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Perspective

Photoreaction Drives Efficient, Precise, and Sustainable Additive Manufacturing

Published as part of Chem & Bio Engineering virtual special issue "3D/4D Printing".

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Cite This: *Chem Bio Eng.* 2024, 1, 414−426

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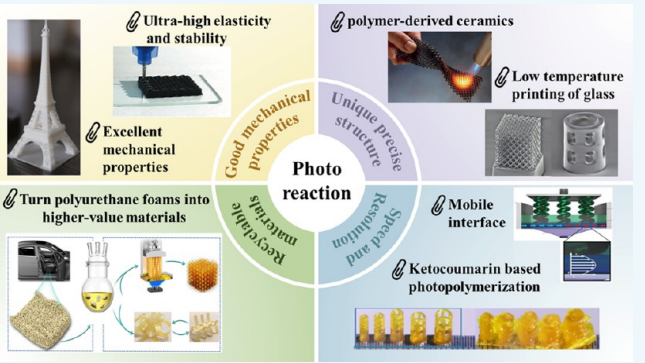
ABSTRACT: Additive manufacturing, normally referred to as three-dimensional (3D) printing, has been maturing rapidly in recent years and widely utilized in various industrial fields, because it can create predesigned functional products with sophisticated structures that are basically difficult to achieve using traditional methods. Among all 3D printing technologies, vat photopolymerization has attracted much attention because of its outstanding advantages such as fast printing speed, high precision, and ease of formulating. In recent years, many breakthroughs in photopolymerization based 3D printing have been achieved by photoreaction design regarding photopolymerizable monomers, photoinitiating systems, inhibition functions, light sourcs, etc., but challenges remain. This Perspective attempts to highlight these great advances regarding the promotion of printing efficiency, accuracy, and sustainability. At the end, several challenges, such as longer-wavelength printing, printing of functional materials, and multimaterial printing, are discussed, which must be carefully addressed to meet the increasing requirements of future high-performance additive manufacturing.



KEYWORDS: *3D printing, photoreaction, printing speed, resolution, sustainability*

1. INTRODUCTION

Additive manufacturing, commonly known as 3D printing, has been extensively employed to create a variety of functional objects with complex structures and intricate geometries. Basically, it is implemented by printing materials in a successive manner according to the sliced 3D digital model (Figure 1).[1,2] Compared with traditional precision machining technologies based on material removal, cutting, or other "subtractive" manufacturing processes, 3D printing has subverted the traditional industrial system.[1,2] 3D printing is a "bottom-up" process that gradually builds up materials to achieve "free manufacturing" of parts. With the help of computers, even the most complex and delicate structures can be fabricated in 3D printing. Therefore, 3D printing technologies have enabled a wide range of promising engineering applications, including but not limited to solar evaporators,[3−5] energy storage,[6,7] mechanical dissipation,[8,9] chemical reactors,[10,11] microfluidic devices,[12−14] and bioscaffolds.[15−20] Generally, 3D printing can be accomplished by vat photopolymerization,[21] fused deposition,[22] inkjet printing,[23] selective laser sintering,[24] direct ink writing,[25] and other technologies. As more and more 3D printing materials are being developed by scientists, 3D printing is beginning to go beyond the production of plastic products, with a wide variety

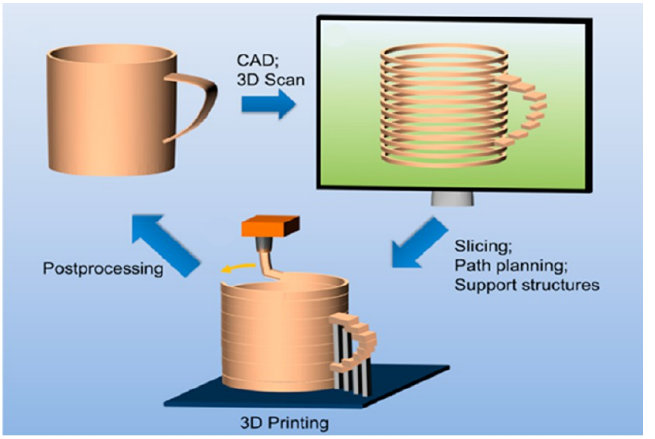


Figure 1. Basic principles of additive manufacturing. (Reproduced with permission from ref 2. Copyright 2017 American Chemical Society.)

Received: December 29, 2023
Revised: April 20, 2024
Accepted: April 23, 2024
Published: May 6, 2024

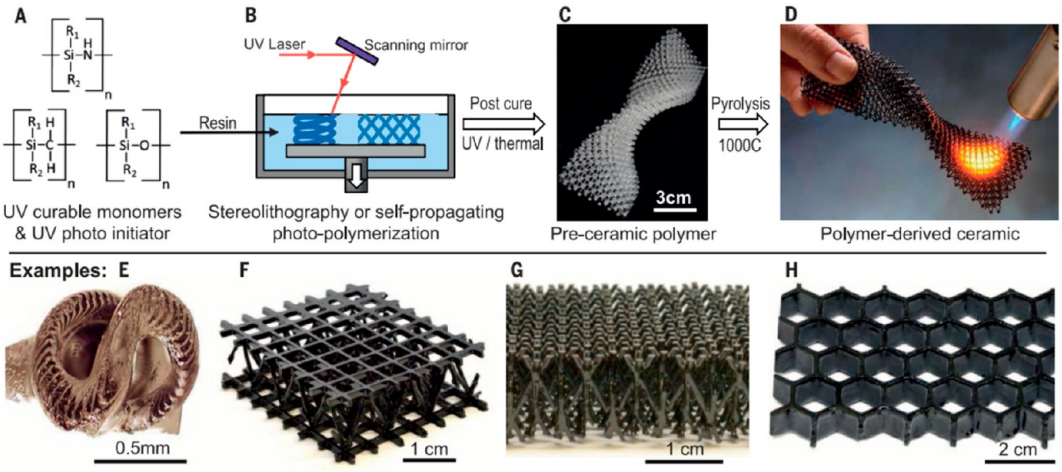


Figure 2. Additive manufacturing of polymer-derived ceramics. (A) UV-curable preceramic resin. (B) 3D printing of resins. (C) Pre-ceramic polymer. (D) Polymer-derived ceramic. (E) Printed cork screw. (F and G) Printed microlattices. (H) Printed honeycomb. (Reproduced with permission from ref 35. Copyright 2016 American Association for the Advancement of Science.)

