# Synthesis of ZnO nanowires by solvothermal method and fabrication of ZnO nanowires film via microfiltration method

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In our work, we synthesized zinc oxide (ZnO) nanowires (NWs) by a simple solvothermal method. Zinc acetate and NaOH were used as the precursors and ethanol as the solvent. The synthesis process is one-step and could produce a mass of ZnO NWs with small diameters and high aspect ratios. This solvothermal method is not critically sensitive to the growth temperature from 100 $^{o}$C to 150 $^{o}$C. For the majority of synthesized ZnO NWs, the lengths and dimensions are around 1 um ~ 10 um and 10 nm ~ 40 nm, respectively. We also discussed the effect of solvents on the morphologies of synthesized nanomaterials between solvothermal and hydrothermal methods. Then, we employed a microfiltration method for the fabrication of ZnO nanowires film (NF). Consequently, ZnO NWs were stacked on the microfiltration membrane forming a thin nanoporous film. After dried in room temperature, the thin ZnO NF could be wholly stripped off from the membrane. The ZnO NWs and NF were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM). The XRD and SEM figures show that the ZnO NWs are single crystals with wurtzite crystal structure.

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*Keywords:* ZnO, Nanowire, Solvothermal, Filtration, Film

## 1. Introduction

One-dimensional (1-D) ZnO nanostructures have attracted vast and persistent interest, owing to their great potential applications in many fields, such as UV photo detectors [1], field-effect transistors (FETs) [2] and nanogenerators (NGs) [3]. A variety of methods [4] have been introduced to synthesize 1-D nanostructures, including chemical or physical vapor deposition (e.g., vapor-solid, vapor-liquid-solid, solution-solid method), wet chemical methods (e.g., hydrothermal methods, solvothermal methods), RF magnetron sputtering, template-assisted methods, etc.

Wet chemical methods which can be used for synthesizing ZnO NWs include hydrothermal methods [5], solvothermal methods [6], deposition method [7], and Sol-gel method [8]. We favor hydrothermal/solvothermal methods because they are relatively low coat, less hazardous, and easy for scale up. However, most hydrothermal methods failed to synthesize NWs with small diameters (< 50 nm) and high aspect ratios (> 20). And hydrothermal orientation growth methods always need two-step processes, in which a seed layer must first be synthesized on a substrate for oriented growth [9].

In this paper, we report a simple one-step solvothermal method for the synthesis of ZnO NWs. Zinc acetate and ethanol were used as the Zinc source and the solvent, respectively. NWs with small diameters (< 50 nm) and high aspect ratios (> 20) were synthesized successfully. Based on ZnO NWs, we employed a simple microfiltration method for the fabrication of ZnO NF.

## 2. Experimental

### 2.1 Synthesis of ZnO NWs

We synthesized ZnO NWs by a simple one-step solvothermal method [10]. Zinc acetate dehydrate ($Zn(Ac)_2 \cdot 2H_2O$) and sodium hydroxide (NaOH) were used as the precursors and ethanol as the solvent. All reagents (From Tianjin Fengchuan Chemical Reagent) in the experiments were analytical grade and without further purification.

The typical procedures were as follow. First, 0.6585 g (0.02 M) Zinc acetate dihydrate was first dissolved into 150 ml ethanol. Ultrasonic wave stir was used to dissolve the reagent. Then, 2.4 g NaOH (0.4 M) was added into the solution, followed by ultrasonic wave stir for 1 h. Consequently, we got a white homogeneous suspension liquid which was transferred into a Teflon lined vessel. The vessel was then sealed into a stainless steel autoclave. Finally, the autoclave was placed into an oven and heated at 100 $^{o}$C for 24 h. After the reaction, the autoclave was cooled at room temperature for 1 h ~ 2 h. As a result, the ZnO NWs were precipitated at the bottom of the vessel.

The supernatant was carefully taken out of the vessel, leaving the precipitate at the bottom.

