



Cite this: *Mol. Syst. Des. Eng.*, 2022, 7, 1017

Received 17th April 2022,
Accepted 30th June 2022

DOI: 10.1039/d2me00066k

rsc.li/molecular-engineering

Digital light processing 3D printing of hydrogels: a minireview

Hongyao Ding,^{†ab} Min Dong,^{†a} Qiang Zheng^a and Zi Liang Wu^{ib} ^{★a}

The rapid development of three-dimensional (3D) printing of hydrogel materials into sophisticated constructs has led to considerable progress in the fields of tissue engineering, soft actuators/robots, flexible electronics, etc. Notably, digital light processing (DLP) based 3D printing provides a potential strategy to achieve high resolution and elaborate 3D structures that are important for specific applications. In this review, we highlight the recent advances in the field of DLP printing of hydrogels with emphasis on the selection of materials, structure designs, and printing technologies. We then discuss the applications of DLP printed hydrogel constructs in biomedicine, tissue engineering, medical devices, soft actuators, and flexible electronics. Finally, the current challenges and future perspectives of DLP printing of hydrogels are also discussed.

Design, System, Application

This is a review paper, in which we give an overview of the recent advances in the field of digital light processing 3D printing of hydrogels with emphases on printing technologies, materials selection, structure designs, and representative applications. We do not report new materials, new designs, or new applications in this paper.

1. Introduction

Three-dimensional (3D) printing, also known as additive manufacturing (AM), is an emerging rapid manufacturing technology first developed in the late 1980s.¹ The essence of 3D printing is the process of stacking raw materials into the corresponding solid devices according to a 3D digital model predesigned using computer modeling software.^{2,3} Owing to the dimensions and flexibility in endowing materials with micro- to nano-scale structural architectures and new functionalities beyond those of their bulky counterparts,⁴ 3D printing has received growing attention and will continue to favor broad applications including biomedical devices, intelligent systems, energy devices, and soft robotics.^{5–8} With the continuous in-depth research on the forming mechanisms and material systems, various 3D printing technologies have been developed in recent years, including fused deposition modelling (FDM),^{9,10} direct ink writing (DIW),^{11–13} direct inkjet printing (DIP),^{14,15} selective laser

sintering (SLS),^{16,17} stereolithography apparatus (SLA),¹⁸ digital light processing (DLP)^{13,19} and so on.^{20–22}

Among these printing technologies, DLP belonging to light-based printing utilizes projection light to polymerize precursors to obtain pre-designed architectures.^{6,23} In particular, the printing speed of this technology ranges from 25 to 1000 mm min^{−1}, and relies chiefly on the intensity of light power and the sensitivity of the printing material. The resolution of printed structures based on DLP has reached as high as 1 μm by focusing the projected light through an optical system.²⁴ Therefore, DLP printing has attracted growing research interest due to its high printing speed, high resolution, and low cost.^{13,25–27} In spite of extensive progress, DLP-based 3D printing is generally limited to material choices. For example, most of DLP-compatible materials are photocurable rigid thermoset materials.^{5,6,28–36} It is highly required to devise flexible devices with soft and active architectures in the new era of intelligence.

Recent advances in soft materials such as hydrogels with good biocompatibility, processibility, and adaptability have opened up a broad spectrum of opportunities in diverse areas, including drug delivery, tissue engineering, and soft actuators.^{37–46} Combined with emerging DLP based 3D printing technologies, hydrogels have been fabricated into complex architectures such as vascular networks, porous scaffolds, and meniscus substitutes for target

^a Ministry of Education Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, 310027, China. E-mail: wuziliang@zju.edu.cn

^b College of Materials Science and Engineering, Nanjing Tech University, Nanjing, 211816, China

[†] These authors contributed equally to this work.

applications.^{47–50} In response to the growing interest in this area, we aim to provide a general overview for the rapid development of DLP printing of hydrogels. In this minireview, we give a simple introduction to DLP-based printing technologies, summarize recent progress in DLP-based printing of hydrogels into various constructs, and present their applications in the fields of tissue engineering, biomedical devices, soft actuators, and flexible electronics. Finally, we conclude with the discussion of current challenges and future perspectives of DLP printing of hydrogel materials.