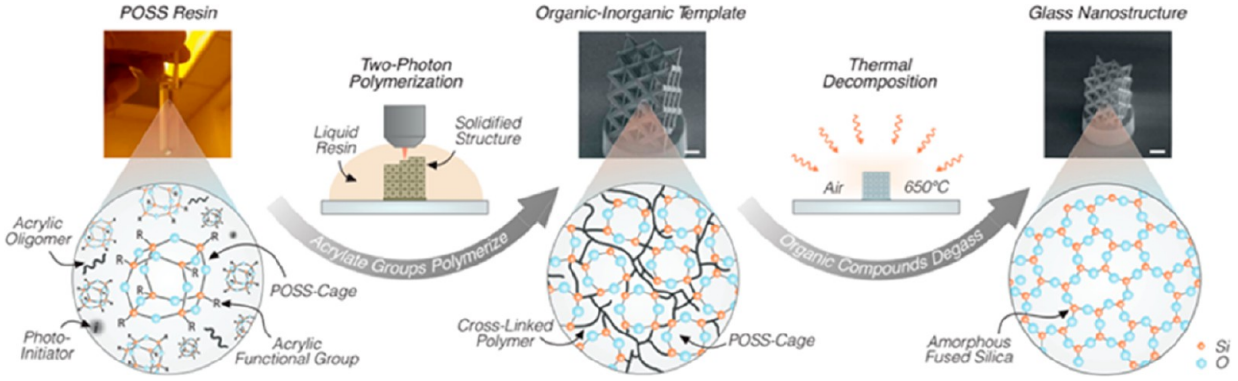


Figure 3. Sinterless, low-temperature route to 3D printing of optical-grade glass. (Reproduced with permission from ref 36. Copyright 2023 American Association for the Advancement of Science.)

of polymers, metals, and ceramics being used in 3D printing.[26] With the growing maturity of the process, materials, and equipment, people gradually realize the great potential of 3D printing and begin to study it in depth. So far, there have been a large number of excellent research results and reviews.[2,27−29]

Among all 3D printing techniques, vat photopolymerization has attracted particular interests. In typical vat photopolymerization, a liquid photosensitive resin is exposed to radiation from a radiant light source, which starts a chemical reaction that joins tiny molecule monomers or oligomers to produce a highly cross-linked polymer. Nevertheless, most monomers or oligomers do not generate reactive species upon exposure to a bright light source; therefore, an initiator is normally added to the resin. Upon light radiation, the initiator produces reactive species (free radicals or cations), which then set off a reaction that polymerizes or cross-links low molecular weight organics.[30] Compared with traditional polymerization methods, the photopolymerization reaction has the advantages of a fast curing speed at low light intensity, short exposure time, less heat production, and the possibility of temporal and spatial control, which makes it the first choice for achieving high-quality 3D printing. In addition, various characteristics of the printed object in photopolymerization 3D printing can be easily adjusted by simply changing the formulation of the photopolymerizable resin, choosing the right initiator or selecting different wavelengths of light.[31] It must be pointed out that the development of precise photocuring systems is currently necessary to achieve efficient 3D printing, and photochemical action plots may be needed as suggested by Barner-Kowollik *et al.*[32,33] Herein, this Perspective attempts to highlight the critical role of photoreaction design for high-quality 3D printing, in terms of producing high performance products with complex structures, creating mechanically robust and environmentally sustainable objects, and simultaneously increasing the printing speed and resolution. Though detailed mechanism in photochemistry is not involved here, we agree that affording predesigned functions (e.g., photoluminescence) into the printed objects and collaborative printing of multi-material gradient structure would be in a crucial future path and need more efforts to control the photochemical reaction.

2. MAJOR ADVANTAGES AND FEATURES OF 3D PRINTING

The most notable advantage of 3D printing is the capability of precisely and swiftly designing and manufacturing more complicated objects than conventional production methods.[2] 3D printing is more cost-effective and quicker than machining prototypes for manufacturing components because 3D printing technology only creates the pieces it needs rather than cutting production.[34] Components can be finished in a matter of hours, making modifications more quickly and effectively. Furthermore, printing materials can be specifically tailored to

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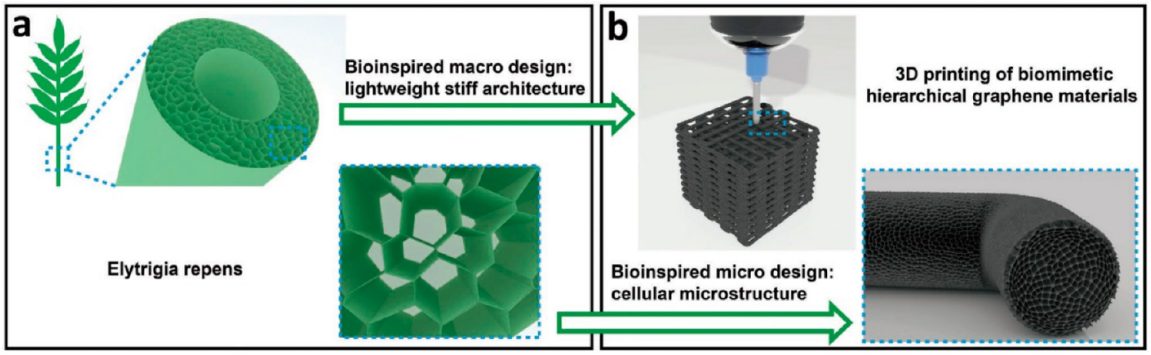

Figure 4. Schematic illustration of 3D printing of hierarchical structures. (a) Grass stems of *Elytrigia repens*. (b) 3D printing of biomimetic hierarchical graphene materials. (Reproduced with permission from ref 37. Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)

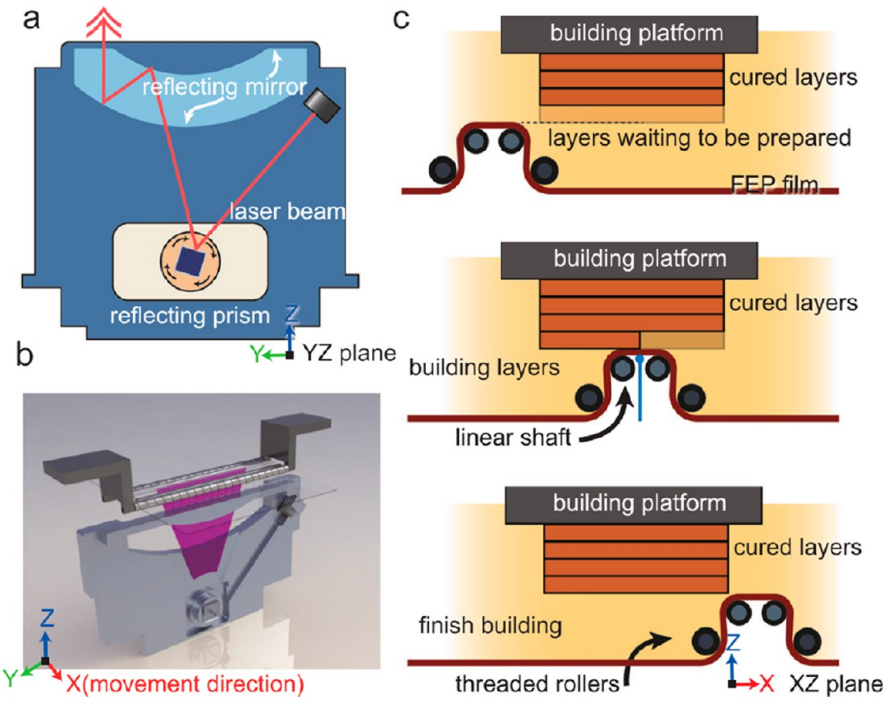

Figure 5. Illustration of "line scanning with synchronous forming and stripping". (a) Laser device in the YZ-plane. (b) Illustration of the entire structure for linear scan-based vat photopolymerization, where the purple sector represents the scanning line and the laser device moves along the *x*-direction. (c) Roller system in the XZ-plane. (Reproduced with permission from ref 38. Copyright 2023 The Author(s).)

accomplish desired qualities, including but not limited to increased mechanical strength, water resistance, or heat resistance.[1] In addition, 3D printing is moving toward environmental protection driven by a material revolution, with an increase in the use of ecologically benign materials.