### 2.2 Fabrication of ZnO NF

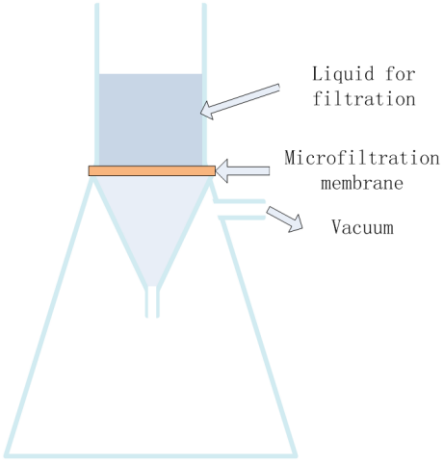


*Fig. 1. A device of vacuum filter used for fabrication of ZnO NFs. The microfiltration membrane is fixed between the top vessel and the bottom vessel. The top vessel contains the liquid for filtering. The bottom vessel is connected to a vacuum pump.*

We employed a microfiltration method for the fabrication of ZnO NF. A device of vacuum filter (Fig. 1) was used to extract the ZnO NWs as well as washing away impurities (e.g., organics and metal ions). Considering the nanoscale NWs, we chose a kind of nylon microfiltration membrane, whose micropores have diameters of about 100 nm. Because the diameter of micropore is so small, liquid will penetrate through the membrane extreme slowly. So vacuum is applied to create a sufficient large pressure between the top and bottom surface of the membrane.

The procedures for fabrication of ZnO NFs were as follows. First, the ZnO NWs precipitate at the bottom of vessel was dispersed uniformly in ethanol (about 200 ml) to form a suspension liquid. Then, the suspension liquid was transferred to the vacuum filter. The liquid was filtered out in about 30 min. Consequently, ZnO NWs were stacked uniformly on the microfiltration membrane. Subsequently, in order to washing away impurities, acetone, ethanol and distilled water was added into the vacuum filer and then filtered out, successively. After dried in room temperature, the ZnO NF was formed on the membrane.

The crystalline characteristics of ZnO NWs and NF were studied by XRD using X-Pert Pro. The crystal morphologies of the samples were investigated by SEM using Hitachi S-4800.

## 3. Results and discussion

XRD was used to investigate the crystalline quality of the synthesized ZnO, as shown in Fig. 2. The positions and intensity of XRD peaks agree well with the standard XRD pattern of ZnO with wurtzite crystal structure (red line, JCPDS: 36-1451) which demonstrates that we have successfully synthesized ZnO crystals with wurtzite structure.

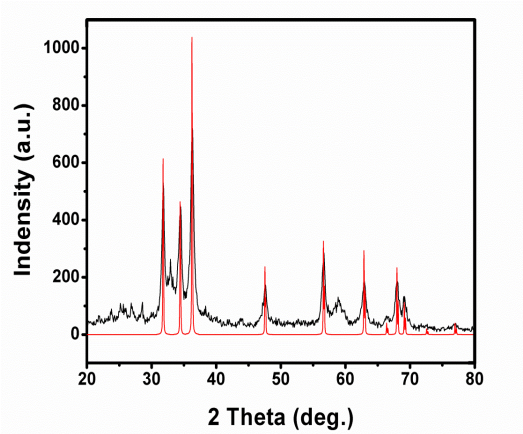


*Fig. 2. XRD pattern of the synthesized sample (black line) compared with the standard XRD pattern of wurtzite structure ZnO (red line).*

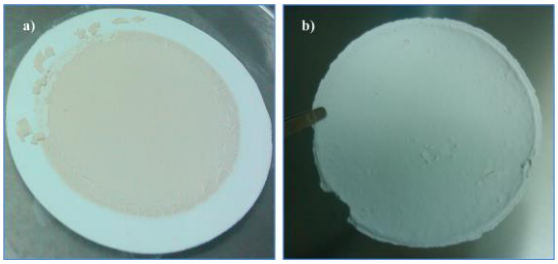


*Fig. 3. Photograph of fabricated ZnO NF. (a) ZnO NF on a microfiltration membrane. Some fragments were cut off from the NF. (b) ZnO NF stripped off from the membrane.*

The picture of fabricated ZnO NF is showed in Fig. 3. The diameters of microfiltration membrane and ZnO NF are 50 mm and 43 mm, respectively. Though the edge of ZnO NF has cracks, most area of the NF is an integrated film and can be wholly stripped off from the membrane. Fig. 3a is ZnO NF on a microfiltration membrane, and Fig. 3b is ZnO NF stripped off from the membrane.

