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Challenges and Opportunities in 3D Laser Printing Based on (1 + 1)-Photon Absorption

Vincent Hahn, N. Maximilian Bojanowski, Pascal Rietz, Florian Feist, Mariana Kozlowska, Wolfgang Wenzel, Eva Blasco, Stefan Bräse, Christopher Barner-Kowollik, and Martin Wegener*

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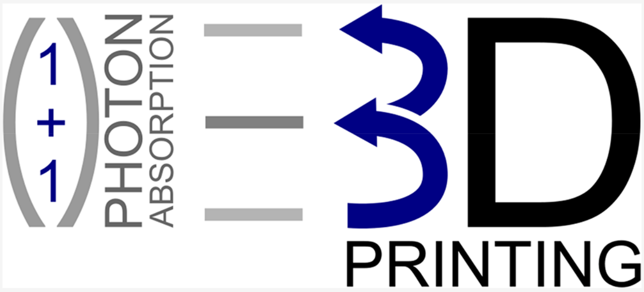

ABSTRACT: Most light-based 3D printing methods rely on optical or chemical nonlinearities to spatially confine the polymerization reaction. In 3D micro- and nanoprinting, this nonlinearity can be provided by two-photon absorption, which describes the simultaneous absorption of two photons. To achieve comparable absorption cross sections for two-photon as in one-photon absorption, short and intense laser pulses with intensities in the range of 1 TW/cm^2 are typically required. Herein, we review three emerging excitation processes that provide a quadratic nonlinearity versus intensity without relying on two-photon absorption: upconversion luminescence, two-step absorption, and triplet−triplet annihilation. We term these “(1 + 1)-photon absorption”. Such processes allow for using continuous-wave lasers at much lower peak laser powers and at much lower cost than those typical for two-photon absorption. We review recent progress, describe current challenges, and outline future perspectives.

KEYWORDS: *photoinitiators, photopolymerization, 3D printing, (1 + 1)-photon absorption, photon upconversion*

INTRODUCTION

In light-based printing (lithography) of objects, molecules called photoinitiators serve as local light-activated switches that trigger specific chemical reactions.[1,2] Most notably, free radical photoinitiators generate primary radicals, which serve as chain starters for radical chain polymerization. Thus, light can locally trigger the polymerization of monomers (photopolymerization).[3] Alternatively, light can induce the reduction of a metal salt (photoreduction) to the metal which is deposited during the metal printing process.[4−6] In two-dimensional (2D) optical lithography of thin layers, one-photon light absorption is sufficient.[7] In certain modalities of three-dimensional (3D) optical printing, 2D layers made along these lines can be stacked, leading to a 3D printed object.[8]

Alternative volumetric optical approaches directly address photoinitiators at a position in 3D space via (i) tight spatial focusing of an ultrafast laser and scanning of that focus,[7,9] (ii) spatial and temporal focusing of an ultrafast laser in projection-based layer-by-layer printing,[10,11] (iii) projecting 2D optical images from various directions in 3D space akin to inverse tomography, called computed axial lithography,[12−14] or (iv) shaping a sheet of light into the plane onto which a 2D optical image is projected with a different color.[15−17] The four described approaches largely differ in printing speed in units of voxels/s and in terms of the accessible minimum voxel size. We refer the reader to recent reviews[18] and to the website in ref 19.

For approaches (i), (ii), and (iv), the photoresins must respond nonlinearly (superlinearly, to be specific) to the local light intensity to reduce the effects of the laser foci’s long-reaching spatial tails, especially along the focusing direction (optical axis), along which the tails asymptotically have a Lorentzian rather than Gaussian shape. Without any nonlinearity, exposure dose accumulates essentially everywhere for complex large three-dimensional objects, rendering 3D volumetric printing impossible. This critical nonlinearity is usually achieved by two-photon absorption, for which the rate of exciting molecules is proportional to the square of the incident light intensity. However, chemical nonlinearities can play an important beneficial role as well.

For (iii), one-photon absorption suffices, but a nonlinearity is highly desirable to reduce unwanted dose accumulation at certain points in 3D space.[13,20] Two-photon absorption has not been used yet for (iii), probably because the required ultrafast laser systems would be prohibitively large and expensive. Similarly, the cost of femtosecond pulsed laser

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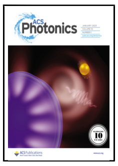

