Parallel Nanoscale 3D Printing with Nonlinear Initiation Depletion

Additive manufacturing of sophisticated 3D nanoscale objects commonly uses femtosecond lasers to photopolymerize a light-sensitive resin using multi-photon absorption. This nonlinear process provides high accuracy and flexibility in advanced 3D fabrication; however, it typically has limited throughput and high tool costs. To achieve a highly nonlinear response in one photon process, the concentrations, and components of the photocurable resin are carefully designed based on the free radical polymerization mechanism. In a typical photo-induced free radical polymerization process, the initiator molecules (In) in the resin absorb photon energy (hν) from the laser, they would be excited from the ground state and generate initiating radicals (R·). These initiating radicals later activate the monomers (M) and launch a live chain reaction to increase the molecular weight and form the polymer. Typically, in this free-radical polymerization process, the conversion rate of the monomers is determined by the accumulative amount of photons absorbed, disregarding the intensity and exposure time of the light, which yields a linear process.

This work makes use of a one-photon-based dosage-nonlinearity to fabricate 3D nanostructures, demonstrating a cost-effective method for 3D nanolithography using a low-cost 405 nm continuous-wave diode laser. Here, we designed the initiating system to have a nonlinear response due to several competing effects including initiation, inhibition, depletion, and diffusion. During the process, radicals initiated outside the voxel would be strongly inhibited by inhibiting radicals, to prevent unwanted polymerization, and these inhibiting molecules can slowly recover by diffusion to maintain the inhibition process. Meanwhile, inside the voxel, initiation radicals are quickly generated by the intense light and take over the inhibition effect.

We developed a parallel 3D nanolithographic tool based on this one-photon nonlinear polymerization process using a 405-nm diode laser and demonstrated successful 3D nanoprintings at a 120-nm resolution by controlling the diffusion of initiation and inhibition, a nonlinear intensity-response polymerization. Compared to multiphoton lithography, this method used diode lasers with milliwatt scale power at a higher scanning speed of 100s-1000s μm/s, which is less expensive and allows parallel operations to further improve the performance. To better understand and control this new process, a multiphysics model is constructed to simulate the intensity-dependent nonlinear response by capturing the laser light propagation, free-radical photopolymerization, and mass transport of participating materials. This model successfully predicted the trend of polymer conversion under different conditions in our results from 3D writing experiments under different average powers and scanning speeds.