# High density growth of ZnO nanorods on cotton fabric enables access to a flame resistant composite

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## Materials and general considerations

#### **Materials**

Polytetrafluoroethylene (PTFE) sheets, 1/8" thick, 6"x6, Nylon 6/6 off white wing nuts, and Nylon pan head slotted screws (1 inch length) were purchased from McMaster-Carr. Bleached desized cotton fabric (#400) was purchased from TestFabrics (West Pittson, PA). Zinc acetate dihydrate (ACS reagent,  $\geq$  98%), triethylamine ( $\geq$  99.5%), ethanol (ACS reagent,  $\geq$  99.5%), isopropyl alcohol (anhydrous, 99.5%), sodium hydroxide pellets (ACS reagent,  $\geq$  97.0%), citric acid (ACS reagent,  $\geq$  99.5%), Triton X-100 (laboratory grade nonionic surfactant), zinc nitrate hexahydrate (reagent grade, 98%), and hexamethylenetetramine (ACS reagent,  $\geq$  99.0%) were purchased from Sigma-Aldrich.

## **Construction of the PTFE frame**

The frames were manufactured from PTFE sheet using a Epilog Mini 24 Laser Cutting System (40W) at the Tulsa FabLab facilities. Dimensions are indicated in the diagram shown in Figure S1. Special safety precautions must be taken during PTFE machining. Thermal degradation of PTFE during laser cutting can produce irritating gases. Furthermore, machined PTFE dust poses a respiratory hazard. Proper ventilation and safety equipment should be employed.



Figure S1. Diagram of PTFE frame (left), manufactured frame (right)

# Scouring of cotton fabric

Before ZnO nanorods were grown, the cotton fabric was cut into square swatches (4 cm  $\times$  4 cm) and scoured to remove wax, grease, and other finishing chemicals. The scouring solution was prepared by first dissolving 5.0 g of NaOH in 20 mL of deionized water followed by the addition of 1.5 g of Triton X-100 and 0.75 g of citric acid. The resulting solution was then diluted to 500 mL with deionized water. In the scouring process, four cotton swatches were then placed in a 500 mL round-bottom flask containing 200 mL of the scouring solution. The mixture was

then stirred at 100 °C for 1 h. At the end of the process, scoured swatches were removed from the solution, rinsed thoroughly with DI water, and dried in air.

# Preparation of ZnO seed solution

First, a 100 mM solution of zinc acetate dihydrate was prepared by dissolving 1.10 g (5.00 mmol) in 50.0 mL of isopropyl alcohol. The resulting solution was then stirred vigorously at 85 °C for 15 min. After this time, 700  $\mu$ L of triethylamine (5.0 mmol) was added dropwise to the stirred solution. The resulting solution, now clear, was stirred at 85 °C for an additional 10 min. After this time, the solution was cooled to room temperature and incubated without stirring for 3 h. The average particle size of the ZnO nanocrystal seed solution was 31.5 ± 10.0 nm, as measured by a Zetatrack (Microtrac) particle size analyzer (Figure S2). We have used this seed solution up to 2 weeks after its preparation with no discernible change in the final ZnO nanocrystals.



**Figure S2.** Size distribution of the ZnO nanocrystals in the seed solution

# Preparation of ZnO growth solution

Equimolar aqueous solutions of zinc nitrate hexahydrate and hexamethylenetetramine were used to grow ZnO nanorods on cotton swatches.

**100 mM Zn(II) growth solution:** Hexamethylenetetramine (7.71 g, 0.055 mmol) and then zinc nitrate hexahydrate (16.4 g, 0.055 mmol) were dissolved a total volume of 550 mL of DI water. This solution [100 mM in Zn(II)] was stirred 24 hours at room temperature before use.

**200 mM Zn(II) growth solution:** hexamethylenetetramine (15.4 g, 0.11 mmol) and zinc nitrate hexahydrate (32.8 g, 0.11 mmol) were dissolved sequentially in DI water (total volume 550 mL). This solution [200 mM in Zn(II)] was stirred 24 hours at room temperature before use.

# Growth of ZnO nanorods on cotton swatches mounted on the PTFE Frame

The scoured cotton swatches were first dip-coated with the ZnO seed solution for 5 minutes and then rinsed thoroughly with ethanol. The dip-coated swatches were then suspended from a wire rack, cured at 120 °C for 1 hour in an oven, and then further conditioned in air for 12 hours at room temperature (Figure S3).



