Colorful 3D Printing: A Critical Feasibility Analysis of Multi-Wavelength Additive Manufacturing

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ABSTRACT: Employing two colors of light to 3D print objects holds potential for accessing advanced printing modes, such as the generation of multi-material objects from a single print. Thus, dual-wavelength-driven photoreactive systems (reactions that require or utilize two wavelengths) and their exploitation as chemo-technological solutions for additive manufacturing technologies have experienced considerable development over the last few years. Such systems saw an increase in printing speeds, a decrease in resolution thresholds, and—perhaps most importantly—the actual generation of multi-material objects. However, the pace at which such reactive systems are developed is moderate and varies significantly depending on the fashion in which the two colors of light are employed. Herein, we address for the first time the varying logic conjugations of light-activated chemical compounds in dual-wavelength photochemical processes in a systematic manner and consider their implications from a photochemical point of view. To date, four dual-wavelength reaction types have been reported, termed synergistic (λ_1 AND λ_2), antagonistic (reversed λ_1 AND λ_2), orthogonal (λ_1 OR λ_2), and—most recently—cooperative (λ_1 AND λ_2 or λ_1 OR λ_2). The progress of their implementation in additive manufacturing is assessed individually, and their concurrent and individual chemical challenges are identified. These challenges need to be addressed for future dual-wavelength photochemical systems to progress multi-wavelength additive manufacturing technologies beyond their current limitations.
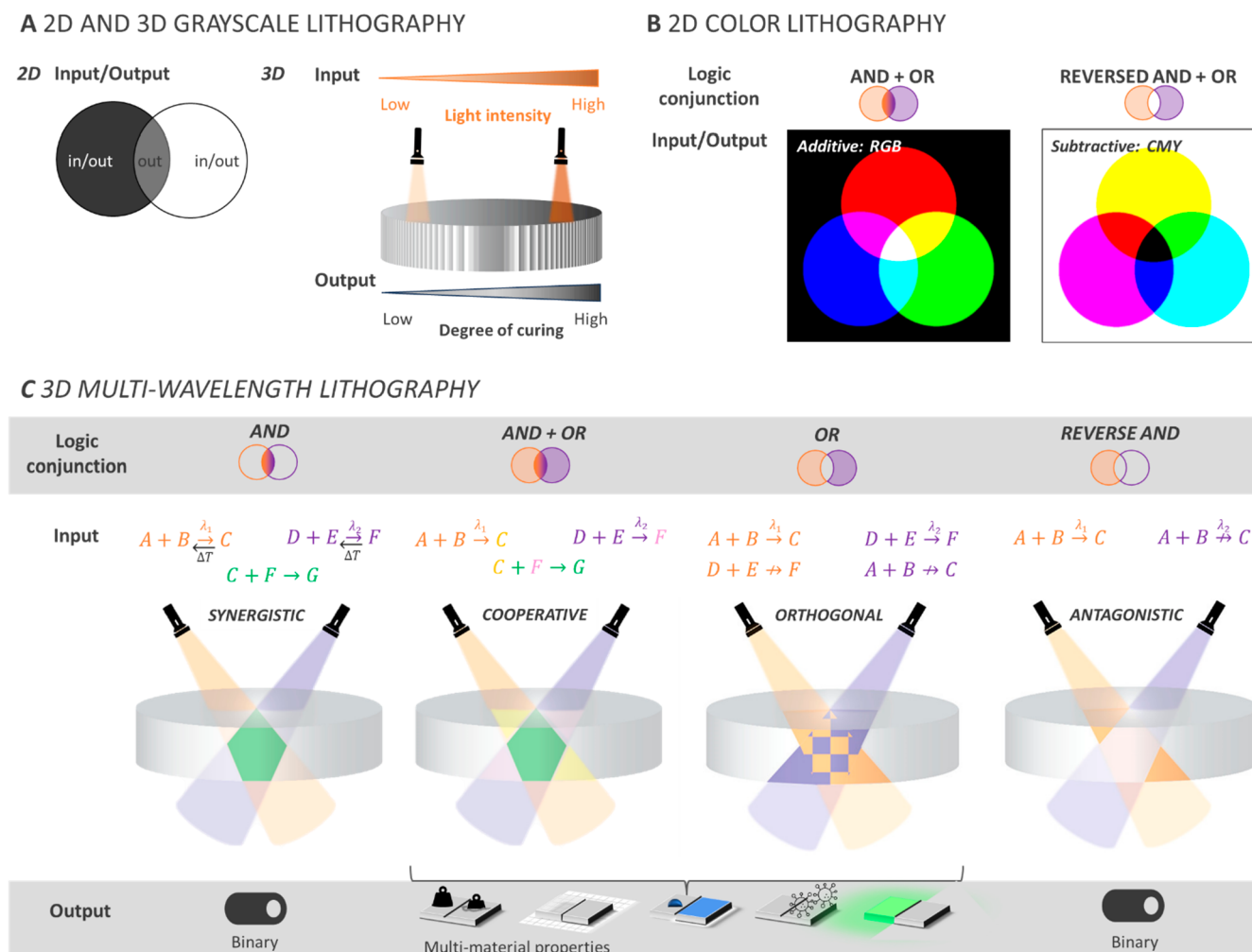
While standard office and at-home desk printers have been able to print colorful images for a long time, this technology was once unheard of.[1] Today, we are on the verge of experiencing an analogous technological transformation in the realm of three-dimensional (3D) printing by utilizing multiple wavelengths or wavelength regimes for light-based additive manufacturing.[2] Hereby, the level of complexity is strongly increased for both the input and output of the printing process (refer to Scheme 1).

