Flow Analysis of 2-photon 3D Printing in situ Material Exchange

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Since the past few years advancements in two-photon polymerization (2PP) have allowed for the fabrication of 3D structures with features at the nano-/micro-scale offering unparallel precision and versatility, making it particularly suitable for applications in fields like microelectronics, optoelectronics, photonics, biomedical engineering and more. Simultaneously, the incorporation of multiple materials in a single printing process enhances the functionality and versatility of the printed objects. This capability is crucial for creating composite materials, multi-material devices, and structures with tailored properties for specific applications.^{1,2}

Here, we demonstrated the successful fabrication of a cuboidal structure using the MergeOne (HETEROMERGE) exchange system³ and examined the flow analysis using a 25x immersion fluorescence microscopy (ZEISS) system. The multi-material exchange system (Fig. 1) has successfully printed the desired structures with no errors in printing and with great alignment precision. Utilizing the multi-material exchange system, a cuboidal structure with dimensions of $200 \ \mu m \times 200 \ \mu m \times 200 \ \mu m$ was fabricated with 50% in height of the structure made of green (MX500) and blue (MX444) fluorescent print material, respectively. The same multi-material exchange system was utilized to understand the flow analysis. The results of this work helped to understand the real-time exchange happening during the 2PP-based 3D printing process.

Here, the phase separation of different fluorescent materials was clearly visualized along with the remaining previous material being visible as a background signal when new material flows in (Fig. 2). It was also seen how the interaction of liquid with the surface of structure resulted in the dragging of liquid. Later, a flow streak in the fluidic shadow of the structures was observed which showed the flow of previous remaining material gathered at the edge of the flow direction after the inward flow of new material. After some time, the successful exchange of new material was observed along with minor traces of old material (Fig. 3). By this the timing and completeness of the exchange process is determined.

¹ Z.C. Ma, Y.L. Zhang, B. Han, Q.D. Chen, H.B. Sun, Small Methods, 2, 2366, (2018)

² M. Schmid, S. Thiele, R. Kirchner, and H. Giessen (submitted)

³ R. Kirchner, Y. Yu, M. H. Wong, S. Toukabri, and J. Knorr, in *Proc. SPIE PC12412*, 2023, PC1241206



Figure 1: Schematic representation of in-situ material exchange through the HETEROMERGE printhead during writing using an open fluidic system to inject liquid and to actively remove liquid with a volume synchronized inward and outward flow.



Figure 2: The whole cuboidal structure was fabricated of 50% MX500 (base monomer, photoinitiator, and green fluorescent dye) as well as 50% MX444 (base monomer, photoinitiator, and blue fluorescent dye) (A) The top 50% is fabricated of MX444. This layer is seen clearly and since this material combination is not fluorescent in the red spectrum, and the reflection from the bottom half of the cuboidal can be observed. (B) The flow of MX535 replacing MXpure (no fluorescent) being both without photoinitiator can be observed along with a clear visual of phase separation between both the materials across the structure. Note: all observations were made in red fluorescent channel for convenience of distinction.



Figure 3: (A) After 1-2 minutes of the flow of MXpure (observed in the green channel), the particular laminar flow effect of MX535 (in white) can be noticed which was generated due to the resistant flow behavior. The high interaction of MX535 along with the glass substrate and surface of the structure also promoted such behavior. (B) After 1 additional minute of MXpure, the cleared MX535 can be seen with some minor stains and traces along the edges of the structure. This is due to the laminar flow behavior with zero flow at boundaries.