The SEM images of the fabricated ZnO NF in fig. 4 showed that the synthesized ZnO NWs have small diameters (10 nm ~ 40 nm) and high aspect ratios (> 20) and the NF is a nanoporous film. The diameters distribution of ZnO NWs is shown in Fig. 5. The diameters of most nanowires were around 20 nm to 30 nm, which shows that the synthesized nanowires have a uniform morphology.

Fig. 4a, 4c, 4e are SEM images of top view of ZnO NF which shows that the NWs are stacked together uniformly and form a flat surface. Fig. 4b, 4d, 4f are SEM images of cross-sectional view of ZnO NF. The high magnification images of the NF (Fig. 4c-4f) show that the ZnO NWs are densely stacked forming a nanoporous film without big cavities.

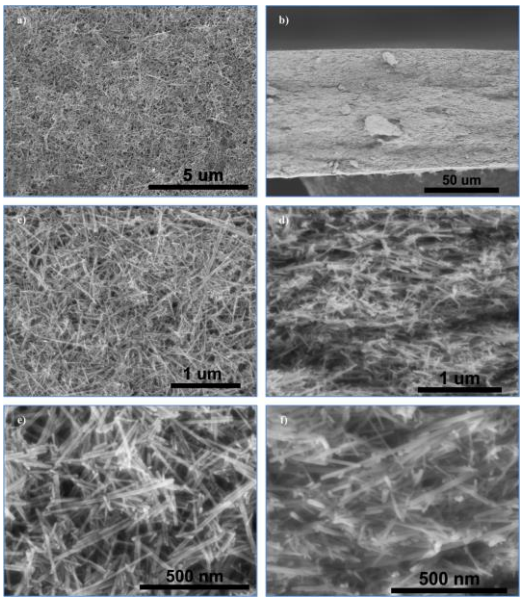


*Fig. 4. SEM images of the top view (a, c, e) and cross-sectional views (b, d, f) of synthesized ZnO NF.*

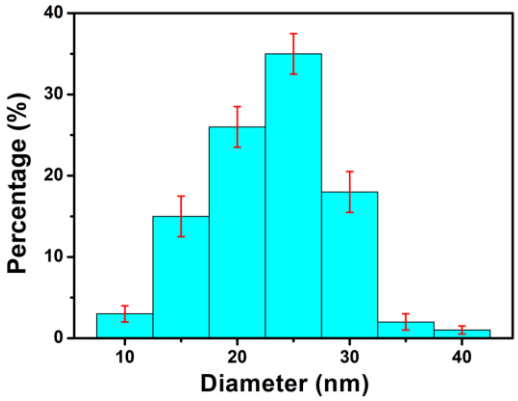


*Fig. 5. The diameters distribution of the synthesized ZnO NWs. The diameters of most nanowires were around 20 nm to 30 nm. (The growth temperature is 100 °C).*

In our experiments, we found that this solvothermal method is not critically sensitive to the growth temperature. As we changed the growth temperature from 100 °C to 150 °C, ZnO NWs could always be synthesized without big morphology differences. Fig. 6 shows that the diameter ranges of the synthesized ZnO NWs with different growth temperature from 100 °C to 150 °C. In fig. 6, we can see that the average diameters and the diameter ranges of ZnO NWs are almost the same, only the diameter ranges were slightly narrowed as the temperature increased. And we seldom found other kinds of nanostructures except NWs in the synthesized samples. So we believe that this solvothermal method is a reliable method for mass production of ZnO NWs with small diameters and high aspect ratios.

