

Supporting information

In Situ XANES Spectroscopy of ZnO Nanowire Growth During Chemical Bath Deposition

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1. Synthesis of Zinc Hydroxide Phases

δ -Zn(OH)₂ (PDF#00-020-1436)

A 500 mL aqueous solution of 0.015 M Zn(NO₃)₂ and 0.15 M NH₄OH was prepared.¹ (NOTE: The Zn(NO₃)₂ stock solution was added to the NH₄OH solution, not vice versa). The solution was stirred at 450 rpm at room temperature for 30 minutes. At the end of 30 minutes, the solution sat unstirred for ~10 minutes to allow the setting of precipitates. The solution was decanted by removing ~300 mL of the supernate with a syringe. The remaining suspension was vacuum filtered and rinsed with DI water multiple times. A suspension of 4.5 g of precipitates per 100 mL DI water was prepared and sealed in a borosilicate jar. The suspension was shaken vigorously and placed in a preheated oven at 60 °C for 1 h (unstirred). At the end of 1 h, the heated suspension was vacuum filtered and rinsed multiple times and dried at 30 °C overnight. This preparation makes ~350 mg of δ -Zn(OH)₂ powder.

γ -Zn(OH)₂ (PDF#00-020-1437)

A 500 mL aqueous solution of 0.043 M Zn(NO₃)₂ and 0.43 M NaOH was prepared (NOTE: The Zn(NO₃)₂ stock solution was added to the NaOH solution, not vice versa). The solution was stirred at 450 rpm at room temperature for 30 minutes. At the end of 30 minutes, the solution sat unstirred for ~10 minutes to allow the setting of precipitates. The solution was decanted by removing ~300 mL of the supernate with a syringe. The remaining suspension was vacuum filtered and rinsed with DI water multiple times. A suspension of 4.5 g of precipitates per 100 mL DI water was prepared and sealed in a borosilicate jar. The suspension was shaken vigorously and placed in a preheated oven at 60 °C for 1 h (unstirred). At the end of 1 h, the

heated suspension was vacuum filtered and rinsed multiple times and dried at 30 °C overnight. This preparation makes ~700 mg of γ -Zn(OH)₂ powder.

ϵ -Zn(OH)₂ (PDF#00-038-0385)

Stock aqueous solutions of 1 M Zn(NO₃)₂ and 4 M NaOH were prepared.² 20 mL of the 1 M Zn(NO₃)₂ stock solution was transferred to a 100 mL beaker in an ice bath. 30 mL of the 4 M NaOH stock solution was gradually added to the beaker. 50 mL of DI water was added to the beaker to bring the total volume to 100 mL. The solution was transferred to a 250 mL borosilicate jar beaker and magnetically stirred at 450 rpm for 2 h at 25 °C. At the end of 2 h, the jar was placed in a 65 °C water bath for 5 h (unstirred). The resulting suspension was vacuum filtered and rinsed with DI water multiple times and dried at 50 °C for 1 hr. This preparation makes ~2 g of ϵ -Zn(OH)₂ powder.

