectively. The upper left and lower right inset images of (c) are the TEM image of an individual nanorod and the corresponding Fourier transform power spectrum, respectively.

2.67 g of PVA were dissolved in 200 mL of deionized water. Meanwhile, 1.26 g of diethylenetriamine was dissolved in 200 mL of deionized water. After 10 min of stirring, these solutions were mixed. Subsequently, the mixed solution was heated and kept at 95 °C in a 500 mL beaker. A 30 mL sample of ZnO seed was then added to the mixed solution, and the resulting solution was kept at 95 °C for 3 h. Finally, the product was cooled, rinsed with deionized water, and dried.

To obtain hectogram-scale ZnO nanorods, the concentrations of the reactants were multiplied 25 times and the reaction was repeated 10 times in a 20 L vessel while the other conditions were kept unchanged.

Figure 1 shows the morphological and structural characterizations of the ZnO nanorods prepared by seed-assisted chemical reaction at 95 °C at a molar ratio of 0.03 of ZnO seed and zinc source. From Figure 1a, a large quantity of uniform thin rodlike nanostructures can be observed. Moreover, straight ZnO nanorods about 20 nm in width and 800 nm in length are clearly shown in the upper left inset of Figure 1a. Large-scale thin ZnO nanorods are confirmed by the field emission scanning electron microscopy (FESEM) image, as shown in the lower right inset of Figure 1a. The X-ray powder diffraction (XRD) pattern of the ZnO nanorods is shown in Figure 1b. All the diffraction peaks can be indexed as hexagonal ZnO with lattice constants $a = 3.249$ and $c = 5.206$ Å, which are consistent with the values in the standard card (JCPDS 36-1451). Figure 1c displays the typical high-resolution transmission electron microscopy (HRTEM) image of the straight ZnO nanorod shown in the upper left inset of Figure 1c. The HRTEM image clearly reveals only the fringes of (002) planes with a lattice spacing of about 0.259 nm, indicating that the ZnO nanorod is single crystalline in nature, which is in accord with the Fourier transform power spectrum inset in Figure 1c. Furthermore, it is indicated that [0001] is the growth direction of the ZnO nanorods.

To clarify the role of PVA in the synthesis of ZnO nanorods, ZnO nanostructures prepared by seed-assisted chemical reaction at 95 °C without addition of PVA are shown in Figure 2. From the transmission electron microscopy (TEM) image, it can be seen that the nanorods are just about 200 nm long, much shorter

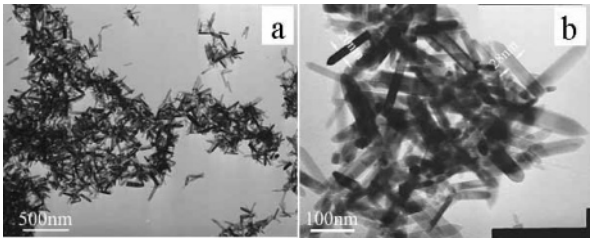

Figure 2. TEM images of ZnO nanorods prepared by seed-assisted chemical reaction at 95 °C without addition of PVA.

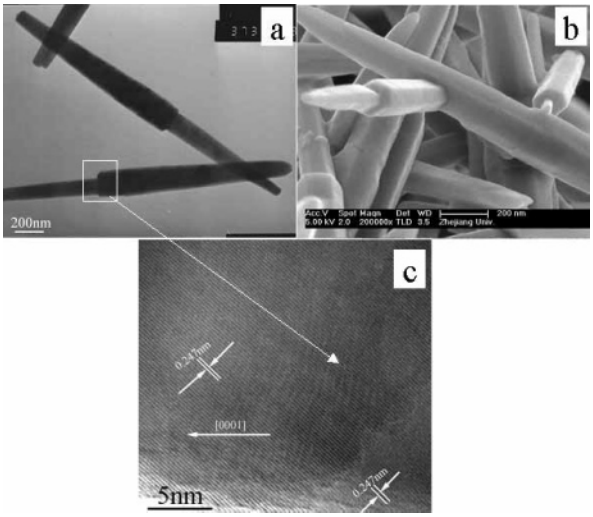

Figure 3. Morphological and structural characterizations of ZnO nanostructures prepared by seed-assisted chemical reaction using PVA as a dispersant at a molar ratio of 0.003 of ZnO seed and zinc source: TEM image (a), FESEM image (b), and HRTEM image (c) of javelin-like ZnO nanorods.

than those obtained by the PVA-assisted reaction, definitely indicating that PVA can enhance the length of ZnO nanorods. Moreover, it was found that the addition of other dispersants such as poly(ethylene glycol-100) (PEG-100), poly(ethylene glycol-2000) (PEG-2000), and poly(vinylpyrrolidone) (PVP) could also promote the length of ZnO nanorods. However, when using PVA as a dispersant, the length of ZnO nanorods is the longest, the aspect ratio of about 40 is the largest, and the diameter is the most uniform, around 20 nm. Therefore, the dispersant not only enhanced the length of ZnO nanorods but also improved the lateral size uniformity of ZnO nanorods. It is believed that the dispersant acted as a spatial obstructor, thus suppressing interdiffusion of reactants, which enabled enough reactants to grow along the *c*-axis direction.