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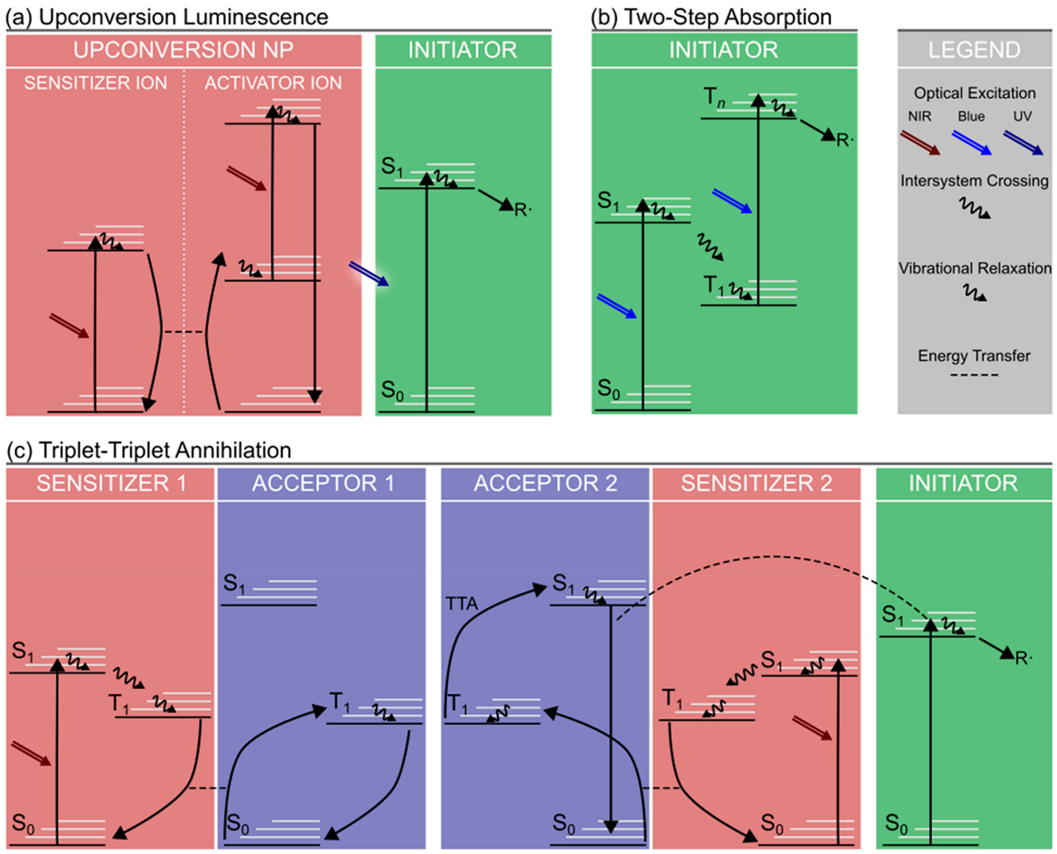

Figure 1. Energy-level diagrams for three reported (1 + 1)-photon absorption mechanisms. (a) In an upconversion nanoparticle (NP, red subpanel), the first absorbed photon excites an ion. The excitation energy is transferred to a second ion (dashed horizontal line). The ion is then further optically excited by a second photon. Note that many other photon upconversion excitation schemes exist.[22] Photoinitiator molecules (green subpanel) are optically excited by ultraviolet (UV) photons emitted by excited upconversion NPs.[23−26] Alternatively, the energy from upconversion NPs can be transferred to photoinitiator molecules via a nonradiative energy transfer, e.g., Förster resonance energy transfer (not shown). (b) In two-step absorption,[17,27] a reluctant photoinitiator is optically excited via an excited singlet to an inactive triplet state. In this state, the photoinitiator can absorb a second photon, which provides sufficient energy to trigger a polymerization reaction. The same energy-level diagram applies for a (1 + 1)-photon excited photochromic molecule.[16] (c) In triplet fusion upconversion, two sensitizer molecules are optically excited by near-infrared (NIR) photons.[28−30] Both sensitizers undergo intersystem crossing to the triplet manifold, from where the excitation energy is nonradiatively transferred to two acceptor molecules. Two excited acceptors can undergo triplet−triplet annihilation, promoting one acceptor to a high-energy excited singlet state. This singlet state transfers energy to an initiator molecule, leading to a polymerization reaction. The energy transfer from the acceptor to the initiator can happen either nonradiatively[30] or radiatively.[29] Acceptor- and photoinitiator-free triplet−triplet-annihilation polymerization has been reported as well.[28]

systems also prohibits a more widespread adoption of 3D printers based on approaches (i) and (ii), creating a demand for nonlinear excitation mechanisms that do not rely on two-photon absorption and costly ultrafast lasers.

The present perspectives article aims at describing recent work on replacing canonical two-photon absorption with mechanisms in which effectively two photons must be absorbed to trigger a chemical reaction. However, with these mechanisms, intense ultrashort lasers are not necessary and rather continuous-wave lasers or even other continuous-wave light sources such as light-emitting semiconductor diodes or lamps can be used. Herein, we nickname such processes “(1 + 1)-photon absorption”. Further, we discuss scientific challenges and future opportunities.

■ REPORTED (1 + 1)-PHOTON ABSORPTION MECHANISMS

We note that related processes for light emitters are well-known under the umbrella term “upconversion luminescence”.[21,22] Here, the absorption of a first photon excites a molecule or a nanoparticle from its ground state to an intermediate state. Subsequently, absorption of a second photon brings the molecule or nanoparticle to a higher excited state, from where luminescence can occur at an optical wavelength shorter than that of either of the two absorbed photons. One should be aware, however, that the notion “upconversion” is also used in a different sense, unrelated to this work, associated with nonlinear optical susceptibilities.[21]

To date, three conceptually different types of processes that are suitable for (1 + 1)-photon absorption in 3D light-based printing have been published. They are illustrated in Figure 1. Let us briefly describe each.

