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3D Laser Printing Based on Two-Step Absorption

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Abstract *We review our recent work on using two-step absorption instead of two-photon absorption for 3D laser printing. This includes single-color two-step absorption for focus-scanning 3D laser nanoprinting based on inexpensive low-power continuous-wave blue laser diodes and two-color two-step absorption for parallelized light-sheet 3D microprinting. ©2022 Martin Wegener*

Introduction

3D laser printing based on scanning a diffraction-limited laser focus through the volume of a photosensitive resin [1] inherently requires an effective nonlinearity to suppress the tails of the laser focus that otherwise accumulate ("proximity effect") and prevent one from printing complex truly three-dimensional objects. In early experiments, this nonlinearity has been provided in optical form by two-photon absorption (see references in [1]). Later, it has become clear that chemical nonlinearities contribute as well, with or without optical nonlinearities. However, the vast majority of applications of 3D laser printing has been based on two-photon or multi-photon absorption. This especially includes commercial 3D laser printers.

To make two-photon absorption efficient, high intensities of light are necessary, which are commonly achieved by tightly focusing femto- or picosecond laser pulses into the resin [1]. Typically, such light sources are costly and large in volume, preventing further miniaturization of 3D laser nanoprinters and slowing down further spreading of this technology.

Here, we review our recent work on replacing two-photon absorption by two-step absorption.

Single-Color Two-Step Absorption

By two-step absorption [2] we refer to a process in which a first photon is absorbed via one-photon absorption, leading to the population of some intermediate or idle (triplet) state of the photoinitiator molecule after vibrational relaxation and intersystem crossing. Ideally, no chemical reaction of any sort is triggered from this idle state. After absorption of a second photon, again via one-photon absorption, the electron is excited from the idle state to some higher excited (triplet) state, from which radicals are generated and photo-polymerization is initiated. Under appropriate conditions [2], the population of the molecule's upper excited electronic state is thereby proportional to the square of the local intensity of light for both, two-step absorption and two-photon absorption.

By using benzil as photoinitiator, BTPOS as scavenger, and PETA as monomer, we have demonstrated 3D laser nanoprinting by scanning the focus of a semiconductor continuous-wave laser diode emitting at 405 nm wavelength with powers well below 1 mW [2]. The achieved spatial resolution surpasses that of 3D laser printers based on two-photon absorption at around 800 nm fundamental wavelength [2].

This work [2] opens the door to drastic miniaturization and cost-cutting of 3D laser nanoprinters.

Two-Color Two-Step Absorption

The speed of 3D laser printing can be boosted by effectively printing with a large number of foci or independent pixels in parallel. This can be accomplished [3] by means of light-sheet 3D printing [1]. Herein, images of a first color (blue) are projected into a plane that coincides with the plane of the light-sheet focus at a second color [3]. The first color mediates the first step in the two-step process, the second color the second step, requiring a different kind of photoinitiator [3] than for one-color two-step absorption [2]. Thereby, we effectively print with 33,000 independent pixels in parallel, leading to a print rate that approaches 10^7 voxels/s [3]. At this print rate, 3D microstructures can be printed in the blink of an eye.

Two-Step Absorption and Depletion

If time permits, we will also present the status of our ongoing work on combining two-step absorption with a depletion mechanism [4]. In analogy to stimulated-emission-depletion (STED) optical microscopy, depletion-mode two-step absorption might allow for breaking the optical diffraction barrier. This would seem especially important for applications of 3D printed architectures in nanophotonics.

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