

Dimensional tailoring of hydrothermally grown zinc oxide nanostructures in a continuous flow microreactor.

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### **Highlights**

- Hydrothermal growth of ZnO nanostructures in a continuous flow microreactor (CF $\mu$ R).
- Demonstrated dimensional designing of nanostructures as well as areal density, length, diameter and shapes.
- Variety of ZnO nanostructures (nanorods, nanotubes, nanopencils, nanosheets etc.) were deposited on ITO-PET substrates.
- The effect of reaction parameters on growth and morphology were analyzed.

### **Reagents and materials**

Zinc nitrate hexahydrate, hexamethylenetetramine (HMTA), polyethyleneimine (PEI), citric acid, cobalt nitrate hexahydrate, ammonium hydroxide and ethanol were purchased from Sigma-Aldrich and were ACS grade. In-SnO<sub>2</sub> : PET (ITO-PET, transmission >80% in the visible spectrum; sheet resistance 60  $\Omega$ /square) from Sigma-Aldrich was used as substrate.

### **ZnO seed layer.**

The formation of ZnO seeds began with the dissolution of 5 mM zinc acetate dihydrate in ethanol by stirring for 3 h at room temperature and aging for 72 hrs at room temperature. This solution was deposited on the precleaned ITO-PET substrate using spin coating technique. at a speed of 2000 rpm for 60 seconds. Two seed layers were deposited on all the substrates. After the deposition ITO-PET substrate was sintered at 180 °C for 24 hrs on a hot plate and allowed to cool down to room temperature. An air plasma treatment for 2 minutes was done to facilitate the hydrophilicity before placing into the Continuous flow microreactor (CF $\mu$ R) assembly.

### **Continuous flow microreactor (CF $\mu$ R).**

The home-built Teflon CF $\mu$ R used for ZnO nanowire deposition is shown schematically in Figure 1 (a and b). It consists of a 4 × 13 × 30 mm deposition chamber, with a total volume of 1.5 mL. An aluminum plate over an ITO-PET substrate was pressed to seal the microreactor. This assembly was then bolted together to prevent leakage. The substrate faces downward in the reactor to prevent any precipitate from settling onto the growing nanostructures. A ceramic heating plate with an embedded microthermocouple was pressed against the back surface of the Teflon microreactor opposite to the substrate surface. Another thermocouple is inserted in the Teflon CF $\mu$ R. The temperature was controlled with a PID controller which was able to maintain set point to within  $\pm 0.1$  °C. Syringe pumps were used to flow each of the aqueous precursors into microreactor's magnetic mixer with a 200  $\mu$ L chamber, and the well-mixed solution was then lead into the deposition chamber of CF $\mu$ R.

### **Deposition of ZnO nanostructures.**

ZnO nanostructures were deposited at 90 °C from aqueous solutions of zinc nitrate and hexamethylenetetramine (HMTA) at concentrations of 100 mM to 12mM. PEI solution of 2mM to

8mM was also used. Each precursor solution was degassed by helium flushing for 30 min prior to being pumped into the microreactor. The reaction chamber was filled with an initial charge of precursor solution before heating starts. Total flow rates of 1  $\mu\text{L/s}$  to 10  $\mu\text{L/s}$  were used. Here, we have the advantage of maintaining precursor concentration in the deposition chamber by just varying the flow rate instead of preparing the various stock solution. CFuR has a mixing chamber before the deposition chamber, which in fact facilitate the uniform heated precursor solution in deposition otherwise faster flow rates would resulted in uneven temperature down the length of the reaction channel if the precursor solutions are not heated until they enter the microreactor. The precursors did not precipitate in the mixing chamber as the residence time is very less compared to reaction initiation time.

### ***Dimensional Tailoring of Nanostructures.***

We have grown nanorods on the ITO-PET substrate in the CFuR for two hours. After two hours, the flow rate was altered to provide a higher molar composition of HMTA and PEI in the reaction medium. At this point, usual growth of nanorods was hampered due to the excess deposition of PEI on ZnO surface. At the same moment, HMTA-induced ammonium ions into the reaction-deposition solution leads to subsequent decrease in nanorod diameter at each layered growth. This phenomenon resulted in the conical shape formation. But a further increase in HMTA-PEI composition, exponentially decreases the nanorod diameter and hence formed a pencil shape structure. It is pertinent to mention here that in CFuR, reactant composition does not change with time and thus there is no way of changing the shape of nanostructure as the reaction proceeds, as in the case of traditional synthesis. To alter the shape, we must manipulate the flow rate and thereby changing the reaction composition. Figure S1 shows the methodology adopted to prepare the various shapes of ZnO nanostructures.