■ UPCONVERSION LUMINESCENCE

We start with a nanoparticle or molecule exhibiting upconversion luminescence (see Figure 1a).[21] Efficient upconversion nanoparticles consist of an inorganic host matrix doped with lanthanide ions (see Figure 2a) such as Yb^{3+}/Er^{3+} or Yb^{3+}/Tm^{3+}.[22] Suppose that the photon energies or wavelengths of the two incident photons are in the visible or

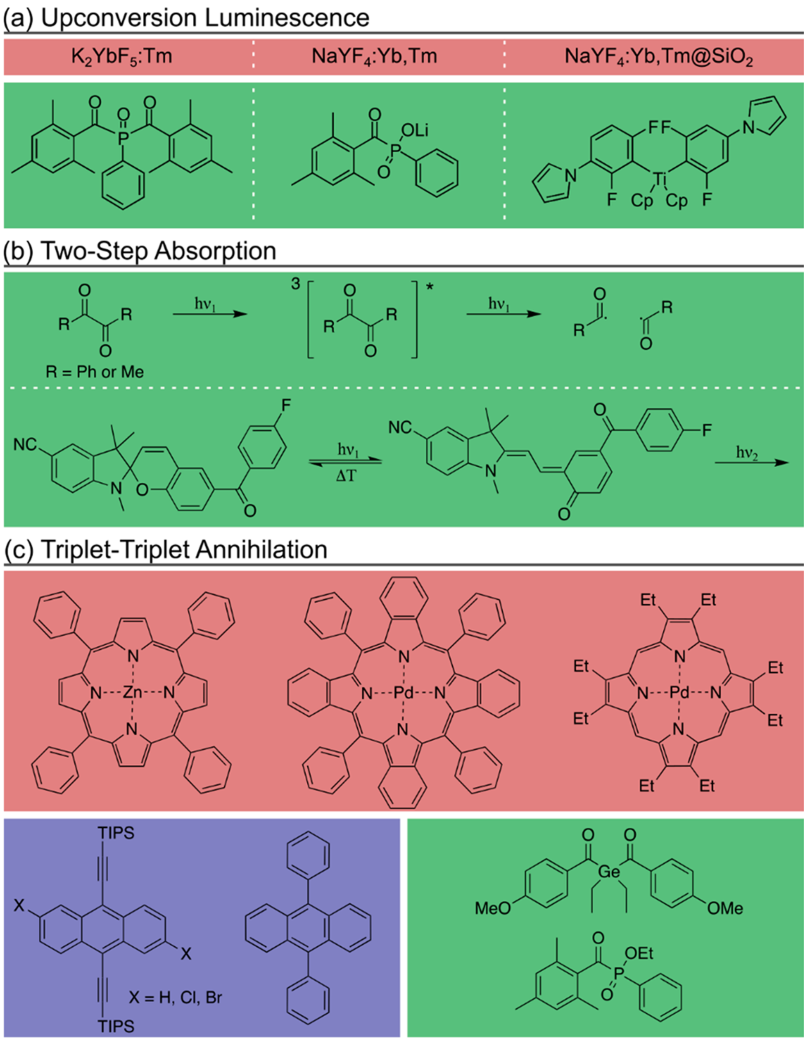

Figure 2. Chromophores used in (1 + 1)-photon-absorption-based 3D printing. Red panels indicate upconversion nanoparticles or porphyrin-complexes, blue panels indicate acceptors, green panels indicate free radical photoinitiators. (a) Left: K_2YbF_5:Tm and Irgacure 819.[23] Middle: $NaYF_4$:Yb,Tm LAP (Lithium phenyl-2,4,6-trimethylbenzoylphosphinate).[25] Right: $NaYF_4$:Yb,Tm@SiO_2 with a titanocene photoinitiator (bis(cyclopentadienyl)bis[2,6-difluoro-3-(1-pyrryl)phenyl]titanium).[38] (b) Upper row: A diketone (benzil or biacetyl) is excited via two-step absorption to yield free radicals.[17,27] Lower row: Spiropyran isomerizes after absorption of a photon to merocyanine. Upon absorption of a second photon, the polymerization is initiated via an amine co-initiator (not shown).[16] (c) In zinc(II) *meso*-tetraphenyl-porphyrin, energy is upconverted via intramolecular triplet−triplet annihilation, i.e., without a separate acceptor molecule. The polymerization is then initiated by an electron transfer from the second excited singlet state of the porphyrin directly to an acrylic monomer (not shown).[28] The sensitizer palladium(II) *meso*-tetraphenyl-tetrabenzo-porphyrin transfers its energy to the acceptor, triisopropylsilane-anthracene (TIPS-anthracene, in blue), which emits a blue photon after a triplet−triplet annihilation. The blue photon excites the photoinitiator Ivocerin (bis(4-methoxybenzoyl)diethylgermanium) (green panel).[29] The acceptor palladium(II) octaethyl-porphyrin sensitizes the acceptor diphenylanthracene, which then emits a blue photon. Irgacure 2100 (a mixture of Irgacure 819 and TPO-L) is used as photoinitiator.[30]

near-infrared spectral region and that they are identical. Under these conditions, the emission probability of an ultraviolet photon can be proportional to the square of the intensity of the incident visible or near-infrared light—as would be the case for two-photon absorption.[31] More generally, also higher non-linearities are possible.[31] The effective nonlinearity can also depend on the intensity of light.[32] If the photoinitiator molecules are homogeneously dissolved in the photoresin, the emitted ultraviolet photon can propagate over distances determined by the absorption length of the surrounding medium, the photoresin. Typically, this absorption length cannot be made very much smaller than 10 μm. Within this length, the ultraviolet photon can excite an ordinary photoinitiator molecule by one-photon absorption (see Figure 1a and 2a), triggering the desired chemical reaction.[23−26,33−37] Thereby, the absorption length limits the achievable minimum printed feature sizes. If the upconversion nanoparticles are coated with the photoinitiator molecules, this limitation does not apply. In this manner, ref 32 has recently obtained 2 μm printed line widths.