On the input side, the printing technology as well as the logic conjunction of the light-activated chemical compounds can lead to vastly different chemical outcomes. The light-activated reactivity of a chemical compound relies on the altered potential energy surface of its excited state compared to its ground state.[3] For wavelength orthogonality, reaching this altered energy surface via single-photon excitation is key, as multiphoton excitation exhibits a distribution of the number of photons, which leads to the reactive species. Thus, the range of wavelengths, which make the active species accessible, broadens, and the chromatic specificity decreases. Within the realm of single-photon excitation, two types of light sources can be utilized: monochromatic lasers, which only emit one wavelength, or multichromatic light-emitting diodes (LEDs), which emit a distribution of wavelengths within a certain (narrow) range. We note that in addition to wavelength, light intensity is a key parameter that influences the outcome of light-induced reactions. In this context, we refer the reader to literature relating to grayscale printing.[5] While lasers provide a perfect wavelength resolution and potentially high light intensities to drive the reaction, LEDs are more cost-efficient and provide the

opportunity to simultaneously illuminate larger areas for increased printing speeds. Wavelength orthogonality is a behavior that is described as two light sources having diverging effects on a light-responsive molecule.[4] This type of behavior has also been termed chromatic orthogonality in a review by Bochet.[6] While both terminologies, in essence, mean the same phenomenon, we suggest that they should not be used equivalently. For monochromatic lasers, wavelength orthogonality seems to be the more appropriate term, while for the use of LEDs, chromatic orthogonality depicts the reality of orthogonal wavelength ranges more accurately. However, for the sake of having uniform nomenclature in the literature and because the use of LEDs and lasers may occur simultaneously or may be interchangeable for certain objectives, we suggest the general utilization of the more common term wavelength orthogonality.

On the output side, there are several options for the outcome of each of the types of chemical interactions. Synergistically[7−10] and antagonistically[11−14] driven processes obtain binary results: a covalent chemical bond is formed, leading to highly localized material deposition, or the chemical composition of the photoreactive formulation remains unaltered. Compared to single-color additive manufacturing, synergistic and antagonistic

Scheme 1. Different Types of Lithography Showcasing the Increasing Complexity of the Input and Output of Different Printing Processes: (A) 2D and 3D Grayscale Lithography, (B) 2D Color Lithography, and (C) 3D Multi-Wavelength Lithography[a]

[a](A) An early approach to chemically controlling material properties in a spatially resolved manner during 3D printing in an analogy to grayscale printing in 2D. A comparison of (B) logic conjunctions for additive and subtractive 2D color lithography and (C) logic conjunctions for light-activated chemical compounds in a light-based additive manufacturing process and their effect on the output (binary material formation for high resolution and fast printing speeds or multi-material formation). Some graphical elements were adapted from ref 4. Copyright 2021. American Chemical Society.

curing has the potential to enhance the speed and resolution of the printing process. For orthogonal[15] and cooperative[16] printing technologies, curing will occur for any of the applied wavelengths, yet the activated species and thus the materials that are produced will be different at each wavelength. Thus, targeted properties can potentially be generated from the same photoreactive formulation, i.e., the same 3D printing cartridge. These properties are not limited to color, as it is the case in two-dimensional (2D) ink printing; rather, they could be a variety of material properties, such as mechanical properties, transparency, hydrophobicity, or cell affinity.[15]

While the substantial variability of multi-wavelength additive manufacturing promises access to a large variety of soft matter materials and material combinations, the technology is still in its infancy. The field of multi-wavelength postmodifications has progressed significantly,[15,17] paving the way for true dual-wavelength printing. However, only some key examples, as cited above, have been pioneered in the latter case, and most of those have been optimized to a specific set of photochemical reactions. Thus, substantial research is required to develop multi-

wavelength printing into a broadly applicable platform technology. Interestingly, the situation is comparable to the beginning of 2D color images, where each individual image needed to be carefully set with an array of stencils specific to the image. In the following sections, we aim to critically evaluate the chemical and technological challenges that need to be addressed in order to advance multi-wavelength additive manufacturing from a case-by-case optimized printing process to a highly potent platform technology with exceptional variability.

