



High Throughput Growth of Zinc Oxide Nanowires from Zinc Powder with the Assistance of Sodium Chloride

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Sodium chloride (NaCl) was found to be very helpful in producing single crystal zinc oxide (ZnO) nanowires in gram quantities. The growth involves heating the mixture of zinc powder and NaCl to 600–700 °C in flowing gases of oxygen and argon. A conversion efficiency of 70–80% (Zn to ZnO) was achieved when NaCl was used, and 5–10% without NaCl. The NaCl was completely removed by soaking and rinsing the mixture in water a few times. Photoluminescence spectra using excitation of 325 nm showed a very strong emission only in the visible frequency range, indicating that the surface states dominate the emission.

Keywords: ZnO Nanowires, Growth, Photoluminescence.

COMMUNICATION

Ever since the report of the successful synthesis of zinc oxide (ZnO) nanobelts¹ and nanowires,² there have been extensive efforts in the synthesis, characterizations, and applications of ZnO-related nanostructures,^{3–11} and were described in detail in a review.¹² A variety of morphologies of ZnO have been reported including nanobelts,^{1,13} nanowires,^{2,14–16} single-crystal nanorings,¹⁷ nanohelices,¹⁸ hierarchical nanostructures,^{19,20} nanocolumns, and nanoplates,²¹ nanobridges and nanonails,²² nanoneedles,²³ tetrapods, and comb structures.^{24,25} Even though reports on the production of large quantities are also abundant,^{26–28} there has not been a truly simple practical procedure that is capable of producing ZnO nanowires in any morphology, in quantities of many grams. Our previous report²⁶ on large quantity production involves an oxidation process to remove the graphite support that was used to increase the yield, which not only shortens and sharpens the end of the nanowires but also changes the electrical and optical properties due to the extra oxygen incorporated during the oxidation process. In this paper, we report a truly simple procedure capable of producing many grams of ZnO nanowires from Zn powder, which involves the use of sodium chloride (NaCl, 99.0%, Sigma-Aldrich). The NaCl was completely removed by soaking the as-made mixture in water and rinsing a few times. This method did not

change the electrical or optical properties of the nanowires. Even though a few reports were about synthesis of ZnO nanorods or nanoparticles using the assistance of NaCl from other Zn precursors,^{29–34} none of them is about the large quantity growth of ZnO nanowires from Zn powder directly.

The process is based on the thermal evaporation of metallic zinc powder mixed with NaCl powder in a tube furnace at 600–700 °C for 2 hrs with flowing gases of oxygen and argon at 2 Torr. Briefly, 1 g Zn, and 3 g NaCl powders were ground and mixed thoroughly before loading into a quartz boat, then the boat was placed in the temperature region of 600–700 °C inside an alumina tube of a horizontal tube furnace and pumped by a rotary pump. As soon as the pressure is below 0.5 Torr, the power is turned on, the temperature starts to rise, and the flowing gases of argon (25 sccm) and oxygen (20 sccm) are introduced. The vacuum in the alumina tube was kept at 2 Torr during the whole growth period. The center of the furnace was set at 800 °C to establish a temperature gradient at where the mixture of Zn and NaCl was located. The growth normally takes about 2 hrs before it is stopped and cooled down to room temperature. After the samples were taken out, we carried out morphology studies including determining the length and diameter by scanning electron microscope (SEM), crystalline structure studies by transmission electron microscope (TEM) and X-ray diffraction (XRD).