In addition, we found that the molar ratio of ZnO seed and zinc source is the critical parameter to affect the growth of ZnO nanorods. Figure 3 shows the TEM and FESEM images of the ZnO nanostructures prepared at a molar ratio of 0.003 of ZnO seed and zinc source. Javelin-like ZnO nanorods consisting of thin ZnO nanorods with a diameter of 100 nm and thick ZnO nanorods with a diameter of 200 nm were obtained, as shown in Figure 3a. The above-mentioned ZnO nanostructures are more clearly revealed by the FESEM image shown in Figure 3b. From the FESEM image, it is found that two pieces of the ZnO nanorods are discontinuously connected at a flat plane to form a javelin-like ZnO nanorod. The HRTEM image as shown in Figure 3c taken on the regions near the joint of two parts in the javelin-like ZnO nanorod indicates that the lattice fringes of the thin and thick ZnO nanorods are completely identical. However, when the molar ratio was 0.03, uniform straight ZnO nanorods with a diameter of about 20 nm and a length of 800

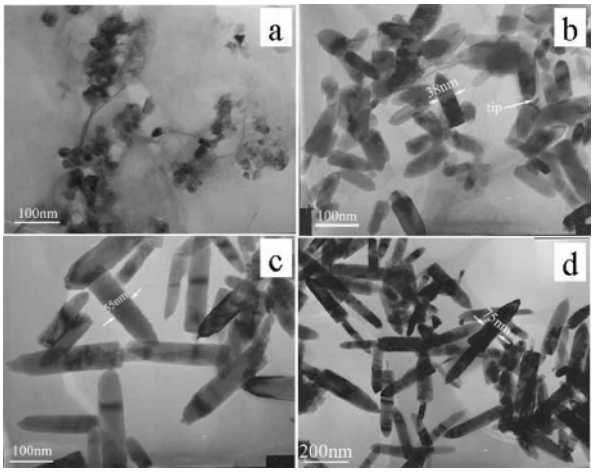

Figure 4. TEM images of ZnO nanostructures prepared by seed-assisted chemical reaction at 95 °C using PVA as the dispersant at a molar ratio of 0.003 of ZnO seed and zinc source for different times: (a) 10 min; (b) 30 min; (c) 1 h; (d) 2 h.

nm were obtained as shown in Figure 1. Therefore, it is very easy to control the growth of ZnO nanostructures by adjusting the molar ratio of ZnO seed and zinc source.

In the synthesis of ZnO nanostructures, the preferential growth of ZnO along the *c*-axis is almost inevitable. For example, in the hydrothermal process, flower-like ZnO nanostructures consisting of ZnO nanorods were obtained due to polar growth as mentioned above.[3e] To avoid dendrite-like growth, herein, the ZnO seeds are employed to direct the growth of ZnO nanorods. When the molar ratio of ZnO seed and zinc source is high, there are enough ZnO seeds acting as nucleating centers. Therefore, the reactants will be quickly depleted to a considerably low level, and the diameter and morphology of ZnO nanorods are nearly determined by the amount of ZnO seeds. This case is very similar to the synthesis of arrayed ZnO nanorods on the substrate covered by a ZnO film.[10] However, when the molar ratio of ZnO seed and zinc source is low, there are not enough ZnO seeds acting as nucleating centers. Therefore, although the ZnO seeds can control the growth of ZnO nanorods along the [0001] direction during the initial stage of ZnO growth, relatively more reactants can promote the secondary growth of ZnO in the following stage, similar to the case we have reported in ref 10. Due to the polar growth of ZnO, the growth direction of ZnO nanorods is from the $(000\bar{1})$ plane with the slowest growth rate to the (0001) plane with the fastest growth rate. It is believed that the ZnO seeds exist on the $(000\bar{1})$ plane, the flat plane of ZnO nanorods. As a result, in the secondary growth process, thin ZnO nanorods also nucleate at the ZnO seeds on the $(000\bar{1})$ plane, and then grow along the (0001) direction, ultimately leading to the formation of javelin-like ZnO nanorods. The morphological evolution of the ZnO nanostructures obtained at a molar ratio of 0.003 of ZnO seed and zinc source and the reaction time are shown in Figure 4, which confirms the above-mentioned analysis. As can be seen, the ZnO nanoparticles were first formed after 10 min (Figure 4a), then thick ZnO nanorods were generated after 30 min (Figure 4b), after 1 h, thin ZnO nanorods were initiated on the flat plane (Figure 4c), and with the extension of the reaction time, javelin-like ZnO nanorods were finally formed (Figure 4d).