3D printing of high-performance products with complex and delicate structures is readily available by predesigning photopolymerizable monomers. As displayed in Figure 2, Eckel et al.[35] developed a resin formulation to obtain UV-active ceramic precursor monomers. The resulting material was called a "ceramic precursor monomer", which was formed through the addition of thiol, vinyl, acrylate, methacrylate, or epoxy to an inorganic host (e.g., silicone, silazane, or carbosilane). This material could be formed into various shapes and sizes by using 3D printing technology. Unlike traditional ceramic powder processing, no sintering step was involved, which significantly reduced the synthesis temperature. After firing, the material transformed into high-strength, fully dense ceramics that can withstand extremely high temperatures exceeding 1700 °C. The strength of the obtained ceramics was 10 times higher than that of similar materials. Bauer et al.[36] developed an acrylate-functionalized polyhedral oligosiloxane (POSS) resin that could polymerize into a continuous network of silica-oxygen molecules, allowing it to be converted into fused silica at only 650 °C (Figure 3). The most attractive advantage was that the method could eliminate high-temperature processing to sinter discrete silica particles into a continuum. In other words, optical-grade glassy nanostructures could be easily achieved by low temperature printing.

While unique structures are obtained, the mechanical properties of 3D printed products are not far behind. Early 3D printing technology has been mostly difficult to meet the needs of practical applications due to the lack of printable materials to provide high mechanical performance. With the development of material technology and printing equipment, scientists have reported many exciting results in this area. For instance, Peng et al.[37] proposed an ink-based 3D printing strategy to prepare ultralight multistage graphene materials

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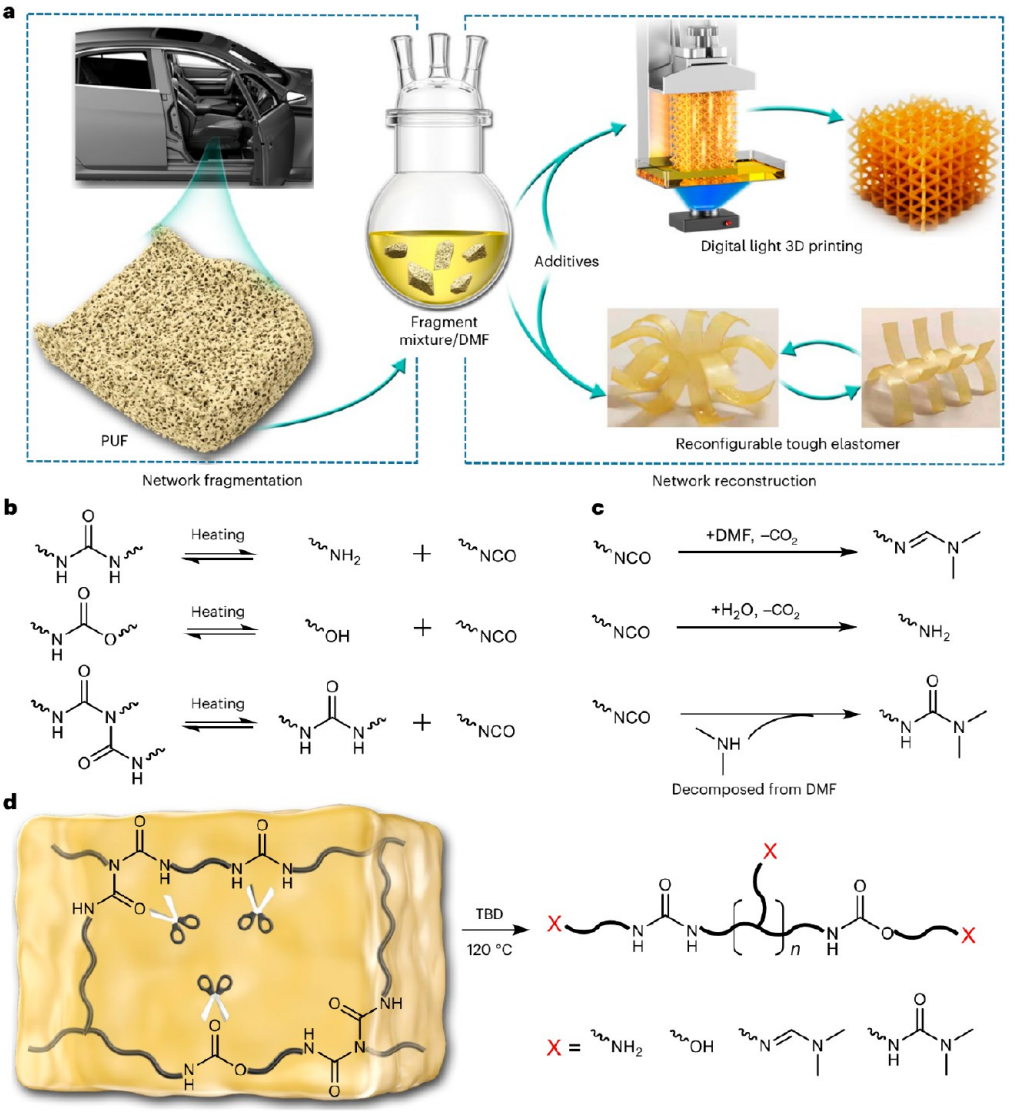

Figure 6. Chemical fragmentation and upcycling mechanism of commodity polyurethane foam (PUF). (a) Upcycling and 3D printing of PUF. (b) Thermal equilibria of the bonds in PUF. (c) Reaction proceeds to the right. (d) Chemical fragmentation of PUF. (Reproduced with permission from ref 40. Copyright 2023 The Author(s) under exclusive license to Springer Nature Limited.)

with ultrahigh stiffness and elasticity (Figure 4). The 3D-printed materials could sustain ultrahigh elasticity and stability under compression forces of up to 95%, primarily due to the produced cellular microstructure and macroscopic scaffold that could provide good mechanical properties at ultralow densities. Wu group[38] developed an innovative method called "line scanning with synchronous forming and stripping" to print photosensitive resin with a high viscosity of over 600000 cps. The printed samples had excellent mechanical properties, good isotropy, high tensile strength of 11.6 MPa, large elongation at a break of 650%, and excellent molding precision (Figure 5).

Employment of efficient photomediated radical reaction can lead to robust 3D printing. Li et al.[39] developed a universal method for 3D printing of nanomaterials using a colloidal nanocrystalline solution as the raw material and corresponding inorganic materials as the "ink". A small molecule cross-linking agent based on photogenerated aziridinyl radicals was designed, and a femtosecond laser was used to initiate photo-cross-linking reactions of ligands on the surface of the nanocrystals. Consequently, stable covalent bonds were formed, enabling the nanoscale 3D printing of a wide range of inorganic nanomaterials. Due to the high inorganic content in the structures, excellent mechanical properties along with tunable optical properties were achieved.

Very recently, photopolymerization based 3D printing has also demonstrated its ability to tackle the problem of environmental sustainability. Under the premise of ensuring the efficiency and product performance of 3D printing, people focus on global environmental and resource issues and are committed to the development of recyclable and environmentally friendly materials. As such, the increasingly pressing environmental burden can be reduced. Xie group[40] reported a highly effective way to turn waste polyurethane foam into higher-value 3D printing materials. The foam was heated to 120 °C for 20 min, during which organic solvents and catalytic agents led to a dynamic opening of the urethane bond, resulting in local "loosening" of the network structure within the foam. Consequently, an un-cross-linked polymer—a non-cross-linked polymer fragment with reactive hydrogen at the end groups, is produced when part of the foam breaks down.