CURRENT STATUS OF MULTI-WAVELENGTH ADDITIVE MANUFACTURING

Progress on the different types of 3D multi-wavelength lithography varies significantly. For binary systems, where the photosensitive resin exists only in either its fully cured state or its original, unaltered state, significant progress has been achieved with respect to the generalization of the AND-type initiating systems, which are generally available for radically curable formulations and, in some instances, cationically curable formulations. We note that in the literature, the term

Scheme 2. Network Formation Strategies in Additive Manufacturing: (A) Photoinitiator-Based Chain-Growth Reactions[a] and (B) Chromophore-Containing Precursors for Step-Growth Reactions[b]
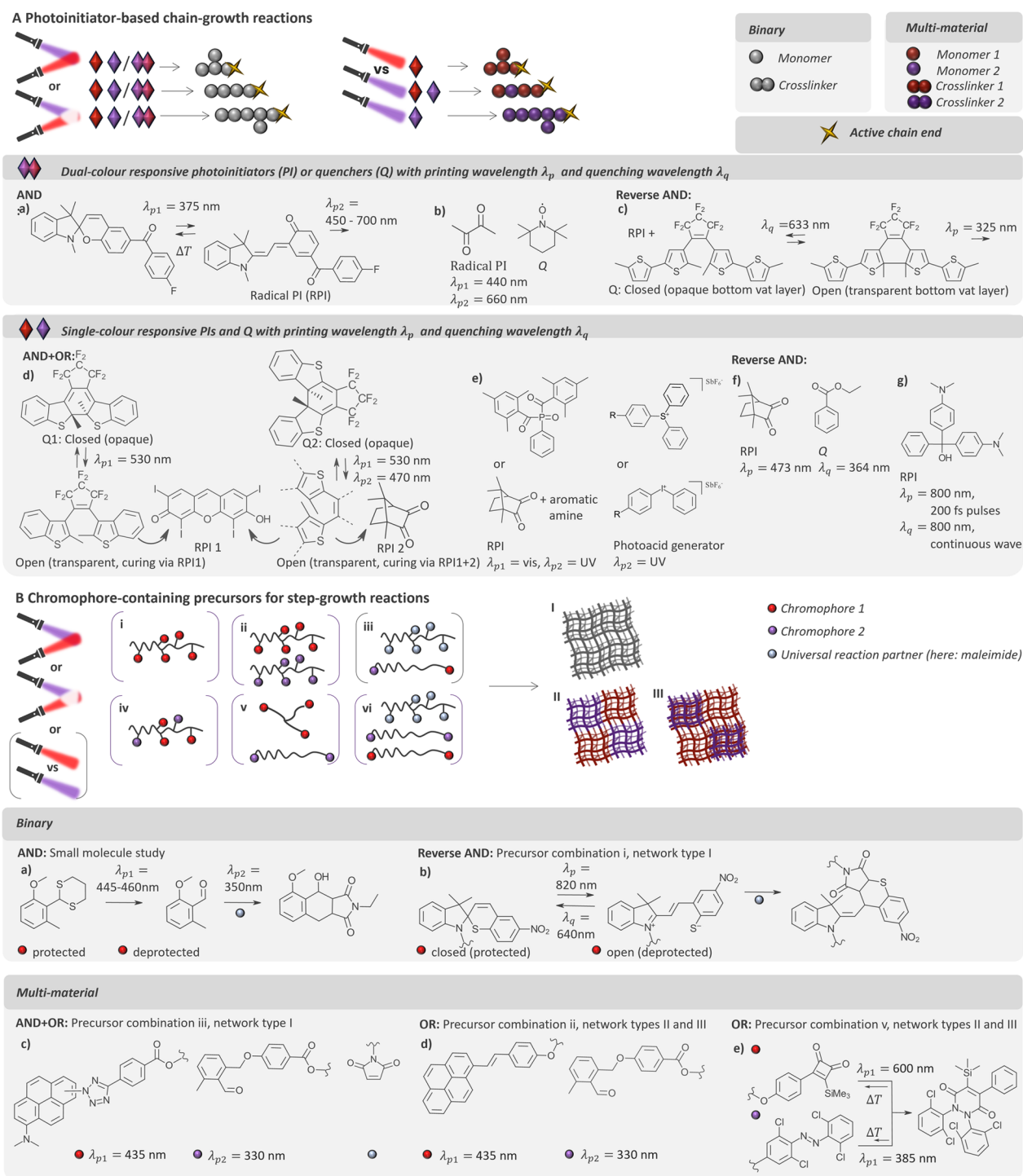
[a]Photoinitiator (PI) -based chain-growth with one dual-wavelength responsive PI for AND-type network formation: (a) spiropyran-protected radical PI,[9] (b) two-color two-step responsive diketone radical PI with TEMPO radical quencher (Q) to inhibit one-color one-step initiation,[8] and (c) open/closed ring isomers of bithiophene.[23] PI-based chain-growth via an interdependent system of single-wavelength responsive molecules for AND-type network formation: (f) a camphorquinone radical PI combined with a benzoate radical Q[24,25] and (g) malachite green carbinol base as a radical two-photon PI, which is effectively quenched by irradiation at the same wavelength with one-photon irradiation.[22] PI-based chain-growth via an interdependent system of single-wavelength responsive molecules for AND+OR-type network formation: (d) similar open/closed ring isomers that were utilized in (c) as solution masks for radical PIs[26] and (e) a radical PI for the radical photopolymerization of acrylates in combination with a photoacid generator (PAG) for the cationic photopolymerization of epoxides.[27] [b]Uncatalyzed light-initiated step-growth through chromophore-containing monomers for binary AND-type network formation: (a) light-stimulated deprotection of α-methylbenzaldehyde (MBA) with subsequent light-induced enolization to activate it for a Diels−Alder cycloaddition (DA-CA) with maleimide (MI) as a universal reaction partner[28] and (b) light-gated DA-CA of spiropyran in its open form with MI.[29] Uncatalyzed light-initiated step-growth through chromophore-containing monomers for multi-material AND+OR-type photosensitive resins: (c) DA-CA of MBA and MI and/or nitrile imine tetrazole−ene CA of a

