

Supplementary Information

3D printing of hollow geometries using blocking liquid substitution stereolithography

Authors: Aftab A. Bhanvadia¹, Richard T. Farley², Youngwook Noh², Toshikazu Nishida^{1*}

¹Department of Electrical and Computer Engineering Department, University of Florida, Gainesville, Florida 32611, USA.

²Nanoptics, Inc., 3014 NE 21st Way, Gainesville, FL 32609, USA.

*Correspondence to: E-mail: nishida@ufl.edu (T.N.)

This PDF document includes:

- Supplementary Notes
- Supplementary Figs. 1 to 5
- Supplementary References

Supplementary Notes

Supplementary Note 1: Selective utilization of the blocking liquid substitution

The blocking liquid substitution process can be used on an as-needed basis. The blocking liquid is substituted into the hollow spaces prior to polymerization of layers that would pose a risk of print-through. Otherwise, the fabrication process can continue to operate in conventional mode. See **Supplementary Note 4** for additional details on how the reported method can be utilized selectively for fabrication of multilevel hollow geometries. In a fully automated fabrication system, the pre-fabrication process planning can utilize the Gong et al. model²⁸ to determine when the blocking liquid substitution should be utilized based on the characteristics of the resin, the layer thickness and exposure condition used for the fabrication process.

Supplementary Note 2: Another HDDA resin

The devices in **Fig. 5A–C** of main text were fabricated using the Secondary Resin for which the working curve is shown in **Supplementary Fig. 2**. This HDDA resin was formulated with TPO photoinitiator and Benetex OB absorber. Beyond a certain dose, the cured depth of this resin exhibits a nonlinear dependence—described as “superlogarithmic behavior” by P. Jacobs²⁶. Therefore, we estimated the D_p of this resin by fitting the working curve equation within the linear regime ($D_p \sim 37 \mu\text{m}$), and over the entire range of exposure doses tested ($D_p \sim 74 \mu\text{m}$) which includes the non-linear regime. Without the blocking liquid substitution process, the channels of the devices shown in **Fig. 5A–C** were confirmed to be clogged.

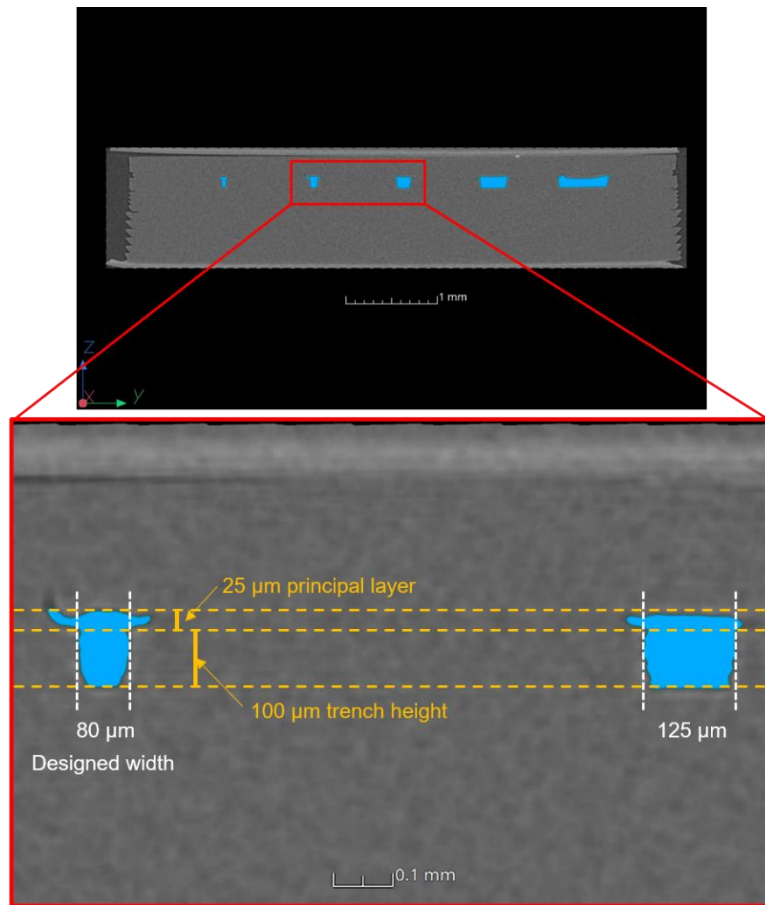
Supplementary Note 3: Fabrication of transparent device using PEGDA

The device shown in **Fig. 5D–E** was fabricated using a PEGDA resin for which the photopolymerization working curve is shown in **Supplementary Fig. 3**. This resin was formulated with TPO photoinitiator and absorbers (Benetex OB and BLS 99-2) which do not cause coloration (e.g. yellowing) within the visible spectrum. The critical features (i.e. trenches and capping layers) of the device were fabricated with a 25 μm layer thickness and an exposure intensity of $\sim 6 \text{ mW cm}^{-2}$. We observed that the PEGDA resin is very susceptible to polymerization within the hollow regions because of the low $E_c \sim 11 \text{ mJ cm}^{-2}$, therefore we formulated the blocking liquid using IPA and BLS 99-2 absorber. The lower viscosity of IPA compared to the PEGDA also facilitated draining of the blocking liquid with ease after the part was fabricated. Without the blocking liquid substitution process, the channels of the device shown in **Fig. 5D–E** were confirmed to be clogged.

