Additive micro-/nano manufacturing of non-sensitized SZ2080™ employing femtosecond-laser VIS-light oscillator

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Introduction

Femtosecond laser direct writing (fs-LDW) is typically achieved using ultrashort pulsed lasers initiating localized non-linear light matter interaction (Fig.1) at a spatially confined volume, where photoinitiators (PI) are commonly used as an essential ingredient to induce cross-linking reactions. However, photo-structuring of pure polymers is often realized using amplified laser systems of longer pulse durations and lower repetition rates enough to cause avalanche ionization triggered photopolymerization [1]. Here, we extend the possibility to apply non-photosensitizied resins and non-amplified laser oscillators of VIS-light [2]. Experimental validation is done by producing benchmarking 3D woodpile nanostructures, micro-scaffolds, free-form micro-object and bulk micro-cube.

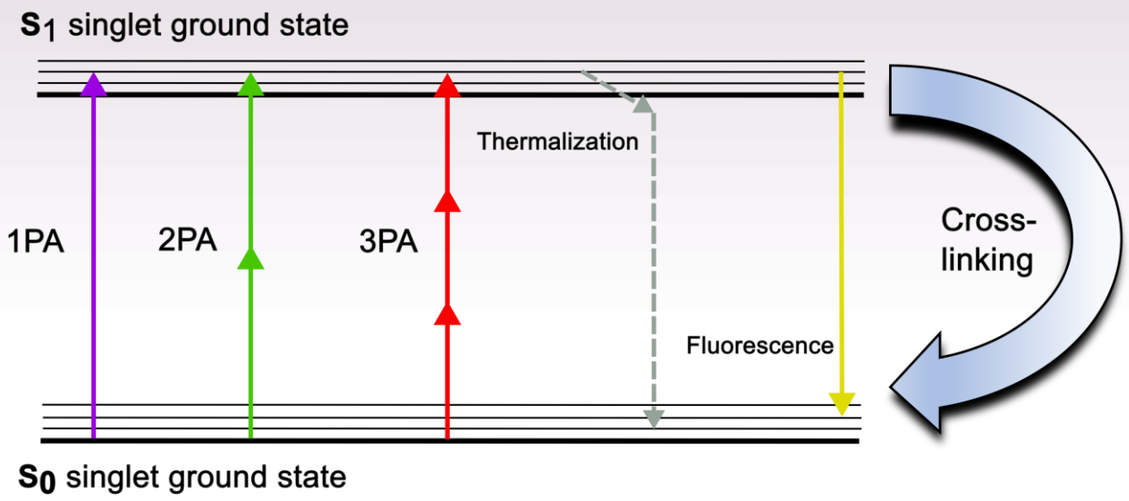

Fig. 1. Possible crosslinking initiation mechanisms.

Materials & Methods

- Fs-LDW is performed using Laser Nanofactory (Femtika Ltd.) (Fig.2)
- Beam focusing via 63x/1.4 NA oil (for woodpiles, “Benchy”, cube) and 20x/0.8 NA (for scaffolds) dry objective lens.
- Hybrid organic-inorganic pre-polymer SZ2080™ (FORTH, Greece).
- Material is drop-casted on a glass slide following pre-baking procedure of up to 90 ° C for 40 min.
- Samples are developed in 4-methyl-2 pentanone for 30 min and subsequently rinsed with isopropanol.

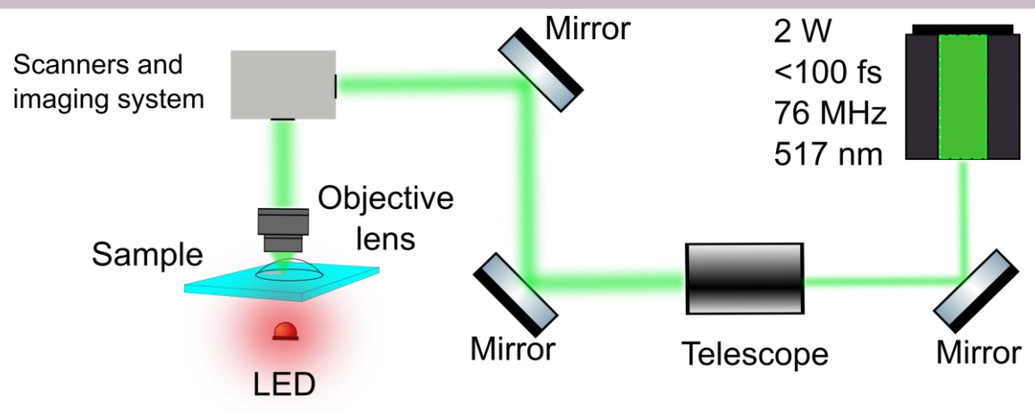

Fig. 2. Simplified schematics of the Laser Nanofactory system.