The accessible spatial resolution is determined and limited by the absorption length. Therefore, deep sub-μm feature sizes are not in reach with this approach. A conceivable remedy to achieve a finer spatial resolution is given by rather transferring the energy nonradiatively from the upconversion nanoparticle to the photoinitiator molecule, e.g., by Förster resonance energy transfer.[24]

Upconversion-luminescence excitation has been used in macroscopic 3D bioprinting applications.[25] Biological tissue absorbs and scatters infrared light less than ultraviolet light, making upconversion-luminescence nanoprinting with near-infrared excitation attractive for in vivo 3D printing.[25] Moreover, upconversion-luminescence polymerization has also been combined with direct-ink writing, an extrusion-based 3D printing method.[38]

TWO-STEP ABSORPTION

For two-step absorption, we distinguish two approaches. The first approach (see Figure 1b) makes use of a photoinitiator that cannot efficiently generate a primary radical after the absorption of a first photon, i.e., a "reluctant" type-I photoinitiator, e.g., a diketone such as benzil (see Figure 2b).[39−41] Herein, the excited molecule undergoes rapid intersystem crossing to the lowest triplet state after the initial one-photon absorption from the ground-state singlet manifold to the first excited-state singlet manifold. "Reluctant" implies that the molecule remains in the triplet state for a certain time without any fast conversion processes. Thus, a subsequent one-photon excited-state absorption in the triplet manifold can excite the molecule to a higher-energy triplet state. This process is similar to upconversion luminescence, as discussed earlier.

However—and in contrast—consider a system that does not lead to the emission of light but rather to the direct formation of primary radicals, which trigger the photopolymerization. We term this process "two-step absorption".[27] If the colors of the two involved photons are the same, we refer to the process as "one-color two-step absorption".[17] In this case, the local excitation rate is proportional to the square of the light intensity at this position. If the colors of the two photons are dissimilar, we speak of "two-color two-step absorption".[17] Here, the excitation rate is proportional to the product of the two corresponding light intensities (as for the case of upconversion luminescence). In the recently published examples of two-step absorption,[17,27] the lifetime of the triplet (intermediate) state has been shown to be in the range of 100 μs or below. Generally, a long triplet lifetime is beneficial for obtaining high photoresin sensitivity. At the same time, it is disadvantageous when aiming at high printing speeds. Therefore, the lifetime has to be carefully balanced between these two requirements.

In the second approach to two-step absorption, photochromic photoinitiation systems are employed.[16,42,43] Let us consider the case of one specific photochromic molecule, spiropyran (see Figure 2b).[16] Spiropyran is completely transparent in the visible part of the spectrum.[16] After absorption of a first photon in the ultraviolet, the molecule photoisomerizes into the merocyanine form, which exhibits a broad absorption spectrum in the visible light regime. After absorption of a visible photon, an excited benzophenone-type moiety is generated that, in combination with a co-initiator, forms primary radicals and a radical polymerization process is initiated.[16] The lifetime of the latent merocyanine state can exceed 5 s.[16] Such a lifetime is close to 5 orders of magnitude longer than the 100 μs time scale mentioned for ordinary two-step absorption.[27] Following our discussion for two-step absorption, a long lifetime makes the resin extremely sensitive, which is critical for printing large volumes per unit time, yet concomitantly imposing a limit on the printing speed. As for upconversion luminescence (see above) and triplet−triplet annihilation (see below), while each of the two involved one-photon absorption processes is linear, the overall excitation is proportional to the product of the two corresponding light intensities and, again, optically nonlinear. In the experiments reported so far, the two colors were dissimilar.[16]

TRIPLET−TRIPLET ANNIHILATION

Two identical sensitizer molecules, e.g., porphyrins (see Figure 2c), are each excited by a photon that brings each molecule from the singlet ground-state manifold to a singlet excited-state manifold (see Figure 1c).[28] After intersystem crossing to the lowest triplet state, the molecule shall not have sufficient energy to trigger a chemical reaction.[29,30] Next, both sensitizer molecules excite two acceptor molecules, e.g., anthracene derivatives (see Figure 2c), in a triplet−triplet energy-transfer process (see Figure 1c).[29,30] The energy of the two excited acceptor molecules can then be combined by the bimolecular process of triplet−triplet annihilation, promoting one of the acceptor molecules to a high-energy singlet state. This combined energy is subsequently transferred, either radiatively (triplet-fusion upconversion)[29] or nonradiatively,[30,44] to an organic photoinitiator molecule, which generates primary radicals, initiating macromolecular growth.[29,30]

Both bimolecular processes, the triplet−triplet energy transfer and the triplet−triplet annihilation process, require a sufficiently large concentration of sensitizers and *excited* acceptors, respectively. As two molecules need to approach each other in space by diffusion, the time scale of the process is determined by diffusion, which depends on the viscosity of the used photoresin. These bimolecular processes are also proportional to the square of the local light intensity. Again, the color of the two involved photons must be the same—unless two different acceptors undergo triplet−triplet energy transfer.