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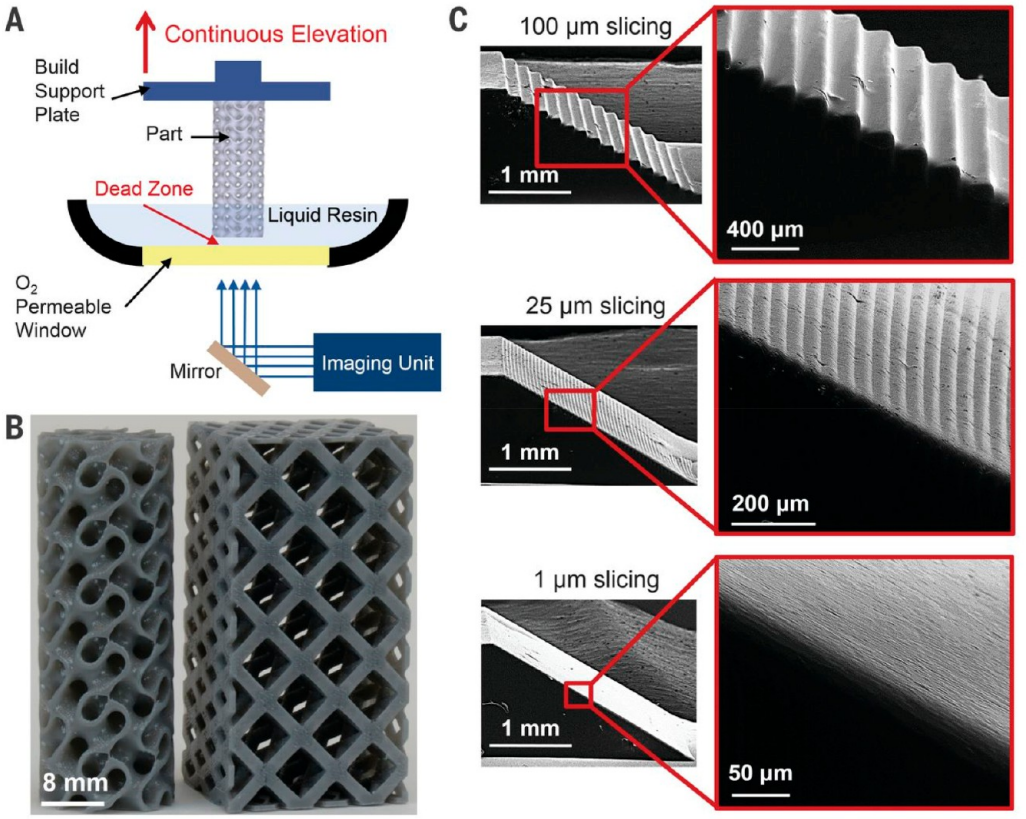

Figure 7. CLIP enables fast print speeds and layerless part construction. (A) Schematic of CLIP printer. (B) Resulting parts via CLIP. (C) Different slice thicknesses at the same print speed. (Reproduced with permission from ref 48. Copyright 2015, The American Association for the Advancement of Science.)

This fragment is then combined with several network remodeling additives to create a photosensitive resin that can be printed in three dimensions and has mechanical qualities that can be adjusted for light-curing 3D printing (Figure 6). This design solves the common conflict between light-curing printing and the final properties of the cured product by allowing the printed single polymer network to reconfigure into an interpenetrating dual network during post-thermal curing. It also makes it possible to recycle thermoset plastic materials to produce high-performance 3D printed products. Many other groups were also committed to this area. Sardon et al.[41] prepared a simple and versatile recyclable 3D printing resin based on a mercaptoisocyanate polymerization reaction. Jarach et al.[42] developed an approach by combing a reversible photopolymerization reaction with a microwave de-cross-linking process, in which solid 3D printed objects could be de-crosslinked by microwave irradiation, enabling multiple printing cycles at low temperatures.

3. PRINTING SPEED AND RESOLUTION

Vat photopolymerization has become a useful technology with a wide range of applications. The current equipment utilizes galvanometer scanning or mask projection technology to control the exposure area. This allows the resin to cure layer by layer and stack within the controllable exposure area, resulting in the generation of 3D objects.[28] However, light passing through the solidified polymer layer is highly likely to trigger undesired transverse photopolymerization during the printing of subsequent layers, resulting in a reduced print resolution. In order to reduce the light penetration and improve the print resolution, it is often necessary to introduce large amounts of non-reactive light absorbers (also known as masking agents). However, under such circumstance, a large amount of light energy is consumed by the non-reactive light absorber rather than the photosensitizer, which results in a sacrifice of print speed. Clearly, although 3D printing technology has rapidly evolved into an integral strategic direction in manufacturing technology, the trade-off between print speed and resolution still limits the potential for fine and efficient printing on a large scale,[27,28,43] and it is essential to seek improvements in both. A large number of excellent reviews have summarized the achievements in terms of improved printing equipment,[44,45] innovative printing strategies,[46,47] and so on. This perspective only focuses on the efforts made by researchers in the field of photochemistry. These efforts have successfully resolved the contradiction between printing speed and resolution and are promising to be used for future research.

Oxygen inhibition of photopolymerization is a breakthrough method to balance printing speed and resolution. The term "oxygen blocking effect" describes how oxygen will interact with the reactive radicals produced during the photoinitiation process to create more stable peroxyl radicals.[30] It inhibits the polymerization process by competing with active radicals during the monomer addition reaction. It is usually necessary to attempt to minimize or remove the oxygen blocking effect during the photopolymerization reaction. However, Tumbleston et al.[48] invented the continuous liquid interfacial production (CLIP) 3D printing technique by utilizing the oxygen blocking effect that one would normally want to avoid

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(Figure 7, Table 1). Due to the oxygen barrier effect of acrylates, oxygen entering the resin bath would inhibit the curing of the part of the resin closest to the bottom, forming a "dead zone" with a thickness of tens of microns. At the same time, UV light cured the photosensitive resin above the dead zone, eliminating the need for slow peeling. In this case, the speed of 3D printing was no longer limited to step-by-step layer formation, and the print speed was increased to 50 cm·h^{-1}, the highest value at the time, with a corresponding increase in print resolution. The CLIP process uses the "dead zone" to achieve the curing layer, window separation, and resin filling. Nevertheless, the "blocking zone" layer has a thickness of less than 20 mm, and the adsorption effect slows down the speed at which resin is backfilled. Additionally, the CLIP process necessitates extremely high resin fluidity, resin filling has emerged as a critical problem limiting the technology's ability to gradually increase productivity. Even if the bonding issue between the curing layer and the restraining surface has been resolved by the CLIP process, it is currently difficult for the printing speed of lifting and pulling to be greater than 100 cm·h^{-1}.

