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# Supporting Information

for *Small Methods*, DOI 10.1002/smtd.202301407

Subtractive Patterning of Nanoscale Thin Films Using Acid-Based Electrohydrodynamic-Jet Printing

*Tae H. Cho, Nazanin Farjam, Kira Barton* and Neil P. Dasgupta**

# Subtractive Patterning of ZnO Thin Films using Acid-Based Electrohydrodynamic-Jet Printing

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## Supporting Information

**Table S1.** ICP-MS measurements of glycerol residue dissolved in DI water solution

| **Sample Description** | **Zn Concentration (ppm)** |
|---|---|
| 50 nm ZnO dissolved in ink solution | 83.55 |
| 1 μL ink dropped on 50 nm ZnO | 17.71 |
| E-jet printed 50 nm ZnO | 1.39 |
| 50 nm ZnO dissolved in 2 wt. % glycerol in DI water | ~0.01 |

Theoretical ppm calculation for ICP-MS

To correlate the measured Zn concentration with the theoretical volume of the removed ZnO from the residual polymer composite, Equation S1 was used:

$$V_{ZnO_{measured}} = \left(ppm_{Zn} * V_{H_2O} * \frac{M_{ZnO}}{M_{Zn}}\right)^{-1} * \rho_{ZnO} \qquad \text{(Equation S1)}$$

where $V_{ZnO_{measured}}$ is the calculated volume of removed ZnO from measured Zn concentration from ICP-MS, $ppm_{Zn}$ is the measured Zn concentration from ICP-MS, $V_{H_2O}$ is the volume of DI water used to rinse, $M_{Zn}$ and $M_{ZnO}$ are molar masses of Zn and ZnO, respectively, and $\rho_{ZnO}$ is the density of ZnO.

To calculate the theoretical volume of the removed ZnO, ZnO thickness was multiplied by the area of the pattern, assuming complete removal through the entire film thickness. The percentage errors between the calculated and theoretical volume of removed ZnO were then analyzed as shown in Table S2. We believe that the large difference in theoretical and measured volume of removed ZnO on e-jet printed sample is due to the droplet casted at the end of printing cycle from residual ink at the nozzle for de-initialization of e-jet.

**Table S2.** Comparison between measured and theoretical volume ($cm^3$) of removed ZnO from acid-based printing

| **Sample Description** | $V_{ZnO_{measured}}$ | $V_{ZnO_{theoretical}}$ | $\%_{error}$ |
|---|---|---|---|
| 50 nm ZnO dissolved in ink solution | $1.85 \times 10^{-5}$ | $2.00 \times 10^{-5}$ | 7.34 % |
| 1 µL ink dropped on 50 nm ZnO | $3.93 \times 10^{-6}$ | $2.67 \times 10^{-6}$ | 47.33 % |

| | | | |
|---|---|---|---|
| E-jet printed 50 nm ZnO | $3.08 \times 10^{-7}$ | $4.00 \times 10^{-8}$ | 670.78 % |

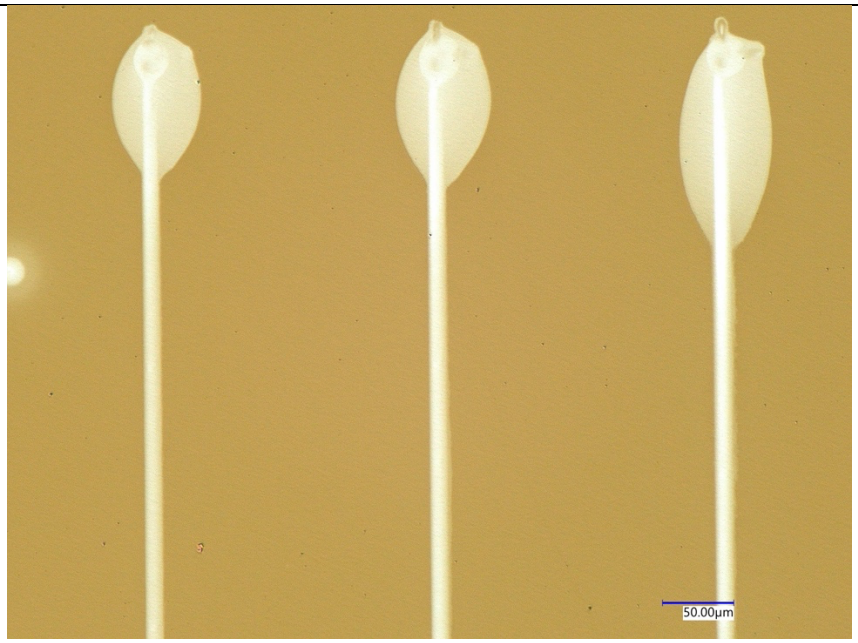


**Figure S1.** Optical microscope image showing the tail of printed pattern, where the residual volume of ink at the nozzle forms a droplet at the end of the line