Scheme 2. continued

tetrazole-based chromophore with MI[30] and (d) two DA-CAs, which occur independently from each other at two wavelengths, with a pyrene- and an MBA-based chromophore.[31,32] Uncatalyzed light-initiated step-growth through chromophore-containing monomers for multi-material OR-type network formation: (d) as explained previously and (e) CA of a *cis*−*trans* reactivity-gated azobenzene and a reversibly photogenerated ketene.[7]

"photoresist" has been adapted as a shortened version of "negative photoresist" from its original use in 2D lithography, and it is used almost interchangeably with the term "photosensitive resin". Herein, we adopt the more intuitive description of "photosensitive resin" for light-driven 3D printing.

Before reviewing the chemical reaction systems for multi-wavelength lithography and classifying them with respect to their logical conjunction, we note that two fundamental network formation strategies are utilized for additive manufacturing (Scheme 2). Traditionally, photopolymerization has been commenced by primary radicals derived from a photoinitiator to initiate the chain-growth of (meth)acrylates or step-growth thiol−ene polymerization. More recently, the cationic photopolymerization of epoxies in parallel to radical photopolymerization has been adopted broadly with the use of photoacid generators, which release radicals and acids upon irradiation. Utilization of chain-growth reactions based on purely non-radical polymerization mechanisms has been implemented in only a few instances so far. For multi-wavelength reactivity, either one dual-wavelength responsive photoinitiator is used (AND-type network formation) or two single-wavelength responsive photoinitiators are used (OR-type network formation). With the rise of click reactions,[18−22] light-triggered network formation has also been achieved using chromophore-containing monomers, which can either undergo uncatalyzed dimerization or react with each other in pairs. For the purposes of this Perspective, we note that radical and cationic photoinitiators are chromophores by definition, as they absorb light efficiently via their extended aromatic structures. However, when we reference chromophore-based printing in this Perspective, we exclude them from this definition to differentiate between the two types of network formation. The network architecture in these step-growth networks is thereby dominated by the monomer architecture, which can be a prepolymer containing several pendant chromophores, a dilinker, or a star-shaped monomer with chromophores at the ends of its arms. The distribution of chromophores within the monomers (AA-BB versus AB step-growth) can also influence the reactivity of the system. For example, homo- or heterotelechelic dilinkers will exhibit drastically different crosslinking abilities: a homotelechelic dilinker can already act as crosslinker with only one color of light, while a heterotelechelic dilinker may only be able to undergo covalent bond formation on both sides if two colors of light are present. Furthermore, the chromophores may also undergo reactions with universal reaction partners, which do not need to be activated by light prior to the reaction.

Some antagonistic printing processes, also known as multi-color photoinhibition lithography, have been established very early on (in 2009) via quenching additives (Scheme 2A,f),[24,25] via one-photon quenching of two-photon initiation (Scheme 2A,g),[22] or via an absorber layer at the bottom of the vat (Scheme 2A,c), which absorbs competitively, at a wavelength orthogonal to the initiation wavelength.[23] Quenching reactions and competitive absorption have always been relevant parameters in photopolymerization, and dyes are routinely used as additives to limit overpolymerization due to light

scattering. Therefore, previous research efforts naturally expanded in the direction of spatially controlled, light-triggered quenching reactions and competitive absorption.

Because the absorption layer on the bottom of the vat can potentially be combined with a variety of polymerizable formulations and a plethora of quenching additives is readily available, these strategies are, in principle, compatible with any type of curing reaction as long as an absorber/quencher can be found, which is inert during photopolymerization and for which the absorption/quenching wavelength regime is orthogonal to the initiating wavelength regime to avoid unwanted absorption at the quenching wavelength.[33] Other limitations regarding printable formulations are the meachanical strength of the resulting structures and the fast reversion of the inhibition for the formulation to become photopolymerizable again.[33] Subsequent antagonistic technologies apply stimulated emission depletion, triplet state absorption, and photodeactivation, which all deactivate the activated species directly via various physical depletion processes that compete with covalent bond formation.[33] These processes are critically dependent on the initiators' properties, and therefore, only a few initiators are available, again limited to radical photopolymerization. Non-radical antagonistic photopolymerization reactions have been reported for spiropyrans (Scheme 2B,b),[29] which have been utilized in a printing process of a prepolymer with pendant spiropyran side chains. These antagonistic printing processes are limited to two-photon polymerization techniques to lower the resolution threshold and have not found application in one-photon polymerization stereolithography or digital light printing.