**Figure S3.** Cotton swatches after dip-coating in ZnO seed solution. The drying rack was mounted directly in an oven and cured at 120 °C for 1 hour.

To mount the seed-treated cotton swatch, it was laid down on one of the PTFE frames and pulled taut while the outer frame was positioned on top of the cotton. The fabric was punctured at the location of each screw hole and then secured in place with the screws and wing nuts (Figure S4). It is critical to ensure the substrate taut throughout the crystal growth process since cotton immobilization has previously been shown to be critical for growth of homogenous ZnO nanorods on flexible substrates.<sup>1–3</sup>



FigureS4.Cottonfabricmounted on the PTFE frame.

Having mounted the cotton fabric, the assembly was then suspended vertically in ~70 mL of the growth solution in a closed glass jar and incubated at 95 °C for 8 or 24 h in an oven (Figure S5). Both 100 mM and 200 mM Zn(II) growth solutions were examined in this experiment. The container was removed from the oven, cooled to room temperature, and then further incubated at room temperature for 10–12 hours. Finally, the frame assembly was removed from the growth solution and disassembled. The cotton swatches, now modified with ZnO nanorods, were thoroughly rinsed with DI water and allowed to air-dry at room temperature (Figure S6).



**Figure S5.** PTFE frame assembly immersed in the seed solution for the growth of ZnO nanorods.



**Figure S6.** Cotton sample after ZnO nanorod growth and removal from PTFE frame.

# Characterization.

Morphology of the materials was investigated using a JEOL JSM 6060 LV field emission scanning electron microscope (FESEM). Length and diameter values are averages of 20 measurements, analyzed using ImageJ software. Crystal structures were analyzed using a Shimadzu XRD-6100 X-ray Diffractometer with Cu K $\alpha$  radiation, employing a scanning rate of 0.02° s<sup>-1</sup> within the range of 2 $\theta$ =10°-70°, operating at 40 kV and 33 mA (1320 W). Thermogravimetric analysis (TGA) was carried out using a Mettler Toledo 851 with a TSO 801RO robotic arm. Quantitative analysis of the weight percent of ZnO contained in the modified cotton samples was carried out using the TGA data. In the event, three pieces were sampled form each treated cotton swatch along with control samples of untreated cotton. The samples were then heated from 40 °C to 600 °C at a rate of 10 °C/min under a nitrogen atmosphere at a flow rate of 40 mL/min. The amount of ZnO grown on cotton samples was calculated by the weight loss of the samples at the end of the heating cycle.

**Figure S7.** SEM and TGA analysis of ZnO modified cotton Crystal growth conditions: 100 mM Zn(II), 8 hr Final ZnO content of composite: 21.9 wt%



**Figure S8.** SEM and TGA analysis of ZnO modified cotton Crystal growth conditions: 100 mM Zn(II), 24 hr Final ZnO content of composite: 36.7 wt%

Side A and Side B were SEM images acquired from both sides of the modified cotton to demonstrate homogeneous coverage on all surfaces of the fabric. The cross-sectional image (lower left) illustrates the hexagonal facets of the ZnO crystals.

Under these conditions, the average length of the nanorods was  $371 \pm 55$  nm and the average diameter was  $188 \pm 29$  nm. These dimensions were averaged over 20 measurements and analyzed using ImageJ software.



Figure S9. SEM and TGA analysis of ZnO modified cotton

Crystal growth conditions: 200 mM Zn(II), 24 hr Final ZnO content of composite: 44.8 wt%

Side A and Side B were SEM images acquired from both sides of the modified cotton to demonstrate homogeneous coverage on all surfaces of the fabric. The cross-sectional image (lower left) illustrates the hexagonal facets of the ZnO crystals.

The average length and diameter of the ZnO nanorods were 816  $\pm$  61 nm and 145  $\pm$  30 nm, respectively. These dimensions were averaged over 20 measurements and analyzed using ImageJ software.





S10. Indexed XRD Figure patterns of highly oriented ZnO nanorods grown on cotton samples mounted on the PTFE frame. These diffraction peaks are consistent with the hexagonally faceted wurtzite structure of the ZnO nanorods. This is а representative XRD pattern for ZnO nanorods grown at 24 hours in a 100 mM Zn(II) growth solution. Similar results were obtained for the ZnO nanrods grown for 24 hours in 200 mM Zn(II) growth solution.