BENCHMARKING THE PRINTING RATE AND VOXEL SIZE

What 3D printing results have been obtained exploiting the processes listed above? Two relevant figures of merit, namely the 3D printing rate in terms of voxels per second and the accessible voxel size, not only are determined by the photoinitiator and the photoresin but also largely depend on the printing approach and—depending on the approach—also on the available light intensities as well as the optical wavelengths, which dictate the diffraction limited focus diameter. In Figure 3, we summarize the published experimental 3D printing results in terms of the two mentioned figures of merit (as far as this is possible from the published literature). The blue-, red-, and green-colored symbols correspond to 3D printing results achieved by upconversion-luminescence, two-step-absorption, and triplet−triplet-annihilation 3D printing, respectively.

From the above (1 + 1)-photon absorption mechanisms, 3D printers exploiting either upconversion luminescence or triplet−triplet annihilation print with rates of 1 voxel/s up to 40 voxels/s.[25,29,30] In contrast, using two-step absorption has led to the largest printing rates.[27] In particular, using light-sheet 3D printing via two-color two-step absorption, printing rates in the range from 10^5 voxels/s to 10^7 voxels/s have been demonstrated.[16,17] As a reference, common tabletop filament-extruder 3D printers achieve printing rates of merely a few hundred voxels/s.[18]

The demonstrated voxel sizes achieved using upconversion-luminescence 3D printing are about 150 μm.[25] For 3D printing relying on triplet−triplet annihilation, the smallest voxel sizes

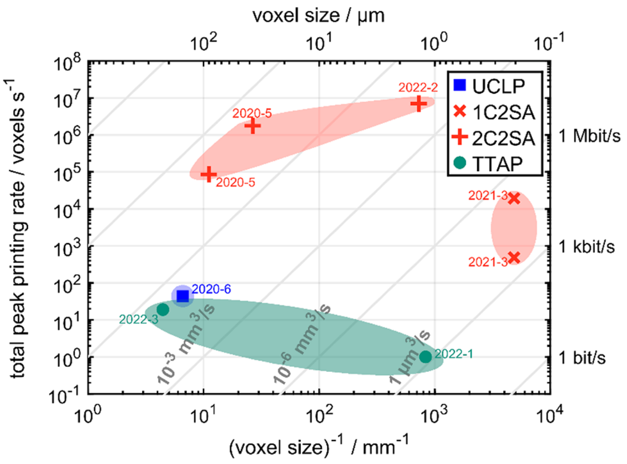

Figure 3. Comparison of the voxel printing rate and voxel size of published (1 + 1)-photon absorption printing results. The different (1 + 1)-photon absorption methods are upconversion luminescence printing (UCLP), one-color two-step absorption (1C2SA), two-color two-step absorption (2C2SA), and triplet−triplet annihilation printing (TTAP). The reference codes are 2020−5[16] (the two data points refer to two different estimates of the printing rate, as outlined in the Supplementary Information of ref 17), 2020−6,[25] 2021−3,[27] 2022−1,[30] 2022−2,[17] 2022−3.[29] For other mechanisms discussed in this perspectives article, the original papers do not provide the information required to represent their results in this chart. A maintained and updated version of this figure is provided on https://3DprintingSpeed.com. This figure is adapted from ref 18 and is available under the CC BY 4.0 license (https://creativecommons.org/licenses/by/4.0/). Copyright (2020) Wiley.

published even range down to almost 1 μm.[30] Overall, one-color two-step absorption at 405 nm wavelength has led to the smallest voxel sizes and the best spatial resolutions for any optical 3D printing approach, especially surpassing previous best values for two-photon absorption.[27] The voxel sizes achieved thereby are even comparable to combining two-photon absorption and depletion mechanisms (STED-inspired 3D nanoprinting), the current top-tier approach for high-resolution two-photon-absorption 3D nanoprinting.[19,27,45] Advantageously, however, one-color two-photon nanoprinting does not require the meticulous alignment of two differently colored and differently shaped laser foci, as is the case for STED-inspired 3D nanoprinting.[45]

Figure 4 shows a gallery of 2D and 3D structures fabricated via the above presented processes and allows for a more qualitative comparison. The structures in Figure 4a−f are fabricated via upconversion luminescence. Figure 4b,c displays colorful structures obtained by combining direct-ink writing and upconversion polymerization by a 50 W laser.[38] The 3D structure in Figure 4f reveals feature sizes of a few hundred micrometers, printed with layer exposure times of 15 s and an excitation wavelength of 980 nm.[25] In Figure 4g,h, results of light-sheet 3D printing via a two-color two-step-absorption photochromic sensitizer are shown.[16] 3D microstructures obtained by one-color two-step-absorption with a 405 nm wavelength laser diode are displayed in Figure 4i−k.[27] Here, scan speeds of 1 to 3 mm/s and laser power values of around 300 μW (or an intensity of ~10^6 W/cm^2) were used. The structures in Figure 4l−s are produced via triplet fusion upconversion. In Figure 4l,m, scanning fluorescence microscope images of 2D structures fabricated using either a halogen lamp (Figure 4l) or a 561 nm wavelength solid-state laser (Figure 4m) are shown.[28] The latter is 3D printed with a focus scan speed of 21 mm/s and a light intensity of ~10^5 W/cm^2. Figure 4n,o shows photographs of a 3D printed benchy structure. There, the total print duration was 1 h 50 min, yielding an estimated scan speed of 2.5 mm/s and a focus intensity of 4.7 × 10^3 W/cm^2 (laser power 3.8 mW) at a wavelength of 637 nm.[29] Finally, the 3D microstructures shown in Figure 4p−s were printed with a white LED, using voxel exposure times of 0.1 s and an intensity of 17 W/cm^2.[30]

■ CHALLENGES

On balance, all (1 + 1)-photon absorption processes still suffer in one way or another from the proximity effect, which is the unwanted dose accumulation arising from multiple exposures at other locations or from exposing large volumes in remotely distant regions. The proximity effect can at least have four different origins.