2. X-ray diffraction of Zinc Hydroxide Phases

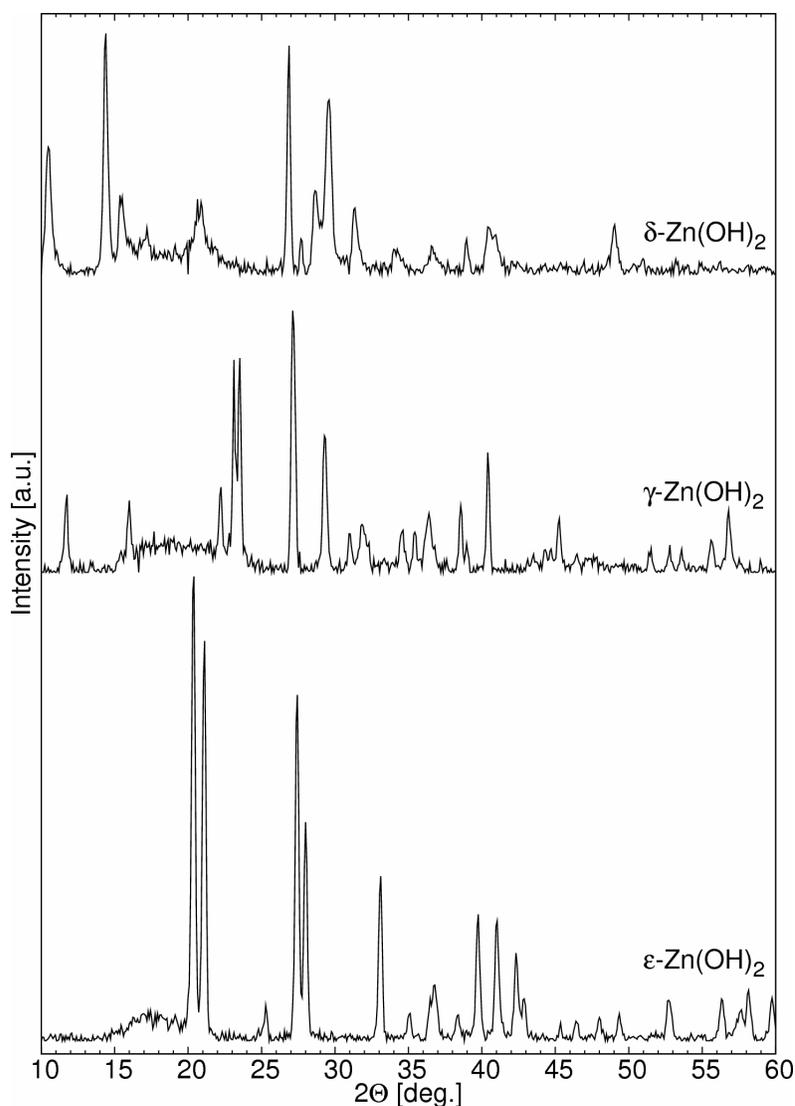


Figure S1. X-ray diffraction 2 θ scans of δ , γ and ϵ zinc hydroxide powders

3. TEM of deposition at 60 °C

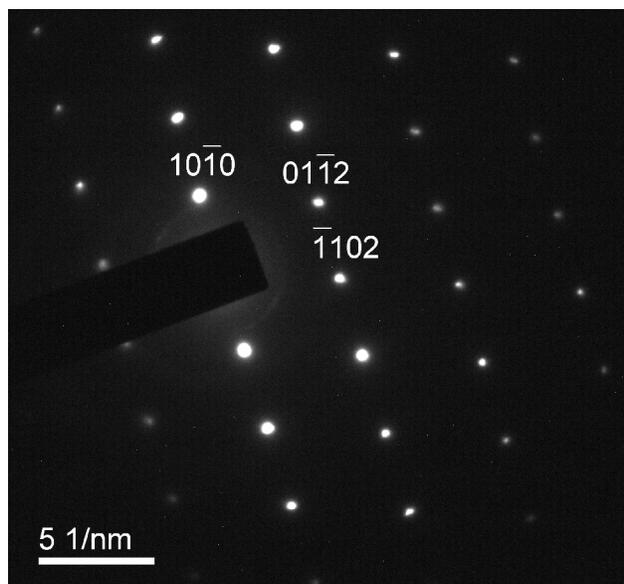


Figure S2. Electron diffraction pattern of hemispherical honeycomb-like structure grown at 60 °C on the CdO seeded polyimide tube. Diffraction pattern shows the deposited material to be crystalline wurtzite ZnO.

4. ZnO Radiation Damage Tests

Consecutive spectra were taken of ZnO nanowires grown in the microreactor at both 60 °C and 90 °C to test for radiation-induced changes. Figure S2 shows the whiteline peaks for XANES spectra of the ZnO nanowires taken while the wires were in air. Each point is a sum of ten consecutive scans, and the error bars represent the standard deviation of that sum. For nanowires grown at both 60 °C and 90 °C, there was no trend in the change in the whiteline, indicating no detectable radiation damage over the 2 h scan period. Figure S3 shows similar scans taken of ZnO nanowires immersed in DI water at room temperature. The wires grown at 90 °C (Figure S3a) show a slight increase in the whiteline over the 1 hour exposure to x-rays, but the increase is within the uncertainty of a single scan (~0.2%). The wires grown at 60 °C (Figure S3b) show a significant increase in the whiteline (about 4% over an hour of scanning). This increase is attributed to the dissolution of ZnO in water and not to x-ray-induced damage. The dissolution rate of ZnO grown at 60 °C is faster than ZnO grown at 90 °C due to the increased number surface defects in the ZnO grown at a lower temperature.

