Two-Step Formation of ZnO Nanotubes by Wet Oxidation and Selective Etching

M D L Balela* and M J A Jose

Sustainable Electronic Materials Group, Department of Mining, Metallurgical and Materials Engineering, University of the Philippines, 1101 Diliman, Quezon City

*Email: mlbalelal@up.edu.ph

Abstract. Zinc oxide (ZnO) hierarchical structures composed of nanorods were grown by wet oxidation of etched zinc (Zn) foils in hot water at 90°C for 4 h. The ZnO nanorods having an average topmost diameter of 490 nm were then selectively etched in 0.5–4 M potassium chloride (KCl) solution at 80°C for 1–4 h to facilitate conversion to nanotubes. Well-formed ZnO nanotubes were obtained after immersion in 1 M KCl solution at 80°C for 3 h. However, increasing the etching time to 4 h resulted in the collapse of the structure. XRD analysis showed that the nanorods and nanotubes were highly crystalline with wurtzite structure.

1. Introduction
ZnO is widely used in many industrial products, including paints, cosmetics, and pharmaceuticals [1]. It is also used as a semiconducting and piezoelectric material due to its wide bandgap energy of 3.37 eV [2]. ZnO has been prepared in a variety of nanostructures, including nanowires [3], nanobelts [3], hierarchical structures [4–6], nanorings [7], and nanotubes [8]. There are many common synthesis routes for ZnO nanomaterials including hydrothermal [9], thermal evaporation [10], chemical vapor deposition [11], metal oxide chemical vapor deposition [12], sol-gel [13], and electrochemical methods [14]. These methods, though effective in producing different ZnO nanostructures, often require expensive equipment and harsh conditions.

Researches in the previous years have been focused on the synthesis of one-dimensional (1D) nanoparticles, such as nanorods, nanowires, and nanotubes [15]. These structures display a large surface-to-area ratio, which is useful for sensing applications (Xu and Wang 2011). However, studies on the photodegradation of methyl orange over ZnO crystals have indicated that the non-polar {100} surfaces of wurtzite-structured ZnO have the highest photocatalytic ability compared to the Zn-terminated (001) and O-terminated (00\overline{1}) basal plane [16]. It suggests that by etching out the polar cores of ZnO nanorods or nanowires will increase the amount of non-polar surfaces exposed [16].

Wet oxidation using hot water has been previously used to modify TiO2 nanostructures produced using the sol-gel method [17]. It has also been used to produce ZnO nanostructures such as nanowires and nanorods on etched Zn foils [4–5, 18]. This process does not require harsh conditions, as it uses water as an electrolyte at relatively lower temperatures than other synthesis methods. This process also makes it applicable for use on substrates with low thermal stability [4–6, 18]. However, there has not been any work that has successfully produced pure ZnO nanotubes from this method. On the other hand, selective dissolution has been successfully used to convert electrodeposited ZnO nanorods and nanowires into nanotubes [19, 20]. This method takes advantage of the inherent characteristics of the
ZnO crystal to allow the adsorption of ions that form highly soluble compounds with Zn along the c-axis of the ZnO nanorods and wires. However, it has only been used on well-aligned electrodeposited ZnO nanotubes [19, 20].

This study investigates the selective dissolution of ZnO nanorod cores produced by wet oxidation of etched Zn foil for 4 h at 90°C. The effects of parameters, i.e., etchant concentration and etching time, on the morphology, and structure will be studied. This study will provide a simple, easily-controllable, low-temperature synthesis method for the formation of ZnO nanotubes.

2. Experimental Methods

Zn foils (Zn, Sigma Aldrich, 99.99%) with 0.25 mm thickness were cut into 1.0 × 1.0 cm² samples. The foils were manually polished using silicon carbide (SiC, 3M) papers of increasing grit sizes, followed by alumina until a mirror finish was achieved. The polished samples were washed with de-ionized water before and after degreasing in acetone (C₆H₅O, RCL Labscan) for 10 min in an ultrasonic cleaner. The foils were etched in a 5% hydrochloric acid (HCl, RTC) in ethanol (C₂H₅O, Univar) solution for 3 min, followed by washing with de-ionized water. The samples were immersed in de-ionized water at 90°C for 4 h to produce ZnO nanorods, then washed with de-ionized water and dried to room temperature. Afterward, the as-produced ZnO nanorods were etched in potassium chloride (KCl, Merck, 99.95%) solution at 80°C to facilitate conversion into nanotubes. The effect of time and etchant concentration was studied by etching at 80°C [19–22] for 1–4 h and in 0.5–3 M KCl, respectively.