First, even with an ideal two-photon absorption process, the squaring of the spatial intensity tails of a laser focus does not completely suppress exposure in the tail regions. In two-step absorption, the effective nonlinear exponent can be two, as for ideal two-photon absorption. The exponent can also be smaller than two and approach unity from above.[27] This behavior can, for example, arise for high excitation intensities,[31] leading to partial saturation of the intermediate energy level. In this case, the proximity effect is more prominent than for ideal two-photon absorption.

Second, photoresin ingredients may be consumed irreversibly in the photopolymerization reaction. For example, oxygen serves as a quencher in many processes. This has two important effects. First, the polymerization threshold laser power increases in the presence of oxygen. Second, oxygen spatially confines the polymerized volume, improving the 3D printing resolution.[46] However, oxygen is consumed in the quenching process. While oxygen diffusion from the surrounding photoresin rapidly replenishes a local oxygen deficit, these processes successively reduce the overall available oxygen within the entire photoresin droplet or cuvette. The oxygen diffusion from the surrounding air into the photoresin is typically slow, enforcing slow printing speeds in order to retain a steady oxygen concentration. The situation is more severe for other quenchers or scavengers, which do not replenish at all from the surrounding atmosphere. Thereby, exposure at one location affects the polymerization threshold even at remotely distant positions in the photoresin.

The latter can be avoided by eliminating irreversible consumption of photoresin ingredients or challenging depletion processes. Hence, improved choices for scavengers are desired. One way to identify suitable scavengers is by tedious analytical screening experiments. A more convenient route could be provided by theoretical predictions of the reactivity between scavengers and photoinitiators. However, we are not aware of any theoretical publication reliably describing the complex processes involving (1 + 1)-photoinitiators, scavengers, quenchers within the liquid monomer on a microscopic level and with predictive power. Improvements in the detailed understanding of photochemical reactions, especially by means of quantum mechanical calculations, are urgently required as theoretical guidance and design might ultimately reduce or even eliminate time-demanding trial-and-error experimentation. For two-photon photoinitiators, density-functional-theory (DFT) calculations have been performed and compared to experiments.[47,48]