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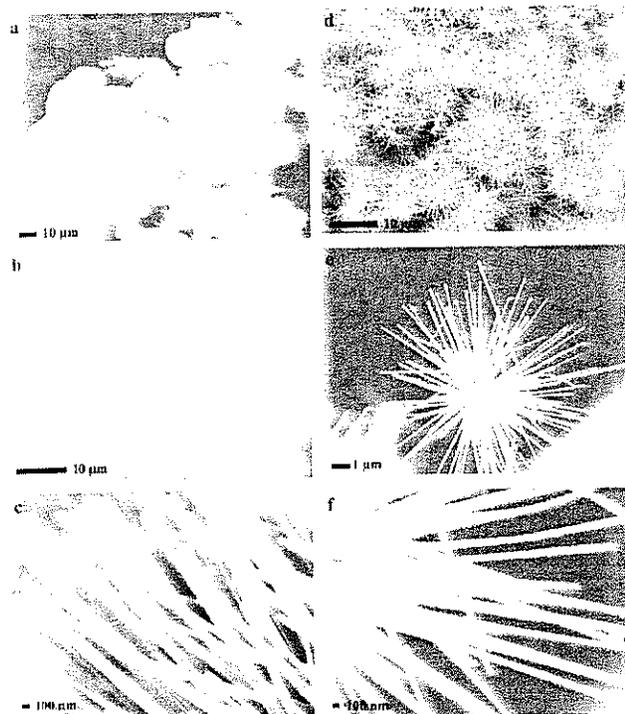


Fig. 1. SEM images of ZnO nanowires at low (a, d), medium (b, e), and high (c, f) magnifications. Images (a)–(c) are for the ball-like nanowires clusters and (d)–(f) flower-like nanowires clusters.

and photoluminescence studies on both the as-grown and NaCl-free ZnO nanowires.

Figure 1 shows the SEM images of the nanowires in low (a, d), medium (b, e), and high (c, f) magnifications. During the SEM examinations, we found there are mainly two kinds of morphologies: (1) ball-like nanowires clusters grown from microparticles shown in Figure 1a and (2) flower-like nanowires clusters grown from a nanoparticle shown in Figure 1d. Figures 1b and 1e show a single ball-like nanowires cluster and flower-like nanowires cluster, respectively. From the low magnification images (a, d), we can clearly see that the ZnO nanowires are about a few μm long. High magnification images in Figures 1c and 1f clearly showed that the diameters of these nanowires are about 100 nm.

Figure 2 shows the TEM images of the as-grown ZnO nanowires. Figure 2a shows a low magnification TEM image of the ZnO nanowires. It indicates that the ZnO nanowires are quite straight and have relatively uniform diameters along their lengths. The diameters are about 100 nm that is consistent with the SEM observations. The energy dispersive X-ray spectrum (not shown here) recorded from a single ZnO nanowire indicates the only presence of Zn and O, which shows that NaCl was not incorporated into the ZnO nanowires, but only acted as the support. Figure 2b shows the typical high resolution TEM image of the ZnO nanowires. The clear fringes indicate that the nanowires are single crystals. The lattice fringe spacing is about 5.12 Å, corresponding to the (0001)