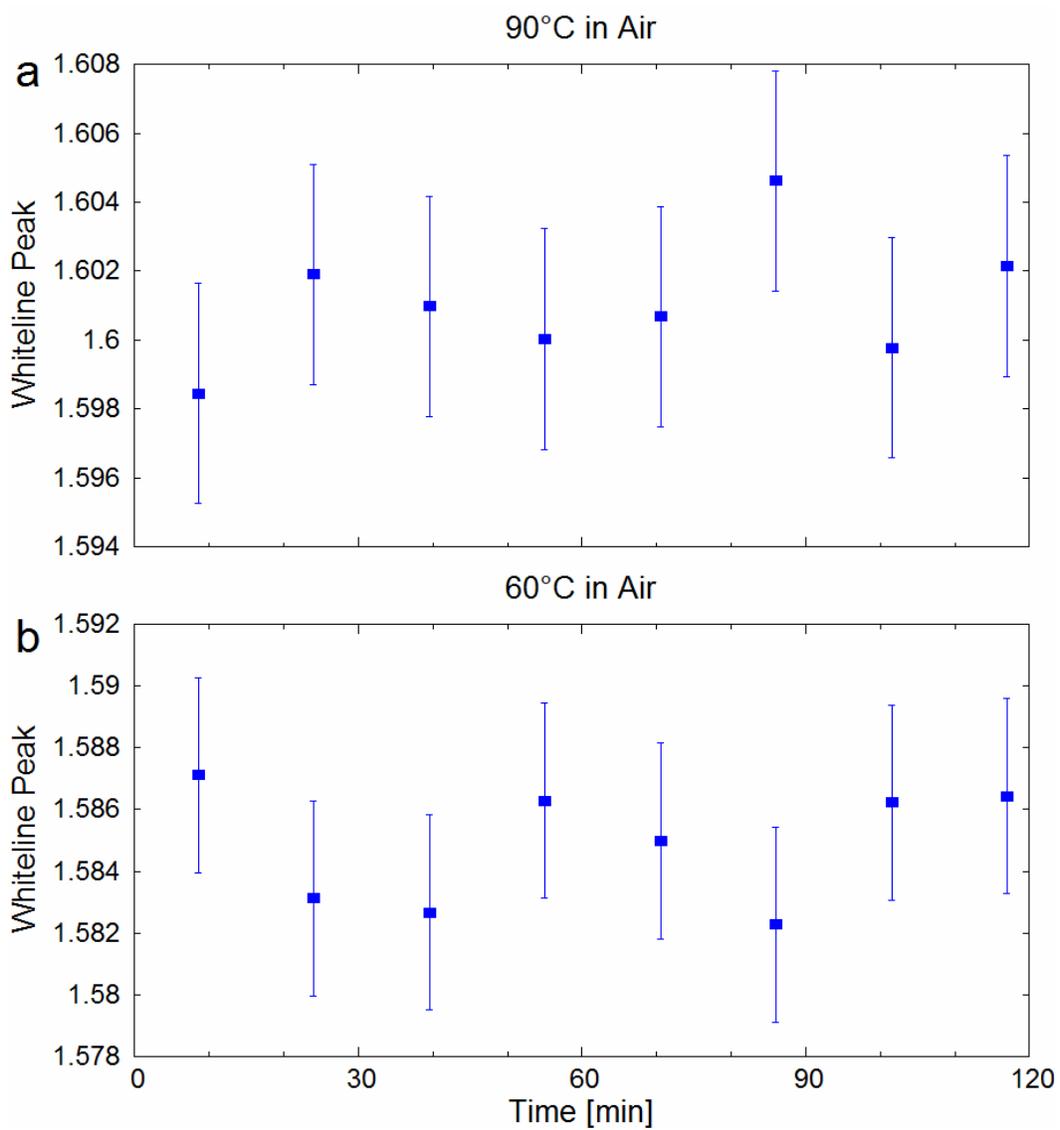


Figure S3. Whiteline peaks for XANES spectra of ZnO nanowires grown at (a) 90 °C and (b) 60 °C. Scans were taken while the wires were dry (blown dry with N₂ and scanned while left open to air) and at room temperature. No radiation damage is observed.