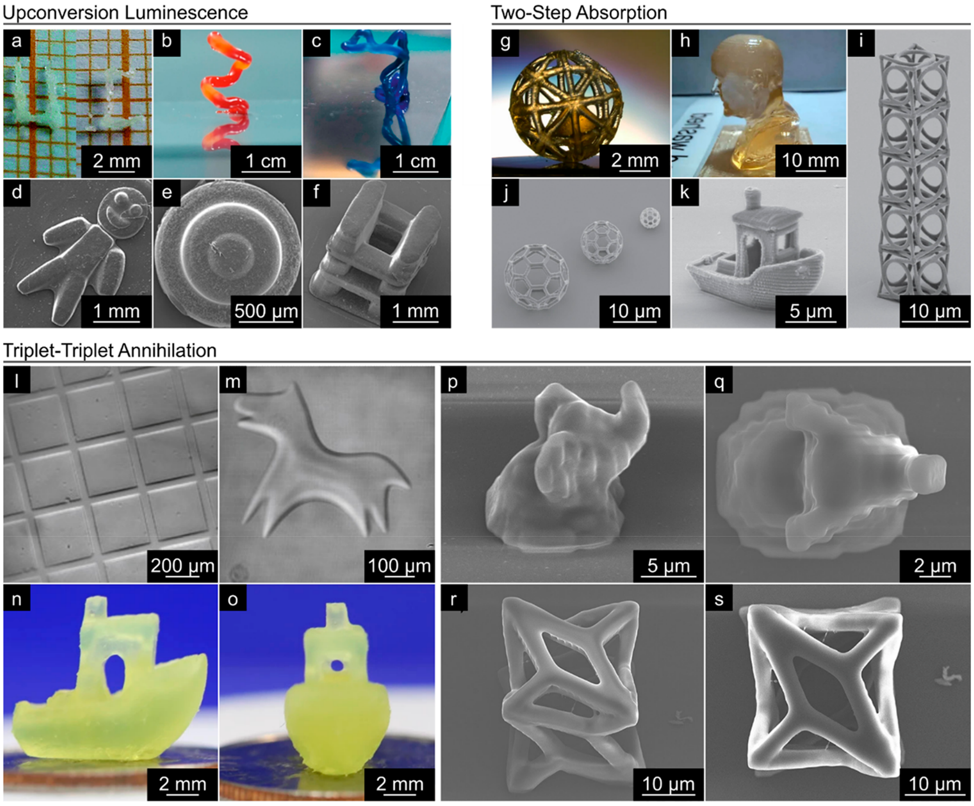

Figure 4. Gallery of selected (1 + 1)-photon absorption 2D and 3D printed structures. (a−f) 2D and 3D printed structure using upconversion luminescence.[23,25,38] The structures in panels (b) and (c) were printed by combining (1 + 1)-photon absorption and direct ink writing.[38] (g−k) 3D structures printed using two-step absorption. The macroscopic structures in panels (g) and (h) were fabricated using light-sheet 3D printing (xolography) using two-color two-step absorption,[16] whereas the microscopic structures in panels (i), (j), and (k) were printed using one-color two-step absorption.[27] (l−s) Fabricated structures using a triplet fusion upconversion excitation.[28−30] Panel (a) is reproduced with permission from ref 23. Copyright (2016) Royal Society of Chemistry. Panels (b,c) are reproduced from ref 38 and are available under the CC BY 4.0 license (https://creativecommons.org/licenses/by/4.0). Copyright (2020) Springer Nature. Panels (d−f) are reproduced from ref 25 and are available under the CC BY-NC 4.0 license (https://creativecommons.org/licenses/by-nc/4.0). Copyright (2020) American Association for the Advancement of Science. Panels (g,h) are reprinted with permission from ref 16. Copyright (2000) Springer Nature.[16] Panels (i−k) are reproduced with permission from ref 27. Copyright (2021) Springer Nature. Panels (l,m) are reprinted with permission from ref 28. Copyright (2020) Elsevier.[28] Panels (n,o) are reprinted with permission from ref 29. Copyright (2022) Springer Nature.[29] Panels (p−s) are reprinted with permission from ref 30. Copyright (2022) American Chemical Society.

Third, for excitation processes involving diffusion of one molecular species, the effective excitation profile is no longer solely determined by the laser focus or the laser foci but also by the associated diffusion lengths.[30] Especially if these diffusion lengths exceed the diameter of the exposed volume, diffusion leads to an increased effective proximity effect.

Fourth, unwanted side reactions from the intermediate state in nonideal two-step-absorption photoinitiators may result in dose accumulation, e.g., via proton abstraction. Such side reactions eventually also lead to polymerization via an unfavorable one-photon channel.[27,49] Overall, this leads to an effective nonlinearity exponent of one, for which dose accumulation in the laser-focus tails is especially detrimental.

In the published results on (1 + 1)-photon absorption, the light intensities used to trigger photopolymerization range from 10^1 W/cm^2 to 10^6 W/cm^2.[28−30] These values are already much lower than the peak intensities of order 10^{12} W/cm^2 encountered in two-photon-absorption 3D nanoprinting.[15] Yet, state-of-the-art light-emitting diodes are capable of emitting about 100 W/cm^2, making them not yet quite suitable for some of the published (1 + 1)-photon absorption printing approaches.

■ ALTERNATIVE NONLINEAR ABSORPTION PROCESSES

In addition to possibly improving the above-mentioned (1 + 1)-photon excitation processes by investigating alternative molecules, one can explore the following conceptually new excitation processes.

Many photoinitiators are, to some degree, solvatochromic or halochromic, i.e., their absorption band shifts with the solvent polarity or the pH value of the surrounding medium.[50−54] Moreover, Norrish type II photoinitiators show a reduced reactivity in acidic aqueous photoresins.[55] Such a pH sensitivity can be exploited to obtain a superlinear behavior by incorporating photoacidic or photobasic molecules into a (water-based) photoresin. Photoacidic molecules undergo reversible proton dissociation upon irradiation,[56,57] allowing a local tuning of the photoresin's pH value and hence the photoinitiator's absorbance. The photoacid can locally switch the photoinitiator from a transparent state to an absorbing state at the excitation wavelength.

An alternative concept is to employ photosensitive polymerization inhibitors. Photoactivatable inhibitors have already been used to suppress the polymerization reaction in stereolithography locally.[58] The opposite mechanism, an optically deactivatable inhibitor, could be used in a (1 + 1)-photon absorption scheme to permit photopolymerization only in a confined volume. For this concept, both the photoinitiator and the photoactivatable inhibitor can be excited via one-photon absorption. Promising inhibitor candidates have been presented,[59,60] but remain to be tested in the context of nonlinear absorption.

At first glance, a further mechanism for (1 + 1)-photon absorption is provided by photochemically masked photoinitiators.[61−64] Absorption of a first photon removes the masking (or protecting) group from a photoinitiator. A second photon excites the unmasked photoinitiator and triggers the polymerization reaction. Here, the unmasked photoinitiator is a stable product. In a 3D printing scenario, all photoinitiators located in the tails of the laser focus become eventually deprotected and thereby effectively turn into one-photon absorption initiators. In other words, the effectively infinite intermediate-state lifetime of photochemically masked photoinitiators is detrimental for applications in the sense of (1 + 1)-photon-absorption 3D printing.

Finally, consider a photoresin in which a thermally activated radical initiator, e.g., an azo derivative, a (hydro)peroxide, or an alkoxyamine-based initiator, is combined with a heat generating dye, e.g., a cyanine borate[65] or a gold nanorod.[66] The local heating necessary to start the polymerization reaction is provided by the one-photon-excited dye molecules or gold nanorods. Thereby, even near-infrared light can be used to trigger the polymerization reaction. While such a photothermal system does not provide a nonlinearity strictly through (1 + 1)-photon absorption, the dissociation rate of the thermal initiator follows an Arrhenius behavior and is thus highly nonlinear.[67] Nevertheless, the voxel size in such a system is governed by the diffusion length of heat, which can become much larger than the laser focus excitation diameter. This aspect could be improved by having a (1 + 1)-photon absorption process in which a photothermal process mediates only one of the two excitation steps.[42]