Table 1. Speed and Resolution of Some 3D Printing Technologies

Printing technology	Speed	Resolution
CLIP	50 cm/h	100 μm
CLIP (fluorinated oil)	43 cm/h	100 μm
CAL	~150 cm/h	300 μm
Xolography	55 mm^3/s	25 μm
Photooxidation of ketocoumarin	5 cm/h	23 μm

A significant limiting element in continuous, high-speed, light-curing 3D printing is the ability to successfully expel the heat produced by the resin polymerization reaction. Other factors influencing the printing speed include curing layer separation and resin reflux in the printing area. Mirkin group[49] found that the heat generated by the photopolymerization reaction increased the local temperature of the resin to 120 °C in the 3D printing process, which seriously affected the kinetics of the photopolymerization reaction and the dimensional stability of the polymer, leading to a decrease in print resolution and material properties. To this end, they filled the bottom of the resin tank with chemically inert fluorine-containing oil and circulated it to significantly reduce the resin temperature and remove the solid particles generated by light scattering, thereby improving the print resolution (Figure 8). At the same time, the fluorine-containing oil also prevented the cross-linked polymers from adhering to the surface of the resin bath, which improved the printing speed. The "liquid−liquid" contact separation mode is realized by this technology through the flow interface of fluorine-containing oil. The flow separation liquid may effectively resolve the adhesion issue between the curing layer and window and dissipate the heat produced by the resin polymerization process. The flow interface's complexity and controllability are drawbacks, and high-speed printing's drag from the flow separation liquid will result in a significant reduction in printing accuracy.

Attempts were also made to improve the 3D printing speed by increasing the initiation efficiency of the photoinitiating system. Bagheri et al.[50] used trisulfide ester compounds as photoinitiating systems to achieve 3D printing based on photocontrolled reversible addition−fragmentation chain transfer polymerization (RAFT) reaction. The printing speed was only 0.05 cm·h^{-1} because of the limited photoinitiation

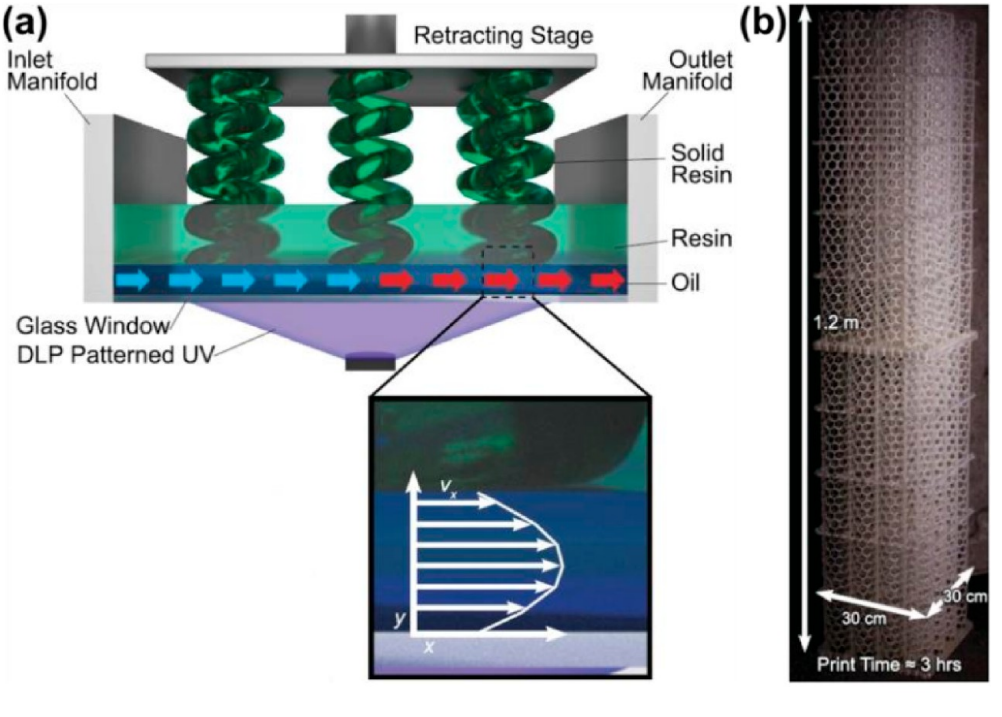

Figure 8. Flow profile of a mobile interface that enables continuous printing. (a) Scheme of high-area rapid 3D printing. (b) Printed hard polyurethane acrylate lattice. (Reproduced with permission from ref 49. Copyright 2019, The American Association for the Advancement of Science.)

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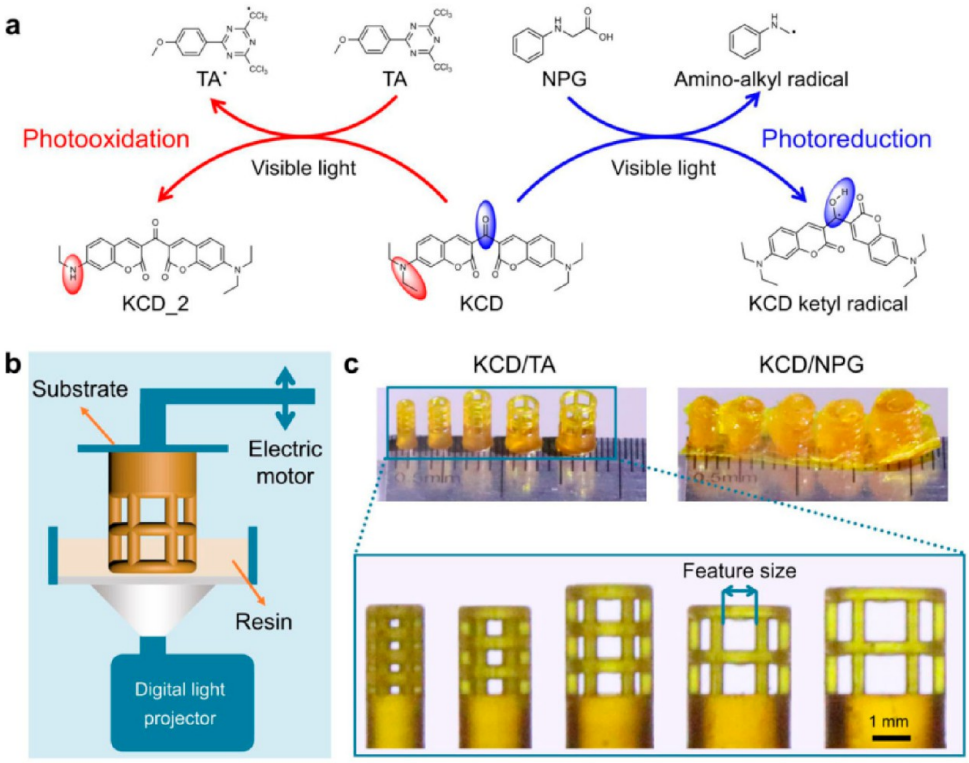

Figure 9. Comparison of print fidelity between KCD/TA and KCD/NPG systems. (a) Reaction of KCD with TA and NPG under visible light, respectively. (b) DLP 3D printing schematic. (c) DLP 3D printing products with varying feature sizes. (Reproduced with permission from ref 52. Copyright 2021 The Author(s).)

efficiency of the trisulfide ester compounds. Subsequently, Zhang et al.[51] introduced the co-initiator triethanolamine to the system with the photosensitizer in order to form a ternary photoinitiation system with the RAFT reagent, which improved the photoinitiation efficiency and then increased the printing speed to 1.2 cm·h^{-1}.