Synergistic printing has been a very recent addition to the multicolor additive manufacturing portfolio, being introduced approximately 10 years after the first antagonistic printing strategies had been pioneered. While both strategies rely on AND-type conjunction photoreactivity, the reversion of the AND-type conjunction in the case of the synergistic system leads to the precondition that network formation only occurs during simultaneous dual-wavelength irradiation. This has been realized with a spiropyran-modified radical photoinitiator in xolography (Scheme 2A,a)[9] and with a diketone, a reluctant Norrish type I photoinitiator, aided by a TEMPO inhibitor in light-sheet printing (Scheme 2A,b).[8] Both of these initiators enable the synergistic curing of radical photopolymerizable formulations. The use of a protected photoenol, which can be deprotected at one wavelength and reacted with a maleimide at a second wavelength, was a first step toward a synergistic chromophore-based reactive system (Scheme 2B,a).[28] More recently, we have introduced an uncatalyzed synergistic pair of photoactive compounds consisting of an azobenzene and a ketene of which, however, the reversibility is insufficient for a printing process at room temperature (Scheme 2B,e).[7]

Dual-wavelength irradiation alone, however, is not a sufficient criterion to meet the synergistic conditions. The simultaneity criterion must also be met. If both simultaneous and sequential irradiation can achieve network formation (AND+OR-type), the system is termed a cooperative system.[30] Such an AND+OR-type multicolor additive manufacturing process is the 3D

analogon to 2D color lithography, which also employs the AND +OR logic conjunction. In cooperative systems, the reversibility criterion for the first irradiation step in synergistic photoreactions is not met, and thus, single-color irradiation yields intermediary products. Therefore, the slight change in the conditions has a significant impact on the outcome: instead of a binary curing versus noncuring outcome (as it is the case for synergistic systems), multi-material printing is achieved. A first system where cooperative network formation was demonstrated was recently published by our team (Scheme 2B,c).[30] In fact, interpenetrating network formation, where one color of light forms one network and a second color of light forms a second network, is an example of a cooperative system, provided that the curing color sequence is irrelevant (Scheme 2A,e). Specifically, three types of networks can form: network 1 in the presence of wavelength 1, network 2 in the presence of wavelength 2, and an interpenetrating network in the presence of both wavelengths. It should be stressed that sequence-dependent dual-wavelength reactivity cannot be utilized for cooperative systems because it implies that only one color of light is necessary for one of the two sequences, as it activates both species.

The restriction of cooperative systems noted above leads to the oldest and arguably best-known dual-wavelength photoreactivity, i.e., orthogonal reactivity, which represents an exclusive OR-type conjunction of two photoreactions. Therefore, orthogonality in its purest form is more specifically referred to as sequence-independent wavelength orthogonality, which implies that one wavelength can only trigger one of two possible reactions and the second wavelength exclusively triggers the second reaction. So-called sequence-dependent wavelength orthogonality implies that one color will always trigger two out of two possible reactions, while the second wavelength triggers exclusively one of the two reactions. Thus, sequential curing can only be achieved if the correct wavelength sequence is applied for curing, in which the higher energy wavelength is utilized as the second irradiation step. Sequence-dependent orthogonality has been implemented in dual-wavelength additive manufacturing in the form of interpenetrating network (IPN) generation.[26,27,34,35] In one approach, the antagonistic concept of utilizing a switchable dye to quench polymerization in one-photon printing was translated to an orthogonal concept, termed solution mask liquid lithography (SMaLL,[26,36] Scheme 2A,e). In contrast to the previous technology, two photoswitches ("solution masks") were distributed throughout the resin to mask the initiators, thus retarding polymerization in its absorbing state while allowing for deep curing in its transparent state (Scheme 2A,d). By simultaneously utilizing two photoswitches, which masked two initiating systems that were sensitive to blue and green light irradiation, respectively, the process enabled multi-material printing of hard IPN and soft (meth)acrylic domains, respectively. In another approach, the combination of two polymerization mechanisms was utilized.[34] Radical network formation was conducted in the visible light range, while the initiation of cationic network formation was conducted in the ultraviolet light (UV) regime, which also triggered radical network formation (Scheme 2A,e). This strategy has been used with other combinations of commercial radical and cationic photoinitiatiors[27,35] and most recently in tomographic volumetric 3D printing, utilizing various commercially available radical and cationic photoinitiators.[35] The reason for the above initiation order is rooted in the poor absorption of visible light by photoacid generators, the photoinitiators

responsible for cationic network formation. An alternative interpenetrating network approach utilizes noncatalyzed photoreactions for sequence-dependent orthogonal curing (Scheme 2B,d).[31] To date, one sequence-independent material-formation process is known (introduced by our group), which is based on the dimerization of styrylpyrene and α-methylbenzaldehyde; this process has been shown to yield tunable interpenetrating network structures as well as disparate multi-material structures (Scheme 2B,d).[31,32] However, the resist has only been utilized in a photomask process, and its realization in a 3D printing process is pending.