Supplementary Note 4: Fabrication of multilevel hollow geometries

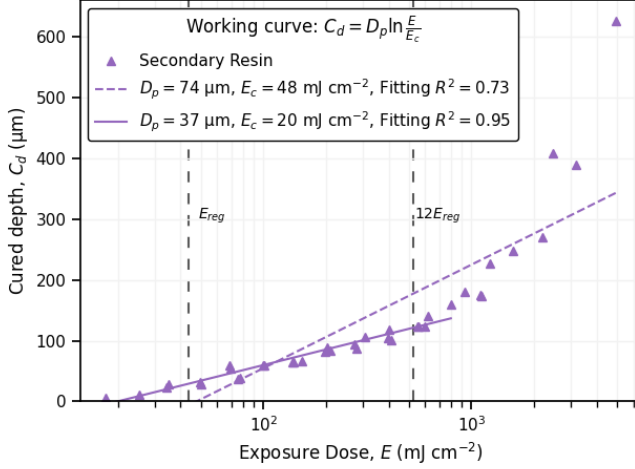
The fabricated device in **Fig. 5C** of the main text corresponds to the CAD model shown in **Supplementary Fig. 4**. This is an example of a device where the hollow geometries span across multiple levels of the device (along the vertical z-axis growth direction). During fabrication of this device, the blocking liquid substitution was utilized three times. The three white-horizontal dashed lines in **Supplementary Fig. 3B** indicate the boundaries of the principal layer facing the hollow region. The hollow regions located on different levels of the device are connected using hollow vias. The vias are formed when the capping layers above the hollow regions (principal layer and subsequent layers) do not fully encapsulate a hollow region which contains the blocking liquid. During the fabrication of the vias, the blocking liquid may diffuse into the resin, however, by formulating a blocking liquid comprising of the same components as the resin, inhomogeneity or contamination effects can be minimized.

Supplementary Figures

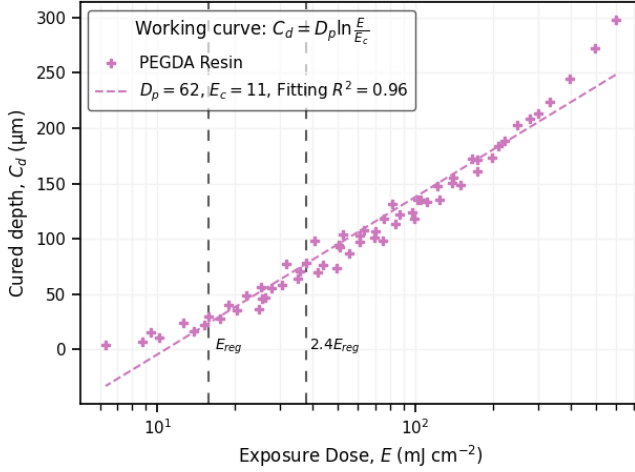


Supplementary Fig. 1. Unpolymerized regions in the principal layer. Cross-sectional view of hollow channels (blue) from a device which was fabricated using a blocking liquid comprising of HDDA + 3.0 [Ab] (see results in **Fig. 3B** of main text). The magnified image (bottom) shows that the principal layer contains unpolymerized areas that are adjacent to the trenches. These unpolymerized areas occur because of the reduced polymerization caused by the blocking liquid that has diffused from Region I into Region II and III of the principal layer (see **Fig. 2** of main text). The unpolymerized area corresponding to Region II results in hollow channel heights to be greater than the designed channel height. The unpolymerized area corresponding to Region III is an indication of poor adhesion of the principal layer.