On the basis of the above-mentioned results, it is known that, once the molar ratio of ZnO seed and zinc source is controlled, the size and morphology of ZnO nanorods are nearly constant with a fixed reaction time. Therefore, it is very easy to obtain hectogram-scale, uniform, and straight ZnO nanorods by only increasing the numbers of moles of reactants. Figure 5 shows the schematic sketch of the reaction vessel and ZnO nanorods obtained at different numbers of moles of reactants. As shown in the image, 0.89 g of ZnO nanorods 20 nm in width and 800 nm in length have been obtained in a 500 mL beaker using 2.67 g of zinc nitrate hydrate as the zinc source, while 200 g of ZnO nanorods with the same dimensions have been prepared by 10 repetitions of the chemical reaction which was held in a 20 L vessel using 66 g of zinc nitrate hydrate as the zinc source. It is believed that the hectogram-scale growth of ZnO nanorods can be accomplished by one repetition of the chemical reaction in a large vessel.

The room temperature cathodoluminescence (CL) spectra of thin straight ZnO nanorods and javelin-like ZnO nanorods were recorded as curves a and b in Figure 6. The sharp and strong

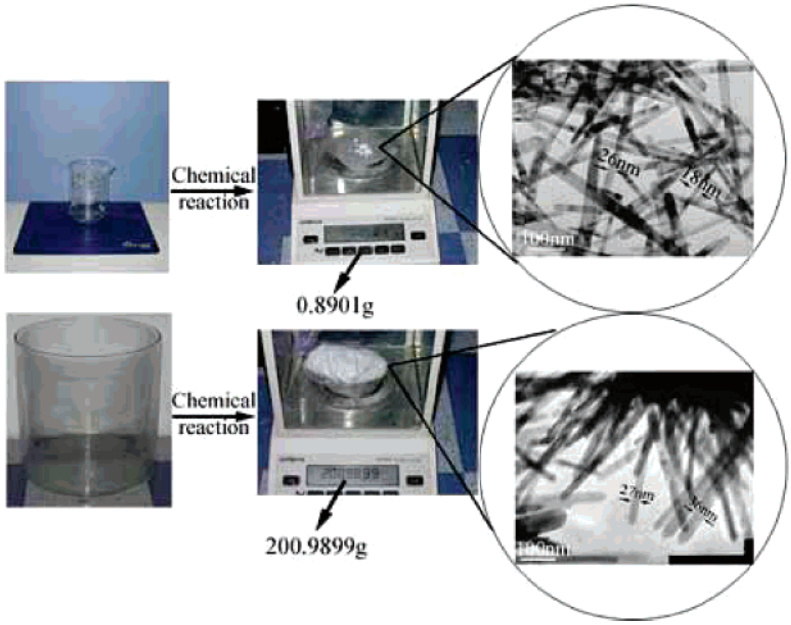

Figure 5. Images of the reaction vessels, readings on the electronic scale, and microscopic morphologies for ZnO nanorods prepared by seed-assisted chemical reaction.

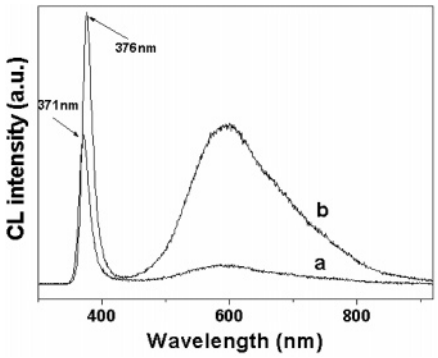

Figure 6. CL spectra of thin straight ZnO nanorods (a) and javelin-like ZnO nanorods (b).

peaks at 376 nm for javelin-like ZnO nanorods and 371 nm for thin straight ZnO nanorods correspond to the near-band-edge emission; they are somewhat blue-shifted as compared to that of the bulk ZnO, likely due to the size effect. Moreover, a broad band peaking at about 600 nm corresponding to defects, e.g., ionized oxygen vacancies in ZnO, is also observed for both samples. The intensity of the broad band for thin straight ZnO nanorods is much lower than that for javelin-like ZnO nanorods, indicating that there are many fewer defects in thin straight ZnO nanorods.

In summary, hectogram-scale growth of uniform, straight, thin, and single-crystalline ZnO nanorods has been achieved by seed-assisted chemical reaction at low temperature (95 °C). The molar ratio of ZnO seed and zinc source plays a critical role in the preparation of thin ZnO nanorods. Dispersants such as PVA act as spatial obstructors to control the length of ZnO nanorods. It is believed that the simple, large-scale, and cost-effective synthesis of straight ZnO nanorods presented herein can find applications in multiple fields such as composite, organic sewage purification and sun block in the future.

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