In light of the presented state-of-the-art additive manufacturing processes, it is obvious that multi-wavelength additive manufacturing has been developed with AND-type printing strategies. Similar progress has been made for the two commonly utilized photopolymerization strategies (initiator-based chain-growth and chromophore-based step-growth reactions) and for the two types of light-activation of the chemical process (one- and two-step multiphoton absorption). OR-type printing strategies, which could enable multi-material manufacturing, are underrepresented. This is surprising, as the concept of wavelength orthogonality is generally more common than the concepts of synergistic or antagonistic reactivity. Furthermore, the few examples of orthogonal multi-wavelength additive manufacturing that exist cannot be generalized to a range of photosensitive resins, as is the case for AND-type systems. Critically, all printing strategies are generally underexplored with respect to (i) single-photon printing technologies, such as stereolithography and digital light printing, and (ii) nonradical photopolymerization mechanisms. In the following section, we will retrace the presented progress to identify the challenges that could explain why certain strategies are underexplored and discuss how these could be addressed.

THE CHALLENGES AHEAD

On the basis of the above literature examination, two major curing strategies were identified for all four types of multicolor additive manufacturing (Scheme 2). On the one hand, classical photoinitiated chain-growth reactions have been utilized to generate complex 3D structures with light. Most of the strategies in this approach utilize radical photoinitiators, yet some use photoacid generators (which release superacids upon irradiation to initiate cationic photopolymerization) or a combination of these two initiator types. On the other hand, light-activated uncatalyzed cyclization reactions have been developed into an efficient step-growth polymerization technique, and their potential in multi-color additive manufacturing has been demonstrated. Curiously, both strategies have proven to be successful despite their obvious and substantial differences. While dual-wavelength-stimulated radical and cationic photoinitiators only need to be added to a potentially broadly tunable radically or cationically curable printing formulation in small amounts, progress in red-shifting their absorption spectra, and more importantly their reactivity,[4] is moderate compared to the finetuned absorptivity and reactivity of chromophores utilized in uncatalyzed cyclizations. On the other hand, the synthetic strategies used to obtain chromophore-derived precursors can be challenging, limiting the available number of photosensitive resins. Thus, the use of chromophore-derived photosensitive resins has generally been utilized in multiphoton printing technologies, where only a small amount of photosensitive resin is necessary for printing. So far, both polymerization strategies have proven to be promising in multi-wavelength additive

Scheme 3. Challenges Ahead for Multi-Wavelength Additive Manufacturing
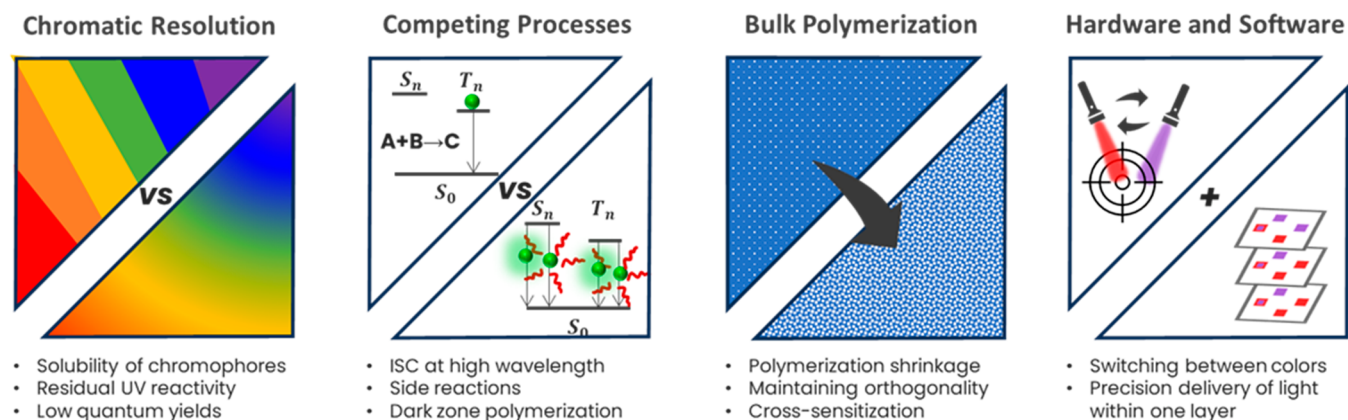
manufacturing. Therefore, multi-wavelength additive manufacturing will benefit from diverse approaches toward photosensitive resin design. Despite the rather varied challenges for initiator- and chromophore-based photosensitive resins, some common denominators can be identified that act as bottlenecks toward a versatile landscape of multi-wavelength 3D-printable photosensitive resins, which will be discussed in this section (Scheme 3).

Limits of Chromatic Resolution. Traditional photochemical reactions are typically driven by UV light. To achieve chromatic resolution, bathochromically shifted (also referred to as red-shifted) photoresponsive systems are required, as only the utilization of the full electromagnetic spectrum allows for sufficiently separated wavelength regimes that drive orthogonal reactions. Furthermore, the penetration depth of light and thus the maximum layer thickness during printing increases with increasing wavelength. Therefore, it is important to understand the molecular features leading to bathochromically shifted absorptivity and, even more importantly, reactivity. Because red light is less energetic than UV light, a molecule's absorptivity is red-shifted in molecules that exhibit a smaller gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital, thus favoring electron excitation already at a low energy input. From a chemical structure perspective, this is achieved through the extended delocalization of electrons, i.e. conjugation.[37,38] The absorptivity of a molecule can additionally be red-shifted by substituting the chromophore with auxophores, which are substituents that increase electron delocalization and thus cause a red-shift by contributing to their lone pairs but are not chromophores themselves. Typical auxophores are hydroxy, amino, and aldehyde groups. However, bathochromically shifted molecules have several challenges related to their application as photoinitiators or side/end group chromophores. We argue that only a deep understanding of photochemical reactivity via action plot analyses of covalent bond forming reactions, as pioneered by our group,[4] will enable the design of ever more reactive red-shifted chromophores.[4] The key reason for the need for action plots lies in our observation that the absorptivity of a chromophore is not a valid predictor for its chemical reactivity.

