Electron and X-ray Beam Direct Write Lithography in Liquids: a Crucial Step Toward 3D Nanoprinting of Soft Materials

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Additive manufacturing with highly focused scanning electron [1] and X-ray beams [2] is a current frontier of 3D nanoprinting technology for inorganic materials. On the other hand, organic soft materials, such as gels are materials of choice for a vast number of biomedical applications such as tissue engineering, soft robotics, biosensing, drug delivery, implantable electronics, etc. Despite of aforementioned advancements, electron or X-ray beam printing is hard to realize as a polymerization (or crosslinking) tool in liquid organic precursor solutions primarily due to: (i) their vacuum incompatibility [3]. Therefore, multi-photon, polymerization technique remains to be the only technology for 3D printing of submicron scale soft matter features [4]. Here we report on solution of this "pressure and material gap" impediments and demonstrate *in-liquid* direct write technique for 3D-sculpturing of hydrogels [5]. The principle of the technique is shown in Figures 1a and Figure 1 b highlights the process of crosslinking induced by solvated electrons and radiolitic radicals (Fig.1 b). The experimental setup is based on microfluidic enclosures equipped with electron and X-ray transparent windows (Fig. c, d). We found that in-liquid crosslinking of hydrogel and urethane-based resins takes place at very low doses: in the order of 1 e/nm^2. The smallest feature size was found to be in the sub-100 nm range and is controlled by the excitation volume and radical diffusion. We defined the experimental parametric space for fine features writing: dose, energy, dwell time, which determine the ultimate feature size (resolution) and demonstrated the potential of this technique on a few selected examples such as live-cell encapsulation, and plasmonic sensing.

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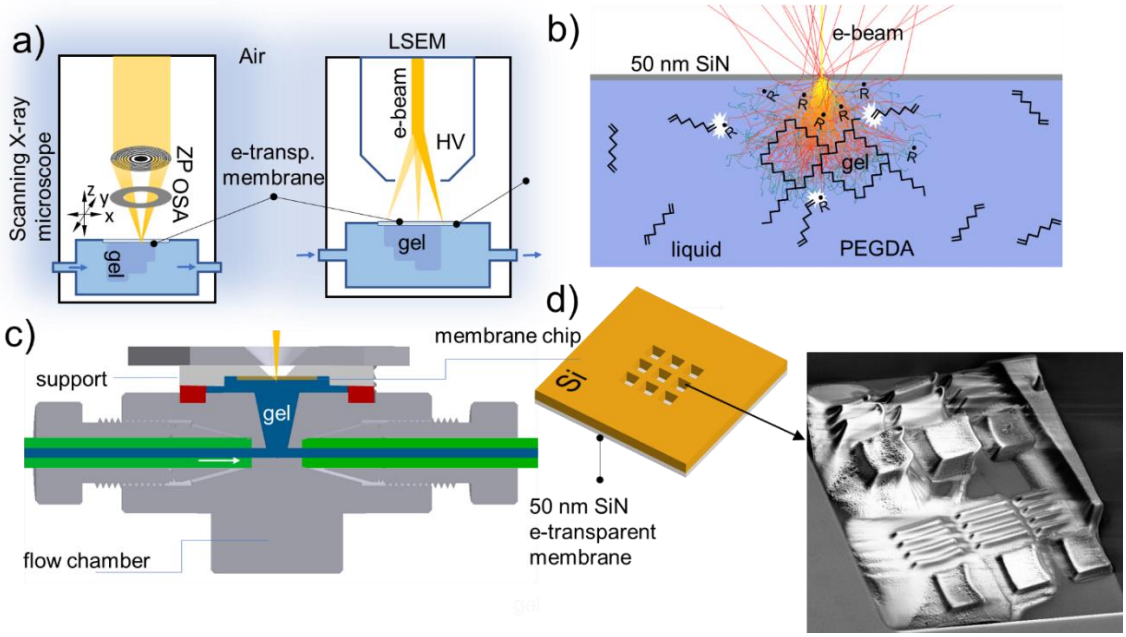

Figure 1. Principe of in-liquid direct writing of high aspect rations of polymers. a) experimental setups for focused X-ray and electron beam printing setups. b) The crosslinking of polymers induced by radiolitic radicals in solution. c) Microflow chamber equipped with array of electron transparent SiN 50 nm thick windows. d) SEM image of the individual 100 x100 μm^2 SiN window patterned with soft X-rays using pre-edge (526 eV) and post-edge (536 eV) O 1s excitations for feature writing.

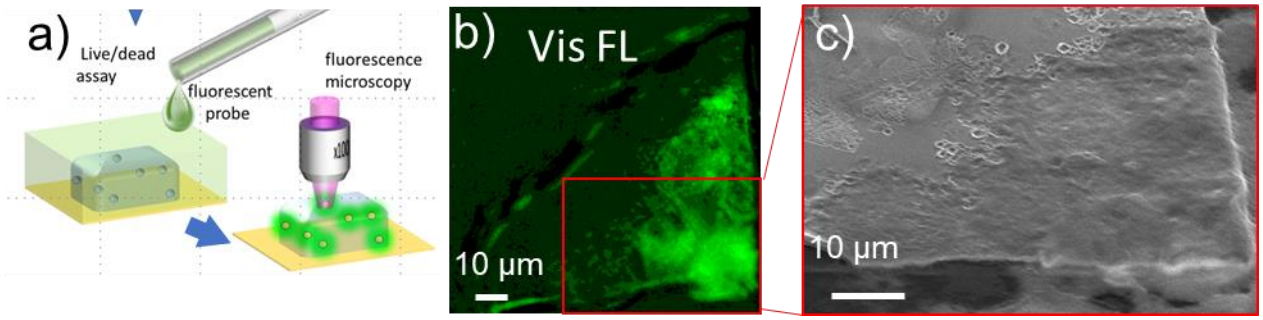

Figure 2. a) E-beam encapsulation of live cells. b) Post exposure fluorescent imaging of the laden cells stained with green dye and imbedded in e-beam cured PEGDA film c) SEM image showing encapsulated cells in the boxed area. All scale bars are 10 microns.