The morphology of the nanostructures produced was observed using a scanning electron microscope (SEM, Hitachi TM 1000, Jeol JSM-5310). The diameters were measured using Image Analysis and Processing in Java (ImageJ) software. X-ray diffraction (XRD, Shimadzu 7000) was used to analyze the structure using Cu-Kα radiation.

3. Results and Discussion

Figure 1 shows the SEM images of the Zn foil after etching and wet oxidation for 0.5–4 h at 90 °C in hot water. The temperature was chosen based on the result of a previous study [5], wherein it was found that oxidation of Zn foil was enhanced at higher temperature. As presented in figure 1 (a), the grain boundaries of the Zn foil were exposed after etching in HCl. White striations were also visible across the Zn grains. These striations are possibly ZnO, which must have formed due to oxidation of the foil during etching. When the etched Zn foil was oxidized for 0.5 h at 90°C in hot water, short nanorods with hexagonal cross-section started to grow along the white striations (figure 1 (b)). It is also apparent from the SEM image that the nanorods grew in clusters, indicating that they may have formed from the same ZnO seed. The ZnO seed layer possibly formed after etching of the Zn foil in HCl [4–6, 18].

Prolonging the oxidation time to 1 h resulted in denser ZnO hierarchical structures. The hierarchical structures are composed of longer nanorods with lengths of about 1 μm as presented in figure 1c. After 4 h wet oxidation, flower-like structures of ZnO nanorods were produced at the surface of the Zn foil as shown in figure 1 (d). At higher magnification, the ZnO nanorods were observed to have flat tops with some nanorods exhibiting hexagonal cross section. The average topmost diameter of the ZnO nanorods is about 490 nm. The nanorod diameter increases along its length, with the largest diameter at the tip. It can be attributed to the diffusion of Zn²⁺ ions towards the Zn-terminated (001). Consequently, more ZnO is deposited on this surface.

Figure 2 shows the corresponding XRD pattern of the ZnO nanorods formed by the wet oxidation process. XRD analysis shows that the ZnO nanorods are of the wurtzite structure, with peaks at 2θ = 31.73, 34.50, and 36.28°. These peaks correspond to the 100, 002, and 101 peaks of ZnO. Other small peaks of ZnO occur at 2θ = 47.61, 56.58, 62.95 and 67.95°. These are the 102, 110, 103, and 200 peaks, respectively. The 002, 100, 101, and 002 peaks at 36.28, 39.02, 43.26 and 54.35° are attributed to the Zn foil. The 101 ZnO peak and the 002 Zn peak coincide at 2θ = 36.28°. The presence of sharp ZnO peaks suggests good crystallinity of the ZnO nanorods.
Figure 1. SEM images of (a) etched Zn foil and after wet oxidation in hot water at 90 °C for (b) 0.5 h, (c) 1 h, and (d) 4 h. Insets are high magnification images of the samples.

Figure 3 shows the SEM images of ZnO nanorods etched in 1 M KCl solution for 1–4 h. When the nanorods were etched in 1 M KCl for 1 h, only a small portion of the nanorod tips was dissolved. Longer etching time resulted in a more pronounced effect on the ZnO nanorods. When the etching time is increased to 2 h, more ZnO nanorods were etched at the center, producing a few ZnO nanotubes. Full conversion to nanotubes was achieved after etching for 3 h in 1 M KCl. The ZnO nanotubes produced after 3 h etching in 1 M KCl have a mean inner diameter of 320 nm and wall thickness about of 85 nm. No significant change in the outer diameter was observed for this sample, suggesting that dissolution occurred in the core. However, further etching to 4 h led to the dissolution of the outer walls of the nanotubes. It indicates that there is an optimum etching time to convert the ZnO nanorods to nanotubes without collapse of the structure. In addition, there is an increase in the outer diameter of the ZnO to about 555 nm. It is possible that fast dissolution of ZnO leads to its redeposition along the walls of the collapsed nanotubes.