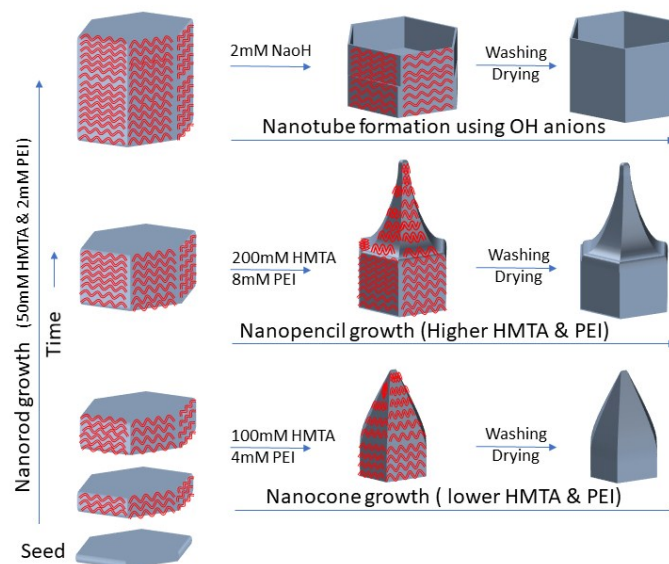


Figure S1 : Schematic of mechanism to produce various forms of ZnO nanostructures. Use of PEI stops the lateral growth by binding to the ZnO surface leading to smaller diameter ZnO rods formation. Hydroxide ions introduced in the fluid stream internally etch nanorods resulting in the formation of nanotubes. Higher amount of ammonium ions through an increase in HMTA increases the axial growth which in presence of PEI subsequently reduces the lateral growth at each cycle and leads to the conical

shape formation. An additional amount of PEI further reduces the diameter at each growth cycle and thus form nanopencil.

### ***ZnO structures formed in the reaction chamber and outflow.***

We observed that ZnO nanorods grow on the ITO-PET substrate. However, as active species,  $Zn^{2+}$ ,  $OH^-$ ,  $NH_4^+$  are everywhere in the reaction medium and would lead to the formation of secondary ZnO nanostructures in the solution. We also observed the nanostructures in the outflow. These were also responsible for the clogging of reaction chamber as well as outflow channel, particularly at lower flow rates and higher precursors molar concentration. Figure S2 shows SEM photographs of few of these structures.

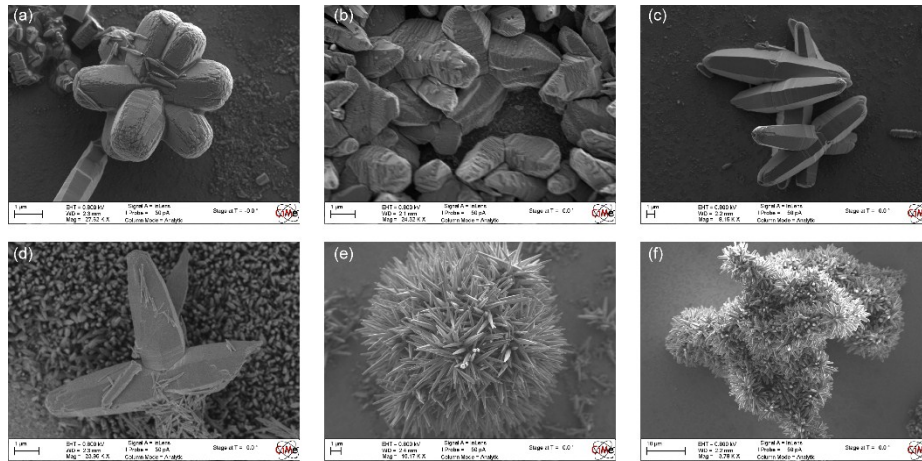


Figure 2 : SEM photographs of various ZnO structures observed in the outflow that were responsible for clogging of channels