**Figure S11.** Calculation of the  $T_{onset}$  of cotton samples containing ZnO nanorods grown in the 100 mM Zn(II) growth solution for 8 h.



**Figure S12.** Calculation of the  $T_{onset}$  of cotton samples containing ZnO nanorods grown in the 100 mM Zn(II) growth solution for 24 h.



**Figure S13.** Calculation of the  $T_{onset}$  of cotton samples containing ZnO nanorods grown in 200 mM Zn(II) growth solutions for 24 h.

## Flame resistance experiments

Cotton samples were clipped to a stainless steel washer (5.0 cm outer diameter, 1.4 cm inner diameter) and clamped 10.0 cm from the tip of a Benzomatic butane torch. Unmodified cotton was exposed directly to the flame and the time to burn through the cotton was recorded. The flame was left on until all of the unmodified cotton visible in the 1.4 cm target had burned and receded from view. The average time for the flame to ignite the cotton was  $1.7 \pm 0.1$  seconds for three trials. The average time for complete recession of the cotton in the target was  $2.9 \pm 0.3$  seconds. Next, cotton modified with ZnO nanorods was subjected to the flame for approximately 2.9 seconds so that it could be compared directly to the unmodified cotton. In all flame tests, the butane torch was filled with fuel before each use. A new washer was used with each experiment. The flame tests were video recorded. Sample video files for the flame test of unmodified cotton and the cotton modified with 44.8 wt% ZnO nanorods are available as part of the Electronic Supplementary Information. After exposure to the flame, the samples were cooled to room temperature and assessed by inspection. Photographs of the samples after exposure to the flame are shown in Figure S15. Note that increasing ZnO content protects the cotton from the flame, with the 44.8 wt% ZnO providing the most significant protection.

## Figure S14: Flame test setup



**Figure S15.** Representative damage to unmodified cotton and cotton modified with ZnO nanorods after direct exposure to flame for  $2.9 \pm 0.3$  seconds.

Unmodified cotton



36.7 wt% ZnO nanorods



44.8 wt% ZnO nanorods



## Prolonged exposure to flame

The flame test described above was repeated for the cotton modified with 44.8 wt% ZnO nanorods. The sample was exposed to the flame until the center of the target collapsed. Typically more than 5 minutes was required for complete collapse of the sample (see representative time course below). While the cotton is not protected from thermal degradation with such prolonged exposure to direct flame, the residual ZnO prevents the spread of flames to the remainder of the cotton sample.

Figure S16: Prolonged exposure of cotton modified with 44.8 wt% ZnO nanrods to open flame



t = 0

t = 2.5 min

t = 5.0 min

Figure S17: Resulting damage from prolonged burn and comparison to unmodified cotton



# **ZnO Modified Cotton Durability Experiments**

A cotton swatch modified with ZnO nanorods (44.8 wt% ZnO) was placed in 250 mL crystallization dish containing hot DI water (85 °C). A stir bar was added and the water was stirred vigorously for 1 hour at 85 °C. The cotton swatch is subject to folding and abrasion from the stir bar throughout this washing procedure. After 1 hour, the cotton swatch was removed and air-dried before analyzing by SEM and TGA. SEM analysis indicated no discernable change in the ZnO nanorod structure and density. Likewise, TGA analysis confirmed negligible loss of ZnO in this abrasive washing procedure (44.8 wt% ZnO before washing; 42.2 wt% ZnO after washing). This experiment highlights the durability of the ZnO-cotton composite. SEM and TGA data are shown below.

Figure S18: SEM analysis before and after abrasive washing at 85 °C



Before washing

After washing and drying



Figure S19: TGA analysis before and after abrasive washing

## References

- (1) Athauda, T. J.; Hari, P.; Ozer, R. R. ACS Appl. Mater. Interfaces 2013, 5, 6237–6246.
  (2) Athauda, T. J.; Ozer, R. R.; Chalker, J. M. RSC Adv. 2013, 3, 10662-10665.
- (3) Wang, R.; Xin, J.; Tao, X.; Daoud, W. Chem. Phys. Lett. 2004, 398, 250–255.