Control of the light penetration via photochemical design is found to be rational to control the print speed and resolution. As mentioned above, reducing the optical transmission depth of the printing resin can help suppress lateral photopolymerization and improve 3D printing resolution. However, the typical method is to add light absorbers (such as Sudan Orange G, Sudan I and Tinafin 171) to the printing resin, but this can reduce the rate of photopolymerization reaction and ultimately slow the 3D printing process. Zhao et al.[52] reported an efficient 3D printing method based on a ketocoumarin photosensitizer. The used ketocoumarin termed KCD underwent photooxidation and simultaneously generated the initiating radical (TA$^{\bullet}$) and deethylated ketocoumarin (KCD_2). KCD had a large maximum molar extinction coefficient at 458 nm, while KCD_2 had a maximum molar extinction coefficient at 448 nm, and the maximum molar extinction wavelength shifted by only 10 nm after deethylation. During the printing process, the initiating radical started the quick photopolymerization that led to fast 3D printing due to the absence of passive absorbers, while the deethylated ketocoumarin limited light penetration to ensure high print resolution (Figure 9). By comparison, the printed feature could not be identified when KCD encountered photoreduction. This method could provide both high printing speed (5.0 cm·h^{-1}) and high printing resolution (23 μm) on an ordinary 3D printer.

Similarly, the Hawker group[53] used photochromic compounds (e.g., diarylethylene) instead of conventional photoabsorbents, which not only inhibited lateral photopolymerization, but also increased the printing speed to 50 cm·h^{-1} (Figure 10). The process was based on the fact that diarylethylene transitioned from a closed ring state to an open ring state when exposed to visible light (530 nm). This results in weakened absorption in the visible region, which allowed the photoinitiating system to absorb light and set off the photopolymerization reaction. Nejadebrahim et al.[54] used the SFH^{+}/PETMP/DPI-PF$_6$ ternary system (Figure 11) as the photoinitiating system for 3D printing. The cyclic regeneration of photosensitizer SFH^{+} eliminated the light absorber, resulting in a printing speed of 1.2 cm·h^{-1}. At the same time, it made the printing resolution in both the xy- and z-directions of 100 μm, five and ten times higher than TPO-based 3D printing, respectively.

Volumetric printing based on light control was also proposed for improving the printing speed. Shusteff et al.[55] introduced a new paradigm for volumetric additive fabrication based on photopolymerization reactions in 2017, successfully constructing complete structures in 1−10 s under medium-power (10-100 mW) light illumination using a low-absorbent resin containing 0.1 % photoinitiators. And in 2019,[56] Kelly et al. developed a computational axial lithography (CAL) method. The CAL fabrication system was capable of selectively curing a photosensitive liquid (methacrylate gelatin hydrogel) inside a container by taking a set of 2D images and projecting them from different angles (Figure 12). This superimposition

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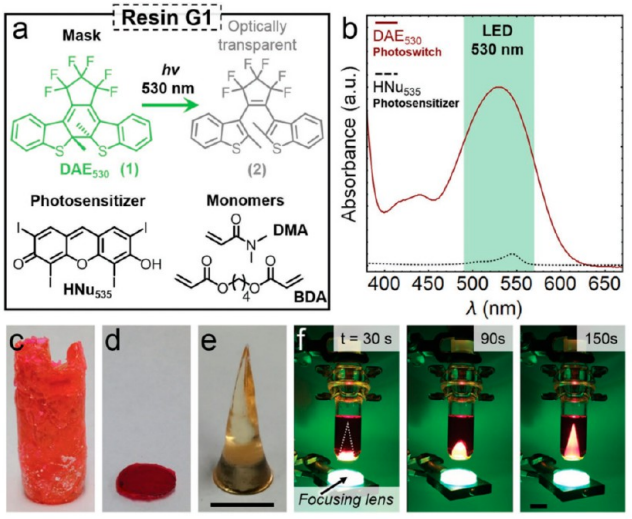

Figure 10. Photochromism controlled 3D printing. (a) Ring-opening transformation of DAE530. (b) Absorbance spectra of DAE530 photoswitch and HNu535 photosensitizer. (c) Printing in the absence of dye or photoswitch. (d) Printing in the presence of a nonbleaching control dye. (e) Object printed with photoswitch and solution mask liquid lithography. (f) Timelapse photographs of the printing process. (Reproduced with permission from ref 53. Copyright 2018 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)

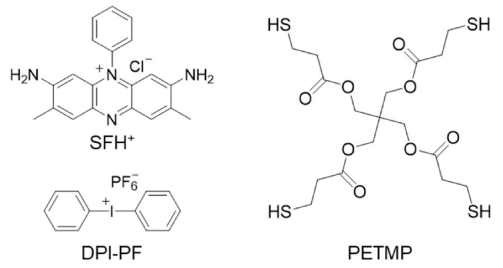

Figure 11. Chemical structure of SFH$^+$/PETMP/DPI-PF as the photoinitiating system for 3D printing. (Reproduced with permission from ref 54. Copyright 2019 The Royal Society of Chemistry.)

of multiple-angle exposures allowed the photosensitive liquid to be cured to the desired geometry in the specified position. This method worked like a reverse computed tomography (CT) scan, in which an X-ray tube rotated around the patient in a CT machine to took pictures of the body's internal organs. The printing time was only 30−120 s with a resolution of 0.3 mm under different accuracies and material conditions.

Compared to CLIP printing, CAL printing is much faster, does not require a support mechanism, can print discontinuous structures, and can also generate new structures outside of existing objects because there is no requirement for media fluidity during the printing process. However, the algorithm for simulating the inverse CT image of the object is quite complex and is not suitable for printing on non-transparent materials.

Regehly et al.[57] proposed a crossing (X) type volumetric 3D printing technique using photoconvertible photoinitiators (Figure 13). The photoinitiators were linearly excited by beams of intersecting different wavelengths, thereby triggering the local polymerization of photosensitive resins in a specific monomer volume to print 3D objects with complex structural features, as well as mechanical and optical functions. More precisely, a specific volume of adhesive resin was exposed to a specific thickness of the crossing light. The wavelength of the first light was chosen to activate molecules known as dual-color photoinitiators (DCPIs). Meanwhile, the second wavelength light projected an image of a section of the 3D object, causing the current layer to polymerize. Next, the resin moved in relation to the fixed position of the light sheet. By doing this, the light sheet in the resin was moved to a new location, allowing the activation and polymerization process to begin again and assembling the thing piece by piece. The technology printed features with a resolution of up to 25 μm and a curing speed of 55 mm^3·s^{-1}.

To further realize the mass production of 3D printing and to solve the problem of significant adhesion between the cured layer of photopolymer resin and the release film, Wen et al.[58] produced a transparent film that effectively resisted photopolymer resins by incorporating micrometer-nanometer-sized layered roughness features and low-surface-energy materials on the surface of quartz glass, which could achieve printing speeds of up to 32 cm·h^{-1} in liquid crystal display 3D printers.