Results

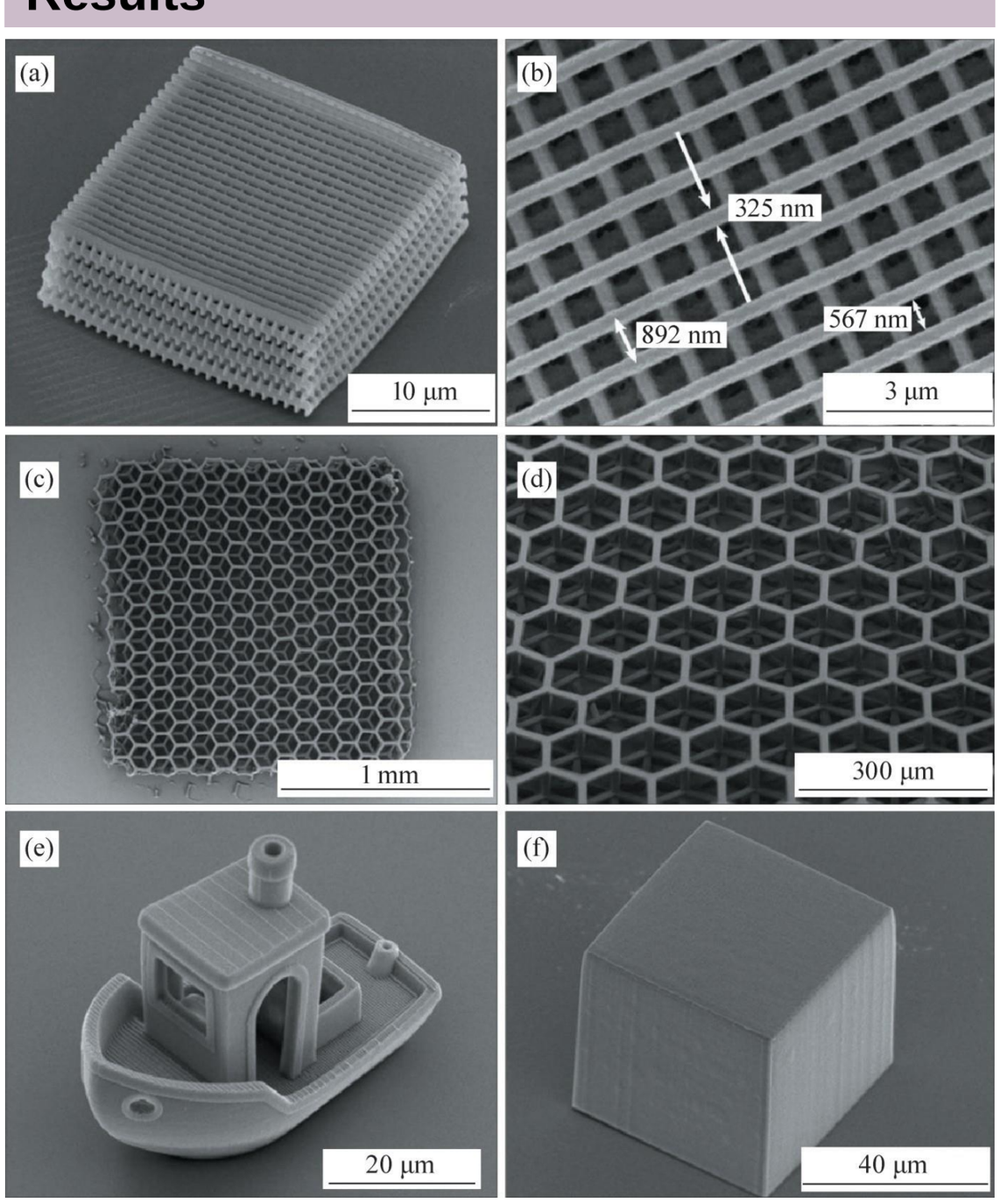

Fig. 2. SEM images of 3D structures: (a) Micro/nano-periodic woodpile; (b) Closeup view from above of (a); (c) Hexagonal scaffold; (d) 45° closeup view of (c); Free-form and bulky structures of (e) micro-“Benchy” and (f) microcube

Discussion

Here based on pure SZ2080™ absorption (Fig, 3) and laser wavelength, most probably 2PA should occur, with potentially some 3PA and negligible amount of 1PA. On the other hand, photo-polymerization mechanism cannot be directly explained by an impact ionization as the used pulses are of 100 fs width and too short to generate electron avalanche [3]. Photopolymerization is also observed using 1035 nm excitation of oscillator, but results are not consistently repeatable, and further systematic study is carried out.

