VOLUMETRIC 3D PRINTING ENABLED BY TRIPLET FUSION UPCONVERSION NANOCAPSULES

Samuel N. Sanders[a,$], Tracy H. Schloemer[a,b,$], Mahesh K. Gangishetty[a], Daniel Anderson[a], Michael Seitz[a], Christopher Stokes[a], and Daniel N. Congreve[a,b;*]

[a]Rowland Institute at Harvard University, Cambridge, MA 02142 USA
[b]Stanford University, Stanford, CA 94305 USA
[$]These authors contributed equally

Two-photon photopolymerization addresses a photopolymerizable resin volumetrically to deliver prints without support structures or layering artifacts in a broad range of materials. This approach scans a focused laser through a resin and takes advantage of the quadratic power dependence of two photon absorption to produce blue light and subsequent photopolymerization exclusively at the focal point. While this approach has advantages, the widespread adoption of two photon photopolymerization is hindered by the need for expensive ultrafast lasers and extremely slow print speeds. Here we present an analogous process, triplet-triplet annihilation driven 3D printing, that enables volumetric printing at a focal point driven by milliwatt-power continuous wave excitation. The key enabling advance is a scalable self-assembly approach that permanently encapsulates nanoscale droplets of photon upconversion solution using just a few nanometer thick silica shell, decorated with solubilizing polymer ligands. These nanocapsules can be dispersed without leakage in a variety of organic media, including 3D printing resins. Crucially, due to the nanoscale dimension of the upconverting capsules, they disperse without optical scatter, allowing a laser to address the entire volume. Further, we introduce an excitonic strategy to systematically control the upconversion threshold to support either mono-voxel or parallelized printing schemes with synthetic modifications. Overall, the proof-of-concept printing presented here paves the way for the attractive benefits of volumetric photopolymerization without the current cost and speed drawbacks hindering widespread adoption.