Some studies have suggested that there exists a minimum diameter for ZnO nanorods for etching to occur [21]. Etching occurs initially along the length of the nanorod and dissolution of the ZnO walls occurs only when the reaction has progressed through the nanorod length. Etching essentially occurs due to the preferential adsorption of Cl⁻ ions on the Zn²⁺-terminated (001) tip of the rod [22]. It forms the highly-water soluble ZnCl₂ compound, resulting in the etching of the cores. The (001) surface is polar, in contrast to the {1̅00} surfaces parallel to the c-axis, which renders the (001) surface more reactive [21]. It promotes the preferential dissolution of the center of the ZnO nanorod. Consequently, the tubular structure can be formed. However, prolonged exposure to KCl leads to the dissolution of the ZnO walls as well. The Cl⁻ ions may still be preferentially adsorbed onto the inner walls of the nanotube, resulting in the dissolution of the walls until the structure collapses. The schematic is shown in figure 4.
Figure 2. XRD pattern of (a) ZnO nanorods formed after wet oxidation of etched Zn foil in hot water at 90°C for 4 h, (b) ZnO nanotubes after etching in 3 M KCl solution at 80°C for 3 h, and (c) ZnO nanotubes after etching in 1 M KCl solution at 80°C for 4 h.

Figure 3. SEM images of ZnO nanorods etched in 1 M KCl solution at 80°C for (a) 1 h, (b) 2 h, (c) 3 h, and (d) 4 h.

Figure 5 shows the SEM images of ZnO nanorods after etching in 1–3 M KCl at 80°C for 3 h. Preliminary studies have shown that no etching occurred on the ZnO nanorods even after 3 h when 0.5 M KCl was used. It is consistent with previous studies that suggest that there is a minimum KCl concentration necessary for etching of ZnO [22]. Using 1 M KCl, there is a complete conversion of nanorods to nanotubes, as presented in figure 5 (a). When the KCl concentration was increased to 2–3 M, the ZnO nanotubes appear shorter than unetched samples. It suggests there is a high concentration of Cl⁻ ions leading to fast dissolution of ZnO nanotubes. Additionally, there is also a thin layer of ZnO covering the etched nanorods. It is possible that after etching has progressed up to the ZnO walls, the Cl⁻ ions may have continued to be adsorbed along the Zn²⁺ terminated surface of the rod. The dissolved Zn²⁺ ions from the etching may have deposited along the lateral sides (parallel to the c-axis) of the rod, forming a new ZnO layer.
**Figure 4.** Mechanism of ZnO nanorod to nanotube conversion by selective etching using KCl.

**Figure 5.** SEM images showing the morphology of nanorods etched for 3 hrs at 80°C in 1 M (a), 2 M (b), and 3 M KCl (c).

Figures 2 (b) and (c) show the XRD patterns of ZnO on Zn foil after etching in 1–3 M KCl solution for 3–4 h. Similar peaks were observed in the etched samples compared to the ZnO nanorods produced by hot-water treatment. There is an increase in the broadening of the peaks after etching. It suggests possible decrease in the crystalline size of ZnO due to dissolution and redeposition of ZnO. Additionally, there is an increase in the intensity of the ZnO peaks after etching in 1 M KCl for 4 h at
80°C. As presented in the SEM image in figure 5d, there could be redeposition of dissolved ZnO along the walls of the collapsed ZnO nanotubes. It could result in the increase in the outer diameter of the ZnO nanotubes, as well as in the intensity of the ZnO XRD peaks in figure 2 (c).

4. Conclusions
ZnO nanorods, produced by wet oxidation of Zn foil in hot water at 90°C for 4 h, were successfully converted into ZnO nanotubes. The conversion was facilitated by selective dissolution along the c-axis of the nanorods by immersion in KCl solution at 80°C. ZnO nanotubes were formed after etching in 1 M KCl solution at 80°C for 3 h. The ZnO nanotubes have a mean inner diameter of 320 nm and average wall thickness of 85 nm. Increasing the etching time to 4 h resulted in the dissolution of the ZnO nanotube walls, causing collapse of the structure. Increasing the KCl concentration to 2–3 M caused the nanotubes to appear shorter, suggesting that the etching has progressed up to the ZnO nanotube walls. At this concentration, there was redeposition of ZnO across the sides of the etched nanotubes. It may be due to the preferential adsorption of excess Cl− ions along the c-axis, preventing the redeposition of ZnO along its length.

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