First, the conditions for red-shifted absorption/reactivity described above lead to large aromatic molecules with tendencies for high steric demand and low solubility. Thus, the use of bathochromically shifted photoinitiators in a polymerizable formulation depends on their solubility in the monomer, which can be challenging but is generally manageable

for the low concentrations in which they are added to the formulation. Bathochromically shifted chromophores as side/end groups in precursor molecules are, by definition, much more highly concentrated in the formulation, leading to even more challenges regarding solubilization. Because di- and multifunctionality of the precursors are a prerequisite to obtain networks in step-growth photopolymerization, the molecular weights of chromophore-based monomers increase drastically with functionality, rendering commonly known chromophore-based monomers solid. Solubility can be aided by nonvolatile solvents such as propylene carbonate in microstereolithographic additive manufacturing, where high-resolution structures with nanometer dimensions (routinely approximately down to 300 nm) can be generated. Therefore, perhaps, the chromophore-based monomer design has only been utilized in multiphoton polymerization processes, the leading technology to obtain 3D structures in the micrometer regime, so far. An alternative for solving the solubilization issues of chromophore-based monomers is the use of hot lithography, which utilizes elevated temperatures for the vat and printing platform to heat the monomer formulation during the printing process.[39]

Second, some form of UV absorption and UV reactivity typically remains for molecules with bathochromically shifted absorption spectra. Short-wavelength light, i.e., light of the UV regime, simply corresponds to a higher energy than light with larger wavelengths. Analogous to the principle that endothermic reactions can only be conducted at temperatures higher than a certain threshold temperature, so too can light-driven reactions often only be conducted at higher energies, i.e. in the UV range. However, analogous to thermally driven reactions, increased energy input above the threshold energy input does not necessarily correlate with reaction yield. Indeed, most photochemical reactions are red-shifted in yield compared to their UV–vis spectrum, which we have already noted above.[4] Thus, to determine wavelength-dependent reactivity, action plots must be recorded, which depict the yield of a photoreaction for a specific wavelength within a certain wavelength regime.[4] In any case, the residual UV reactivity of bathochromically shifted photoinitiators or chromophores counteracts wavelength orthogonality, which in turn makes the tuning of AND- and OR-type photoreactive systems more difficult.

Third, a large bathochromic shift in the absorption spectrum does not necessarily predict high reactivity in the bathochromically shifted wavelength regime. In fact, many reported red-shifted molecules exhibit lower quantum yields compared to UV-active molecules, which can decrease achievable printing

speeds. However, it is important to note that the actual photochemical reactivity of each chromophore must be probed via an action plot.

Competing Excited-State Processes. Side reactions are competing excited-state processes that can be of a physical or chemical nature. Typical chemical side reactions are unintended reactions of the photoreactive molecule, such as degradation on the one hand, and (photo)chemical reactions of molecules, which are present in the formulation but should remain inactive on the other hand. Such side reactions are mainly related to a limited reaction orthogonality. A Jablonski diagram describes all possible competing physical excited-state processes: internal conversion, thermal de-excitation (or vibrational relaxation), fluorescence, intersystem crossing, phosphorescence, and energy transfer.[40] The types of processes that occur for a molecule in its excited state largely depend on its excited-state lifetime, which in turn depends on the molecular structure and the surrounding environment of the molecule.[40] The shorter the excited-state lifetime of a molecule, the less likely it is for that molecule to undergo a chemical reaction and decay via (non)radiative physical side reactions. Among other factors, a molecule with a large extinction coefficient between S_0 and S_1 (i.e., a bathochromically shifted molecule) must undergo efficient stimulated emission from S_1 to S_0 and can have only weak excited state/excited state absorption from S_1, a process in which the molecule is lifted into a higher excited state, from which intersystem crossing—the critical step that induces chemical bond formation—occurs more efficiently.[12] In other words, intersystem crossing can become less likely for bathochromically shifted molecules, potentially lowering the quantum yield for bond formation and thus the printing speed.

While chemical side reactions during the printing process are generally unwanted, as they typically impair wavelength orthogonality, physical side reactions are often intentionally utilized in light-based additive manufacturing if a reactive species with a longer lifetime is produced. The longer the lifetime of this reactive species, the higher the probability that this molecule diffuses out of the illuminated area into the dark zone, causing so-called overpolymerization, i.e., the reduced resolution of the printed structure. Thus, a certain amount of quenching of the reactive species via the physical decay of the reactive species is beneficial for the printing resolution, while quenching that is too efficient reduces printing speeds. Classical quenching includes non-light-based techniques, such as oxygen quenching and radical trapping for radical photopolymerization and the quenching of superacids released from photoacid generators with bases, as well as light-based techniques that utilize a second color of light (antagonistic printing). The quenching of chromophore-containing monomers has scarcely been investigated, perhaps because most of these monomers are already rather bathochromically shifted and thus tend to exhibit short lifetimes without quenching or because most chromophore-containing formulations rely on prepolymers, which are cross-linked via chromophore-pendant side chains that are less prone to migration.