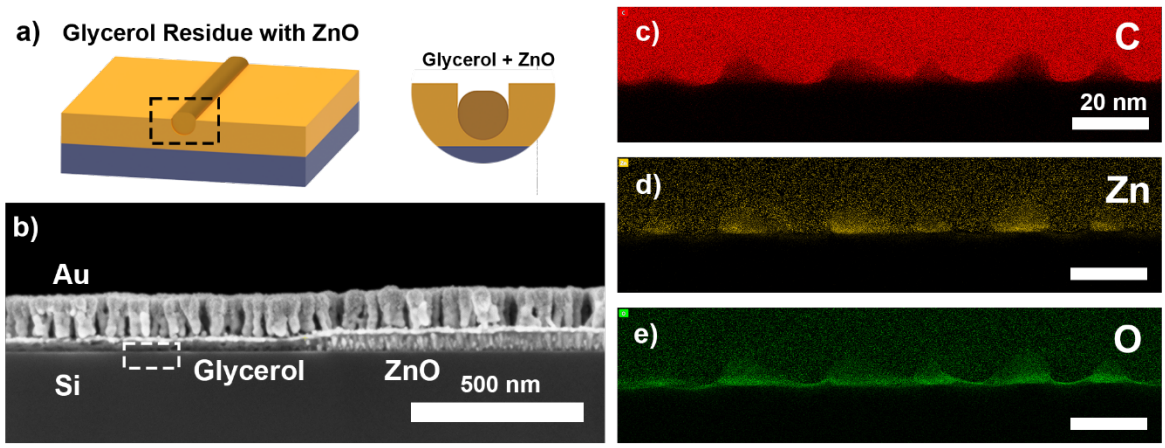


**Figure S2.** (a) Schematic illustration of the sample where black dashed box is the area of interest; (b) cross-sectional SEM image (white box showing the STEM-EDS region); (c-e)

elemental concentrations from cross-sectional STEM-EDS after acid-based e-jet printing, before the residual polymer composite removal

**Table S3.** Summary of acid-based e-jet printing parameters

| **Printing Process Parameters** | **Values** |
|---|---|
| Temperature | 26 ℃ |
| Humidity | 54 % |
| Ink Chemistry | 1M HCl + 2 wt.% glycerol |
| Nozzle | 10 µm size, WPI attached to a metal tube |
| Standoff Height | 30 µm |
| Initialization Pressure | 5 psi |
| Voltage | 680 DCV |
| Stage Speed | 0.1 mm/s |

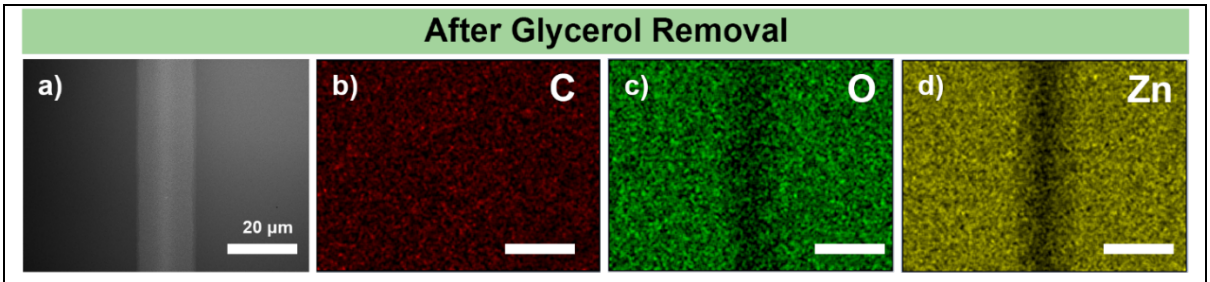


**Figure S3:** Subtractive printing of ZnO using acid-based e-jet: (a) SEM image of printed pattern after polymer removal, and (b) C (c) O, and (d) Zn EDS map scan of etched ZnO trench.

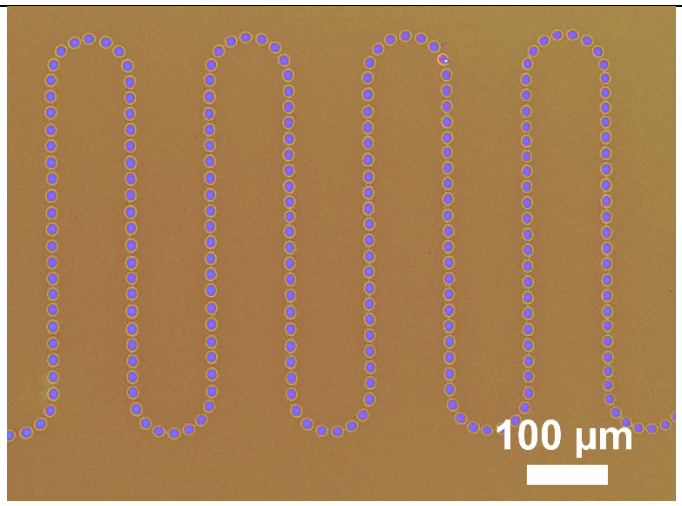


**Figure S4:** Subtractive printing of ZnO with curvature and dotted lines using acid-based e-jet