OPPORTUNITIES

Breaking the Diffraction Barrier. All of the above 3D printing modalities can, in principle, lead to individual printed features (much) smaller than the used wavelength of light. However, the resolution in the sense of minimum distance between adjacent separate features is fundamentally limited by optical diffraction by the second-order Sparrow criterion.[45] Here, "second order" refers to a process proportional to the squared laser intensity. However, the diffraction barrier in 3D laser printing can be broken systematically by invoking depletion processes inspired by stimulated-emission-depletion (STED) microscopy.[45] In STED-inspired 3D laser printing, excited photoinitiator molecules in the periphery of the excitation laser focus are brought back to the ground state by a second, differently colored laser beam. STED-inspired approaches have extensively been investigated in two-photon-absorption-based 3D laser printing.[45,68] The best-published results have reduced the voxel size by about a factor of 2 with respect to the diffraction barrier along all three spatial directions, leading to a reduction in voxel volume by about 1 order of magnitude.[45]

Regarding combining STED-inspired depletion with (1 + 1)-photon absorption, possibilities exist for all of the mechanisms described above. In principle, the canonical STED process works with all three presented (1 + 1)-photon absorption mechanisms. Under normal circumstances, stimulated emission induces only intrasystem electronic transitions, i.e., without changing the molecule's spin-multiplicity. Since typical lifetimes of excited singlet or triplet states are on the order of a few nanoseconds, high optical intensities are required for efficient STED. An alternative mechanism can be exploited for the triplet−triplet-annihilation process and the two-step-absorption process, both of which involve a triplet molecular state. Here, the depletion laser beam can induce a transition from the triplet ground-state to a higher excited triplet-state, from which the molecule returns to the singlet ground state via efficient reverse intersystem-crossing.[69−71] Typical triplet-state lifetimes are on the order of micro- and milliseconds, enabling depletion by comparably low optical intensities. Similarly, certain photochromic molecules suitable for two-step-absorption photoinitiation can return from the activated-state to the ground-state conformation by absorbing a photon of suitable color.[72]

Printing with Tunable Voxel Size. Recently, the concept of grayscale lithography was introduced in two-photon 3D printing.[73] By dynamically increasing the laser power, the volume of the polymerized voxel is adapted to the 3D structure being printed—the volumetric printing rate increases, which is especially useful for structures containing regions with high filling fractions. However, the dynamic range of the voxel size in two-photon 3D printing is limited for two reasons. First, high peak intensities can lead to microexplosions by higher-order multiphoton absorption processes,[74] and second, due to the limited laser power. Both problems are virtually absent in (1 + 1)-photon absorption, which requires low polymerization-threshold peak intensities. Thereby, (1 + 1)-photon absorption 3D printing can potentially achieve large volume printing rates and pave the way toward more scalable 3D printing. However, one must ensure that the proximity effect (see above) does not come in the way.

SUMMARY

We have summarized and compared three conceptually different one-color and two-color photoinitiation mechanisms that can lead to an effective optical nonlinearity other than that of traditional 2-photon absorption. We term such processes "(1 + 1)-photon absorption". Importantly, these do not require pico- or femtosecond lasers, which tend to be large and costly, but rather allow for using compact and inexpensive continuous-wave lasers. When comparing the two important figures of merit, the minimum achievable voxel size and the maximum possible printing rate, of these mechanisms, we find that two-step absorption is presently leading for 3D laser printing. In two-step absorption, a first photon excites an initiator molecule by one-photon absorption from its ground state to an intermediate or idle state, from which a second photon at the same or a different color excites the molecule by one-photon absorption to a yet higher excited state, from where radicals are generated, and the polymerization commences. As future perspectives, we have outlined conceptually distinct (1 + 1)-photon-absorption processes, the need for reducing the proximity effect, and the possibility of combining two-step absorption with depletion processes mediated by a second or third laser color, respectively, to systematically break the diffraction barrier of light for 3D laser printing.

AUTHOR INFORMATION

Corresponding Author

Martin Wegener − *Institute of Applied Physics (APH), Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany; Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany*; Email: martin.wegener@kit.edu

Authors

Vincent Hahn − *Institute of Applied Physics (APH), Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany; Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany*; orcid.org/0000-0003-3229-3285

N. Maximilian Bojanowski − *Institute of Applied Physics (APH), Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany; Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany*

Pascal Rietz − *Institute of Applied Physics (APH), Karlsruhe Institute of Technology (KIT), 76131 Karlsruhe, Germany; Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany*

Florian Feist − *Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany*; orcid.org/0000-0002-2051-5488

Mariana Kozlowska − *Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany*

Wolfgang Wenzel − *Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany*; orcid.org/0000-0001-9487-4689

Eva Blasco − *Institute for Molecular Systems Engineering and Advanced Materials, Ruprecht-Karls-Universität Heidelberg, 69120 Heidelberg, Germany; Institute of Organic Chemistry (OCI), Ruprecht-Karls-Universität Heidelberg, 69120 Heidelberg, Germany*; orcid.org/0000-0002-0849-4223

Stefan Bräse − *Institute of Organic Chemistry (IOC), Karlsruhe Institute of Technology (KIT), 76133 Karlsruhe, Germany; Institute of Biological and Chemical Systems-Functional Molecular Systems (IBCS-FMS), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany*

Christopher Barner-Kowollik − *Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany; Centre for Materials Science, School of Chemistry and Physics, Queensland University of Technology (QUT), Brisbane, Queensland 4000, Australia*; orcid.org/0000-0002-6745-0570

Complete contact information is available at: https://pubs.acs.org/10.1021/acsphotonics.2c01632

Notes

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