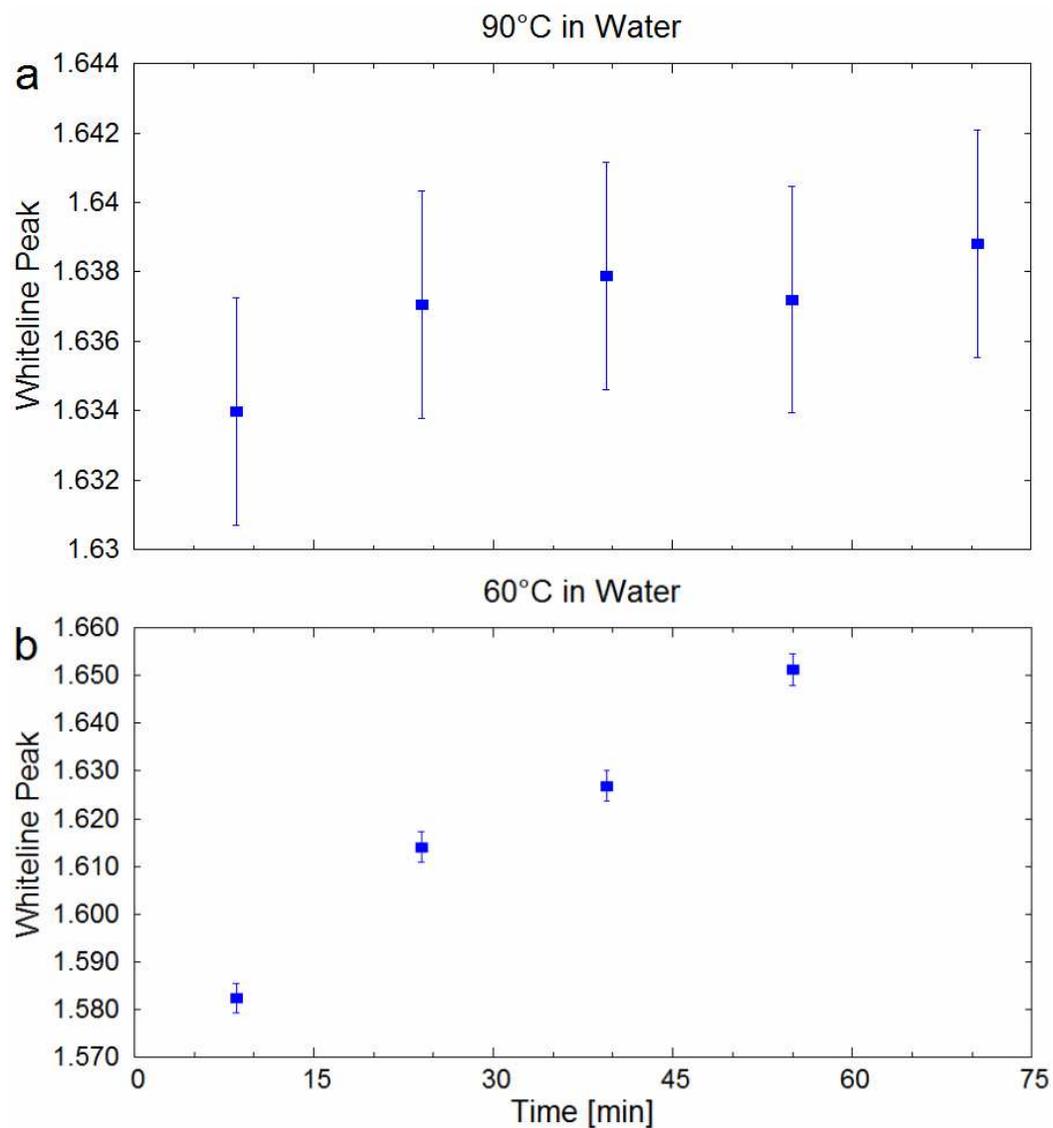


Figure S4. Whiteline peaks for XANES spectra of ZnO nanowires taken while the wires were immersed in DI water at room temperature. Scans are of nanowires grown at (a) 90 °C and (b) 60 °C. No significant radiation damage is observed in either case. The increase in (b) is attributed to faster dissolution of ZnO grown at lower temperature because of the higher concentration of surface defects.

(1) Shaporev, A. S.; Ivanov, V. K.; Baranchikov, A. E.; Polezhaeva, O. S.; Tret'yakov, Y. D. *Russian Journal of Inorganic Chemistry* 2007, 52, 1811.

(2) Ping, L. I.; Ping, Z.; Bin, L.; Zhen-bin, J.; Yu, W. *Chemical Research and Application* 2004, 16.