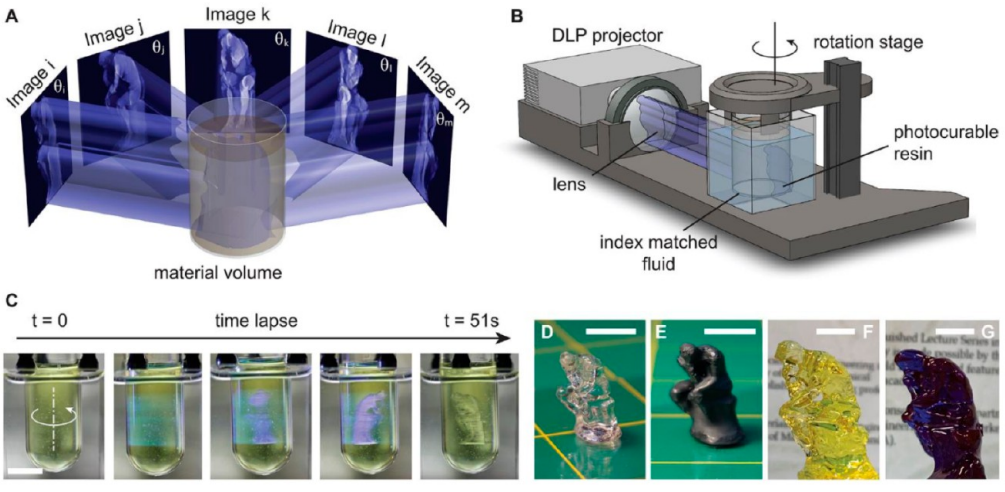

Figure 12. CAL volumetric fabrication. (A) Printing principle. (B) CAL system schematic. (C) Sequential view of the build volume during a CAL print. (D−G) 3D printed products. (Reproduced with permission from ref 56. Copyright 2019 The American Association for the Advancement of Science.)

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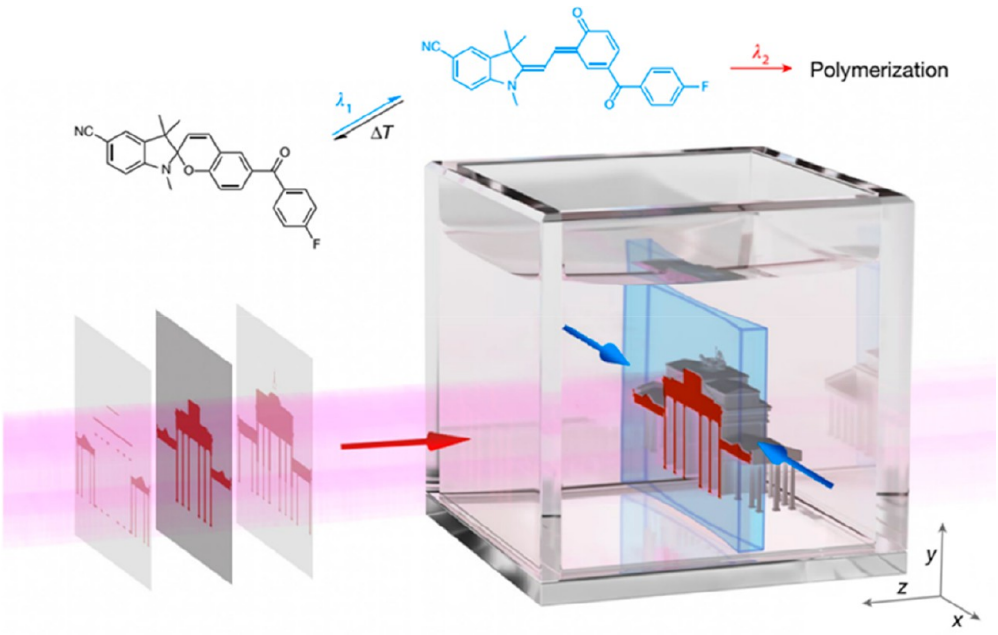

Figure 13. Xolography 3D printing technology. (Reproduced with permission from ref 57. Copyright 2020 The Author(s) under exclusive license to Springer Nature Limited.)

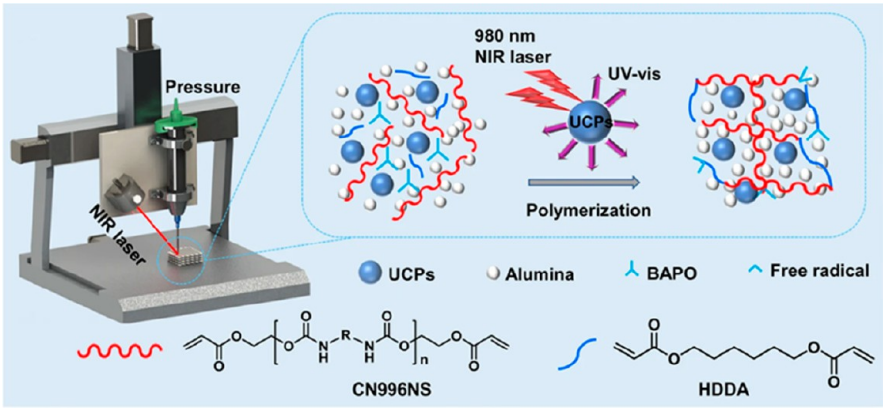

Figure 14. Schematic representation of NIR-assisted direct ink writing. (Reproduced with permission from ref 60. Copyright The Author(s) 2023.)

4. 3D PRINTING WITH WAVELENGTH SELECTION

UV light is a common light source in 3D printing; however, high-energy UV light has poor penetration and a low curing thickness, which makes it unsuitable for printing large objects. Moreover, despite the enormous potential of 3D bioprinting, it is important to recognize that UV light can cause cellular damage and high-energy light can cause genetic instability and chromosome instability in cells. Furthermore, it is impossible to overlook the possibility that extended exposure to intense UV light will cause reactants and products to deteriorate. Because of the aforementioned drawbacks of UV light, researchers have worked hard to develop new curing light sources, such as visible or near-infrared (NIR) light, that will enable higher-quality 3D printing.

Visible light sources are environmentally friendly and do not emit ozone compared to UV light, and LED visible light sources in particular have the advantages of both a low thermal effect and long lifetime, as well as longer wavelengths of visible light with greater depth of penetration and less scattering. In view of the advantages of visible light, Shin et al.[59] proposed a visible light-driven 3D printing method by integrating a novel hexaarylbisimidazole (HABI)-based crosslinker into a red light-curing acrylic resin to make it responsive to visible light. Meanwhile, in order to mitigate the interference of the HABI portion and ensure optical transparency, a red-light-absorbing anthocyanin analogue was used as a photocatalyst to ensure a well-established photobleaching pathway. In this system, a three-component system consisting of anthocyanine derivatives, borates, and iodonium salts successfully realized efficient 3D printing.

Near-infrared (NIR) light has more significant advantages over UV and visible light due to less light damage, lower light scattering, and a higher penetration depth. Zhao et al.[60] recently constructed a new ceramic 3D printing method that couples direct ink writing with an NIR light-induced upconversion particle-assisted photopolymerization (UCAP) process (Figure 14). This method allowed for on-demand curing using NIR radiation at a controlled curing rate, resulting in ceramic structures with flexible geometries and large-resolution feature sizes. Specifically, due to the incorporated upconversion particles into the monomer, these particles radiated UV light to the surrounding area under the excitation