Toward Bulk Polymerization. The larger the size of the printed parts, the more important the concentration of the photosensitive resin becomes. Only monomers included in the photopolymer network contribute to the volume of a printed part. Thus, even neat printing formulations that contain 100% monomer suffer from polymerization shrinkage due to a decrease of the van der Waals distances between the monomers to covalent bond distances within the polymer network. Therefore, any addition of a solvent may be detrimental for maintaining true part shapes, which becomes particularly important for the development of multi-material printing. Here, up to ~50% of the formulation will be uncurable monomers, which are orthogonal to the second type of monomer at a certain wavelength, potentially leading to significant shrinkage. Intricate photosensitive resin design is necessary to overcome this limitation.

The issue of "monomer dilution" also raises questions regarding the fate of unreacted monomers in the final printed object. For example, in IPN-based approaches for hard/soft multi-material printing, uncured epoxy monomers in a visible light-printed part remain present and cause two problems. First, unreacted monomers may migrate out of the part. Second, uncured monomers that remain in the part are likely sufficiently unstable to react at a later stage, turning originally soft sections in a construct into hard sections over time.

Furthermore, it becomes increasingly difficult in chromophore-based formulations to maintain orthogonality at high concentrations, which has recently been shown for cooperative network formation.[30] Because UV-only active monomers and monomers containing bathochromically shifted chromophores are both present in high concentrations, cross-sensitization from bathochromically shifted chromophores to UV-active chromophores is potentially quite efficient. This leads to the originally exclusively UV-active chromophores being active in the visible range. Here, the nonlinear relationship between the molecular distance and the energy transfer efficiency becomes a valuable tool for maintaining wavelength orthogonality via the clever control of the polymerization parameters of intensity and concentration.

Hardware and Software for Dual-Wavelength Printing. Finally, a printing process can only be as good as the sum of its components: the photosensitive resin, the hardware, and the software. Hardware and software play a particularly important role in multi-wavelength additive manufacturing. Precisely delivering light rays or light projections, despite the use of varying wavelengths, poses a challenging engineering and optical problem. Furthermore, multi-material printing requires intricate software that is capable of delivering light of different wavelengths within one printing layer to enable maximum freedom for part design. The first hardware and software components have become available both in the industrial[41,42] and academic sectors,[8,9] taking very diverse approaches into account. Here, we second the call from Fourkas and Petersen to utilize knowledge from other disciplines with related objectives, e.g., the semiconductor industry or holography, and engage diverse disciplines in the field, particularly chemists, physicists, material scientists, mechanical engineers, and software engineers.[12]

PERSPECTIVE

In summary, we have outlined the promise that multi-wavelength additive manufacturing holds: higher resolution and higher printing speeds in AND-type dual-wavelength processes, both of which have already been pioneered, as well as multi-material additive manufacturing in OR-type dual-wavelength processes, for which hardly any precedent exists at the moment, even in its simplest form of dual-wavelength printing. We applaud the diversity of the applied strategies in multi-wavelength additive manufacturing, which will stimulate creative solutions for currently unattainable materials and structures, and we encourage the community to expand this

diversity further. The current challenges presented here and their implications on the outcomes should incentivize researchers from all disciplines to engage in the quest to revolutionize light-based 3D printing in a way that is analogous to the revolution from 2D grayscale to color printing.

Taking the step from dual-wavelength to multi-wavelength printing increases the above-mentioned challenges dramatically. We expect major benefits for OR-type printing processes that utilize several wavelengths to print several material properties in a spatially resolved manner within one process. The increase in complexity can be seen as analogous to traditional orthogonal reactions, where the number of side reactions increases with an increasing number of reaction components, typically controlled through multi-step synthesis,[43,44] and which is currently mimicked in additive manufacturing with multi-step engineering solutions.[45] True multi-property printing within one step would, however, further increase the impact of 3D printing as a manufacturing technology significantly, as one-step multi-property processing is uncommon in the broader context of conventional polymer processing technologies such as solution- and extrusion-based processes. The two most obvious challenges for multi-wavelength printing are obtaining a high wavelength resolution for more than two molecules (only attainable through action plot analysis)[4] and the dilution of differently responsive monomers within the photosensitive resin, further adding to the commonly discussed problems of volumetric shrinkage and shrinkage stress in additive manufacturing. We acknowledge that several more challenges may await in the process of exploring multi-wavelength printing, which cannot be anticipated from the current state-of-the-art practices. Thus, the step from dual-wavelength to multi-wavelength printing should not be seen as an extension of the dual-color printing concept, but rather as a significant stand-alone challenge with worthwhile benefits if achieved.

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Notes

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