Supplementary information
3D printing of hollow geometries using blocking liquid substitution stereolithography

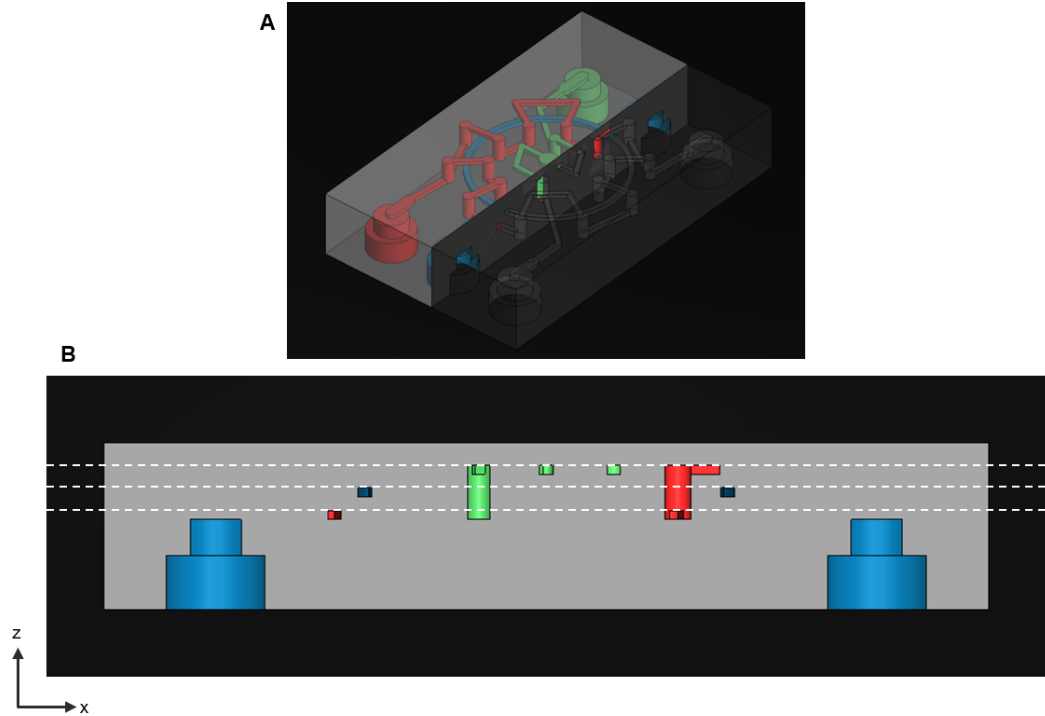


Supplementary Fig. 2. Photopolymerization working curve of another HDDA resin used in this work. This resin exhibits a superlogarithmic behavior²⁶ (see discussion in **Supplementary Note 2**). Two trendlines are fitted to the working curve equation in order to extract the estimated D_p value. First trendlines fits the data over the entire exposure doses tested, while the second trendline fits the data in the lower range of exposure dose where the resin behaves linearly. The vertical dashed lines at E_{reg} and $12E_{reg}$ correspond to regular exposure dose and principal exposure dose, respectively, used for the fabrication of the device in **Fig. 5C** of the main text.

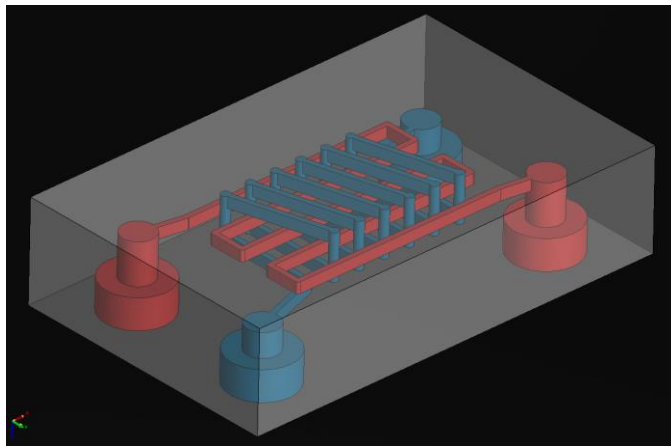


Supplementary Fig. 3. Photopolymerization working curve of a PEGDA resin investigated in this work. The vertical dashed lines at E_{reg} and $2.4E_{reg}$ correspond to regular exposure dose and principal exposure dose, respectively, used for the fabrication of the device shown in **Fig. 5D** and **Fig. 5E** of the main text.

Supplementary information
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Supplementary Fig. 4. CAD model of a device with multilevel channels. This CAD model corresponds to the device shown in Fig. 5B of main text. **(A)** Perspective view of the device where the solid portion of the device is transparent in order to show the internal hollow regions that are colored red, green and blue. **(B)** One cross-sectional view of the model. The horizontal dashed lines correspond to the bottom boundary of the principal layers. Prior to polymerization of the principal layer, the hollow spaces are substituted with the blocking liquid.



Supplementary Fig. 5. CAD model of a multilevel microfluidic device. This CAD model corresponds to the transparent PEGDA device shown in Fig. 5D–E of the main text. The red and blue colored regions illustrate the continuous channel paths that are separate but interlocked within the device.

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