https://doi.org/10.1021/cbe.3c00126
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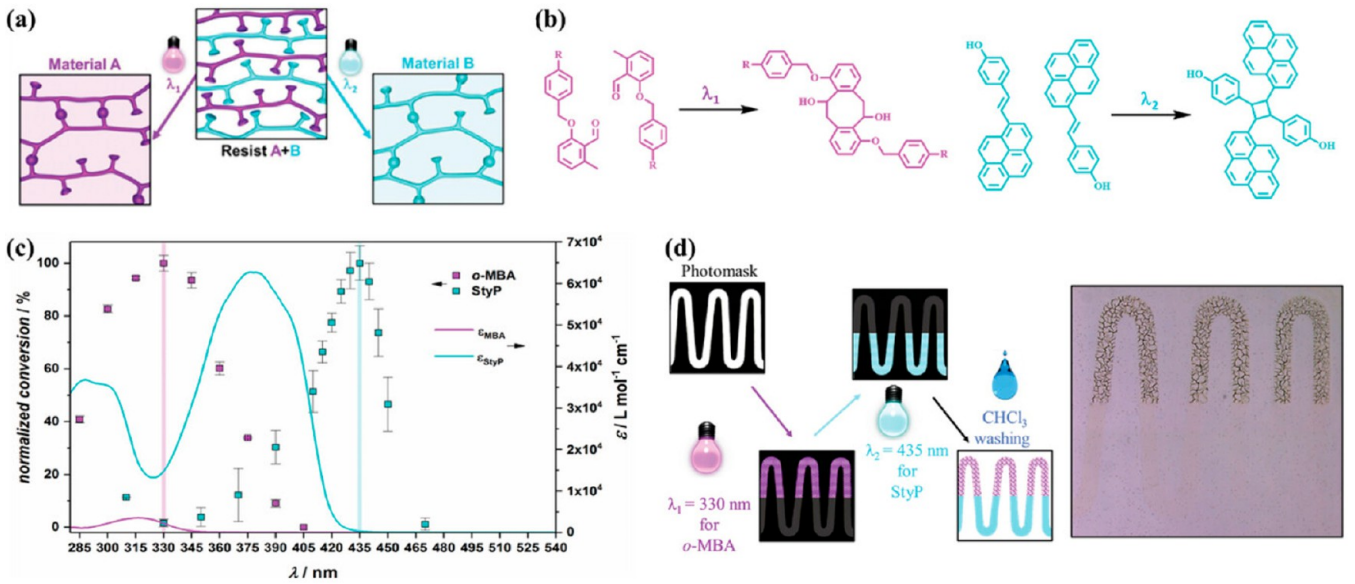

Figure 15. λ-Orthogonal printing. (a) λ-Orthogonal printing of multi-material photoresist under λ_1 and λ_2, respectively. (b) Photoresist consisting of *o*-MBA (left) and StyP (right) for λ-orthogonal printing. (c) Photochemical action plots for implementing the λ-orthogonal printing. (d) Developed photoresist layer after λ-orthogonal printing under 330 and 435 nm, respectively. (Reproduced with permission from ref 33. Copyright 2024, Wiley-VCH.)

of penetrating NIR light, forming a particle-centered limited-domain gradient photopolymerization reaction. The curing system remained in a flow state until a photopolymer network was formed. The technology successfully overcame the limited penetration of UV or visible light in highly solid ceramic pastes. The ceramic pastes could be cured in situ during extrusion using the direct ink writing method without the use of supports by adjusting the irradiation intensity and printing speed.

With respect to the light wavelength control, one should be aware that the highest reactivity may deviate from the absorption maximum, although a higher absorption may benefit the reactivity according to the First and Second Laws of Photochemistry. Thus, according to the research by the Barner-Kowollik group, the utilization of photochemical action plots may be needed for better understanding the relation between photochemical reactivity and absorptivity,[33] as displayed in Figure 15. One amazing added benefit for conducting such photochemical action plots is that one may achieve true λ-orthogonality that seems impossible from the UV−vis absorption spectra. Therefore, multi-material printing would be much easier.

5. SUMMARY AND OUTLOOK

With the continuous innovation of materials and equipment, 3D printing technology has become an efficient, economical, and feasible manufacturing method. After years of development, 3D printing technology has been widely used in manufacturing, aerospace, medical, construction, and other fields, bringing more innovation and development opportunities for various industries. With the help of photochemical technology by designing photopolymerizable monomer, photoinitiating systems, inhibition functions, and light control, 3D printing of recyclable, high-performance materials has made great progress, and the barrier between 3D printing speed and resolution has also been broken, successfully realizing the simultaneous increases.

However, with the demand for mass production in industry, further efforts are needed to realize future high-quality 3D printing. The production of large-volume products is still restricted, the printing cost remains high, the variety of printing materials is limited, and the combination of different methods with both high print speed and resolution is barely reported. In a word, the road ahead for the daily practice of 3D printing still has many challenges; more and more efforts by photochemistry design to enable more precise spatiotemporal control over the photopolymerization kinetics are highly awaited.

Rational chemistry design of the photoinitiating system may be highly awaited to realize efficient 3D printing of functional materials. For instance, carbon dots are new photoluminescent materials with broad availability of raw materials and their 3D printing is a interesting pursuit.[61] Wang et al.[62] successfully prepared liquid crystal carbon dots (LCCDs) by adopting weaker supramolecular van der Waals interactions and grafting flexible alkyl chains on the surface of carbon dots (Figure 16). The liquid crystallization could transform the self-assembled structure of carbon dots from a crystalline phase to a smectic liquid crystal phase. As a result of LCCDs' capacity to form viscoelastic melt at temperatures below 50 °C, solvent-free direct ink writing of LCCDs has been accomplished for the

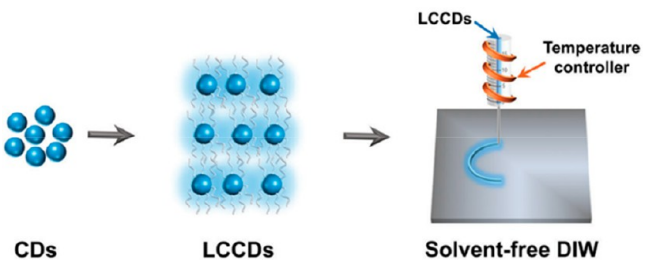

Figure 16. Solvent-free direct ink writing with LCCDs. (Reproduced with permission from ref 62. Copyright 2023 Wiley-VCH GmbH.)

https://doi.org/10.1021/cbe.3c00126
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first time to produce bright red, green, and blue fluorescent lines. Unfortunately, although this study provides a versatile route for the 3D printing of carbon dots, the method is currently extremely difficult to be integrated with photopolymerization as the photoreaction might quench the photoluminescence in the presence of common photoinitiators (e.g., diphenyliodonium hexafluorophosphate).[63]

It is undeniable that there is a mutually beneficial and symbiotic relationship between 3D printing technology and chemistry. The rational and effective use of photochemical materials and subject knowledge can help in the utilization and improvement of 3D printing technology. Aiming at the various shortcomings and limitations of the current UV curing, the innovative development of visible light or an NIR photoinitiation system is a very promising direction for the development of light-cured 3D printing. In addition, endowing printing materials with specific functions and high performance is well-recognized to improve product performance from the source and lay a good foundation for high-quality 3D printing. As such, gradient structure design and synergistic printing of multi-materials will be an important research direction for innovative printing materials. However, how to realize the combination of multi-materials and precise structure design in an appropriate way will be a difficult problem that researchers have to face despite the attractive advances via reaction orthogonialty.[31]

All in all, 3D printing technology is a technology full of potential and innovation. From its origins to its current development and its future outlook, we can see that its impact on human society is becoming more and more far-reaching. Whether it is in improving productivity, reducing costs, promoting innovation, or solving global problems such as environmental and resource issues, 3D printing shows great potential, and its future development is worth looking forward to.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are thankful for the financial support from the National Natural Science Foundation of China (52122316, 52073108, and 52233005), and the support from the Innovation and Talent Recruitment Base of New Energy Chemistry and Device (B21003). We also would like to thank the Open Research Fund (No. 2023JYBKF05) of Key Laboratory of Material Chemistry for Energy Conversion and Storage (HUST), Ministry of Education.

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