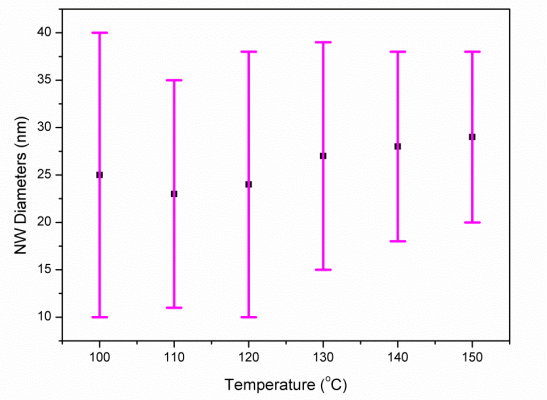


*Fig. 6. The diameter ranges of the synthesized ZnO NWs with different growth temperature from 100 °C to 150 °C.*

Compared with solvothermal method, we also carried out hydrothermal experiments for the synthesis of ZnO NWs at the same process flow and growth condition. The only difference between the solvothermal and hydrothermal method is the solvent. We changed the solvent from ethanol to distilled water. Consequently, we did not find any NWs with small diameters and high aspect ratios in the synthesized samples. Fig. 7 shows the synthesized ZnO nanomaterials by hydrothermal method. In Fig. 7a and 7b, nanoshuttles were synthesized with diameters larger than 500 nm. In Fig. 7c and 7d, the synthesized ZnO NWs have large diameters (>1 um) and merged together to form nanoclusters.

The effects of solvents on the morphologies of synthesized nanomaterials can explain the different results between solvothermal and hydrothermal methods [6].There are four different effects of the solvents: solubility of the precursors in the solvents; polarity of the solvents; saturated vapor pressure of the solvents; possible growth mechanism in different solvents.

The physical and chemical properties of ethanol and water are very similar. Both of which are polar solvents and can dissolve many kinds of inorganic salts. However, there are certain differences in polarity, boiling point, viscosity, vapor pressure, and chemical activities [10]. Compared to ethanol, water has relatively stronger polarity, higher viscosity, higher boiling point and smaller vapor pressure (for closed system) in the reaction temperature (100 °C). The differences of these properties result in the differences during nucleation, growth and ripening of ZnO nanoparticles. In ethanol solvent, lower polarity of ethanol, lower dissolution and higher degree of saturation of the precursor result in faster nucleation and more nuclei generated during the nucleation stage which constrains the crystal growth during the growth and

ripening process. Consequently, particles with smaller diameters are synthesized. In addition, the relative lower polarity of ethanol facilitates the polar facets growth which results in ZnO nanoparticles with high aspect ratios.

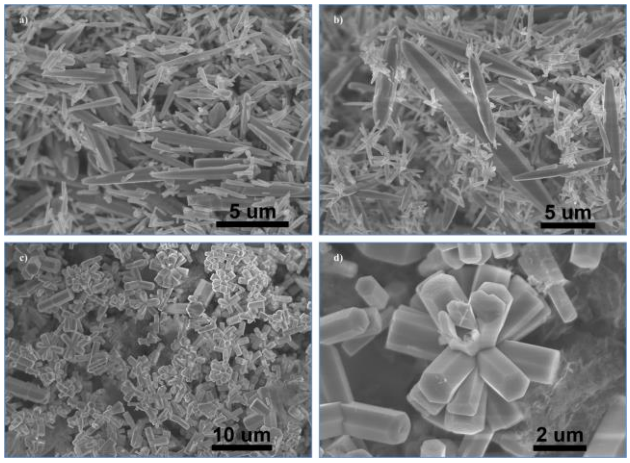


*Fig. 7. SEM images of ZnO nanostructures synthesized by hydrothermal methods. Nanoshuttles (a, b) and nanoclusters (c, d) were synthesized.*

## 4. Conclusion

In our work, we demonstrated a simple one-step solvothermal method for the synthesis of ZnO NWs with small diameters (< 50 nm) and high aspect ratios (> 20). This solvothermal method is not critically sensitive to the growth temperature. This solvothermal method is low coat, less hazardous, an efficient and reliable method for mass production of ZnO NWs. We discussed the effect of solvents on the morphologies of synthesized nanomaterials between solvothermal and hydrothermal methods. We also employed a microfiltration method for the fabrication of ZnO NF, based on the synthesized ZnO NWs. The ZnO NWs are densely stacked together forming a nanoporous film.

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