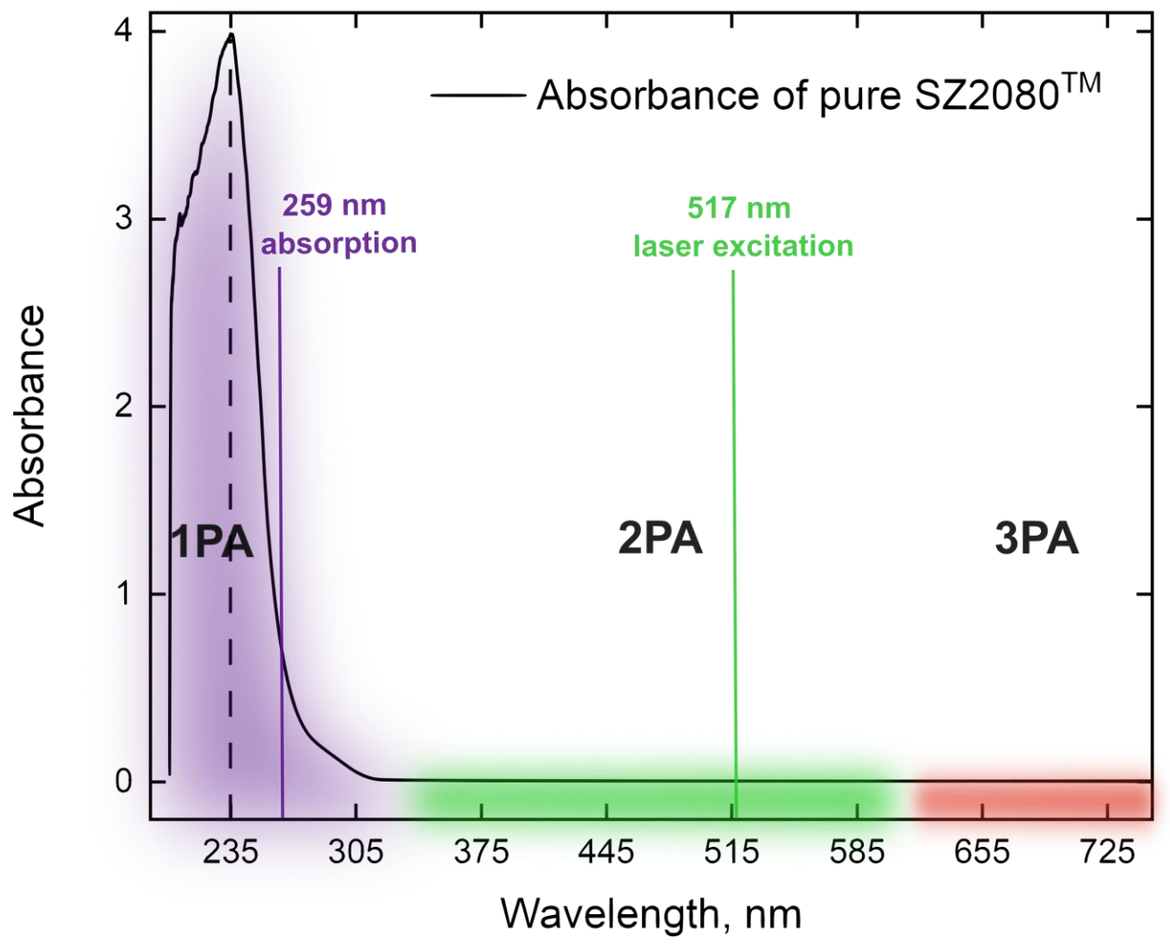

Fig. 3. Absorbance spectrum of pure SZ2080™ (the most probable crosslinking initiation mechanism under applied experimental conditions is caused by a 2PA)

References

1. M.Malinauskas, *et al*. Optics Express, 2010, 18(10): 10209 − 10221.
2. A.Butkus, *et al*. Journal of Central South University, 2022, 29(10): 3270−3276.
3. S. Rekštytė. ” PhD thesis, Vilnius, Vilnius University, 2016, p. 133.

Conclusions

Fs-LDW without PI is validated using 76 MHz repetition rate, 517 nm wavelength, and 100 fs pulse duration exposures. This widens additive nano-manufacturing by adding an option of pure polymers, which is beneficial for micro-optics, nano-photonics, and bio-medical scaffolds.