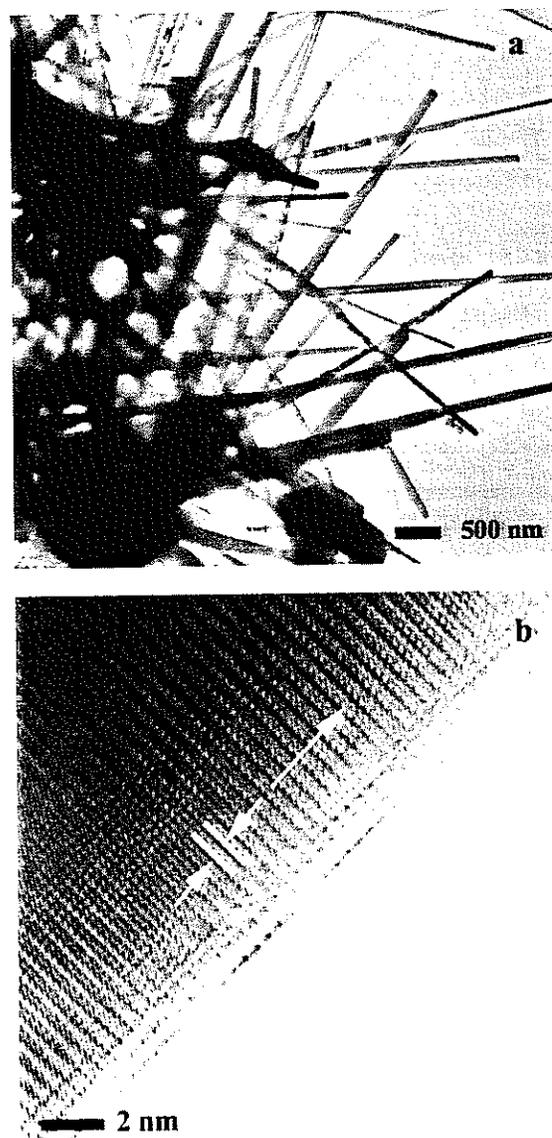


Fig. 2. TEM image at low magnification (a) and crystal lattice image (b) of ZnO nanowires. The growth direction of [0001] and the spacing between (0001) planes are indicated in (b).

plane of the wurtzite structure, and the growth direction is [0001], perpendicular to the (0001) plane.

XRD was used to study the crystalline phases. Figure 3 shows the XRD spectra of the as-grown (bottom) and cleaned samples (top). It is clearly shown that there are two phases in the as-grown sample: ZnO and NaCl, whereas only ZnO exists in the cleaned sample. The spectra matches well with the wurtzite structure of ZnO. The water soak and rinse to completely remove the NaCl is so much simpler than the oxidation procedure in which graphite flakes were used as the support,²⁶ which makes this process very scalable to industrial production of kilograms of ZnO nanowires and applicable to other oxide nanowires.

Photoluminescence spectra were measured and shown in Figure 4 for both the as-grown (filled circles) and cleaned

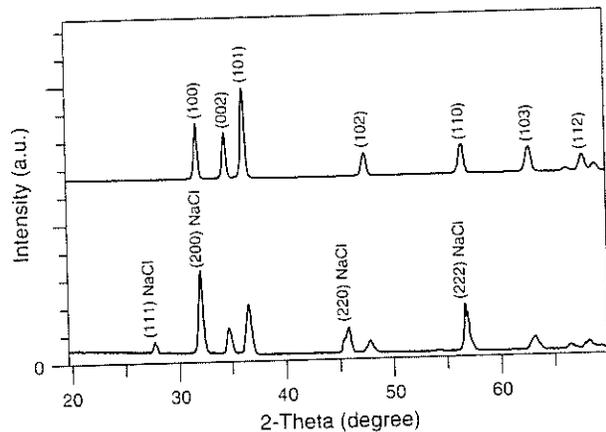


Fig. 3. X-ray diffraction spectra of the as-grown (bottom) and NaCl-free (top) ZnO nanowires. The ZnO nanowires are indexed with the wurtzite structure and the NaCl crystals are also indexed.

samples (open circles). The excitation source was 325 nm. Strong emission was observed in the visible frequency range only, not in the ultraviolet (UV). This indicates that the surface states of the ZnO nanowires dominate the emission when this production technique is used. It is also demonstrated that cleaning the ZnO nanowires with water did not significantly alter the optical properties. However, it is not clear why the growth technique suppresses the UV emission, which is under further study.

We conducted comparative experiments without NaCl and also with other inorganic salts such as sodium carbonate (Na_2CO_3) in order to understand the role of NaCl in the formation of large quantities of ZnO nanowires. Without NaCl, only a small amount of well-aligned ZnO nanorods was produced (about 5–10% conversion of Zn into ZnO, much smaller than the 70–80% when NaCl was used. The conversion percentage was calculated as: Total mass of ZnO nanowires collected after drying divided by that of ZnO corresponding to the Zn powder used). This is shown in Figures 5a and 5b in low and high magnification SEM images, respectively. Neither the ball- nor flower-like

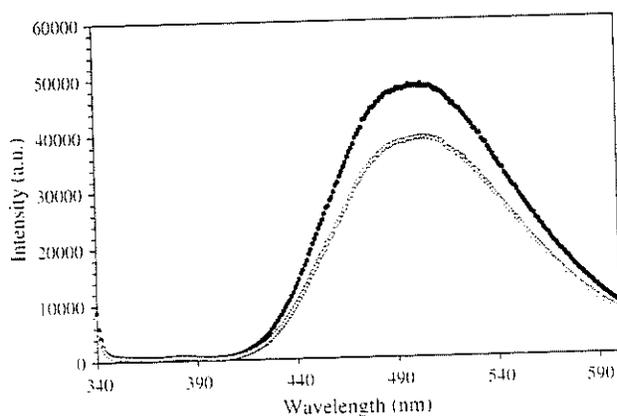


Fig. 4. Photoluminescence spectra of the as-grown (filled circles) and NaCl-free (open circles) ZnO nanowires. The excitation source was 325 nm.

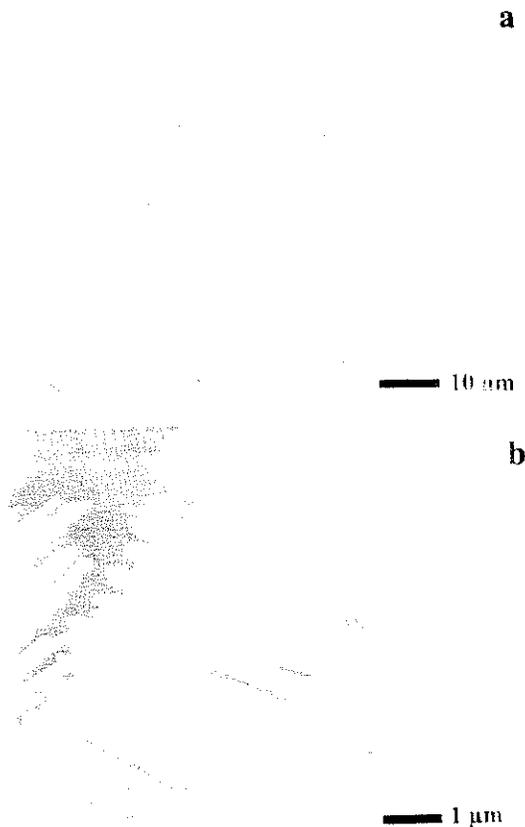


Fig. 5. SEM images at low (a) and high (b) magnifications of ZnO nanowires grown from Zn powder without using NaCl.

clusters were observed. When Na_2CO_3 was used, there was no ZnO nanowire growth at all, indicating the mechanism that the NaCl crystals played in the growth process of ZnO nanowires.

Based on the morphologies of the ball- and flower-like nanowires clusters, we propose the possible growth mechanism when NaCl was used. With temperature increases above the melting point of Zn, Zn starts to evaporate and deposit on the surface of NaCl as ZnO film/islands under the flowing oxygen gas. The ZnO film/islands became the perfect sites for the subsequent growth of ZnO nanowires.³⁵ It is reasonable to assume that the NaCl particles size and shape determines the final ZnO nanowires cluster size and shape. During the grinding of the mixture of Zn and NaCl, some of the NaCl particles were ground into either cubes or rectangular bars or nanometer particles that were the substrates for the subsequent growth of the ball- and flower-like nanowires clusters.

In summary, we have found that NaCl is very useful as the support to promote the conversion of Zn powder into ZnO nanowires in gram quantities with a conversion rate of 70–80%. This should be compared to 5–10% conversion in the case where NaCl is not used, and no growth of ZnO nanowires at all when Na_2CO_3 was used. The NaCl crystals in the product were completely removed by soaking

the mixture in water and rinsing a few times, verified by X-ray diffraction spectra. The ZnO nanowires are highly crystallized single crystals with diameters of 100 nm, and lengths of a few μm . They demonstrate very strong photoluminescence in the visible frequency range.

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