2. DLP printing technologies and materials requirements

2.1. Printer features and operation

A DLP printer includes a projector light and build platform, a vat of liquid resin, and a mobile Z axis.^{5,6} The core component is the digital micromirror device (DMD) embedded in the projector which controls the resolution of projected 2D images sliced from the target 3D object and directly determines the geometric morphology and printing accuracy of the final constructs.⁵¹ Once a layer has been printed, the platform moves vertically for a certain distance and continues to locally cure the precursor by using patterned ultraviolet light. This process is repeated layer by layer until the desired 3D architecture is constructed. According to the moving direction of the building platform, DLP-based 3D printing is generally divided into the “bottom-up” form and “top-down” form.²⁹

2.1.1. “Bottom-up” projection approach. In “bottom-up” DLP printing, the printed object hangs upside down from the bottom of the build platform. During the printing process, solidification occurs at the bottom of the vat, after which the retractable platform pulls upward from the liquid for a certain distance. The robotically controlled focal plane moves vertically for another illumination and photocuring process (Fig. 1a). Notably, the bottom plate of the resin tank needs to be light permeable and covered with an oxygen-permeable

film or perfluorinated film to reduce the adhesion between the printed structure and the printer. For the “bottom-up” projection approach, the prominent advantages are less resin consumption, higher leveling rate of liquid resins, and more diversified adaptability of materials.⁵²

2.1.2. “Top-down” projection approach. In “top-down” DLP printing, the object is printed at the air–liquid interface at the top, and the platform is moved downward into the vat vertically during the printing process (Fig. 1b). The height of the printed object, therefore, depends heavily on the vat depth. The printed object is soaked in the raw material, and the printer cures the top layer of the fluid. This type of printing requires lots of raw materials and is prone to waste.^{13,25} The object size obtained by this method has relatively high resolution and fidelity, because the bottom vat resin not only serves as the supply source to form a new layer for the next printing but also provides buoyant force to support the printed constructs. However, the vibration of solution at the air–liquid interface is a challenging issue that reduces the resolution in top-down projection when compared to the bottom-up approach, which can be mitigated by increasing the layer-to-layer printing interval.²⁹

2.2. Formulation of the precursor solution

In general, processing of hydrogels by using DLP-based 3D printing involves an aqueous solution of photosensitive oligomers or reactive monomers, a photoinitiator activated above 385 nm, a photo-inhibitor, and/or a cross-linking agent.^{24,48,53} Many DLP precursor solutions possess a low apparent viscosity (<5 Pa s) to bring rapid and even replenishment of fresh resin into the processing area for the construction of the next layer.⁵⁴ When the apparent viscosities are higher than 100 kPa s, continuous printing often fails because the partially cured resin with a high viscosity cannot be fully removed from the surface of the printed object. The repeated exposures for subsequent layers can further aggravate this issue of incomplete resin recirculation, sub-gelation polymerization, and eventual

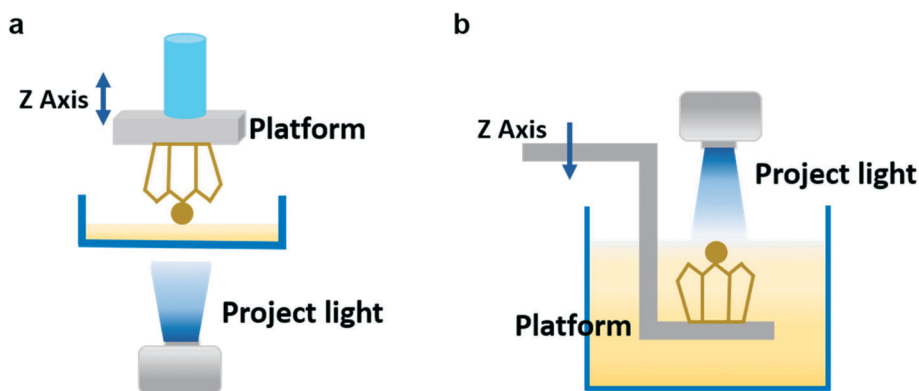


Fig. 1 Schematic illustration for the “bottom-up” (a) and “top-down” (b) printing technologies based on digital light processing (DLP) of photocurable materials.

overcuring. This undesired solidification adds unwanted fillets at the edges or completely fills negative features (*i.e.*, holes, gaps, and overhangs). Beyond the limitation of resolution, highly viscous ink also creates large adhesive or drag forces between the projection platform and printed object during bottom-up DLP. Such adhesive stresses, particularly for large cross-sectional areas, can exceed the strength of the material and cause failure of the printed constructs.⁵⁵

The photoinitiator plays a crucial role in determining the rate of polymerization and, consequently, the resulting properties of the printed construct and the time required for 3D fabrication.^{48,56,57} According to different solubilities in water, photoinitiators are divided into water-soluble photoinitiators and oil-soluble photoinitiators. Oil-soluble photoinitiators commonly used for DLP printing are 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TPO) and phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (Irgacure 819) because of high efficiency. In addition, available water-soluble photoinitiators include 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propanone (I2959) and lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP). However, it still remains a grand challenge to engineer hydrogels with high water content using DLP printing technology because of the absence of more efficient water-soluble photoinitiators to enable fast gelation and continuous printing of the precursors.⁵⁸ In order to alleviate the problem, Pawar *et al.* successfully presented an innovative approach to enable rapid DLP printing of hydrogel precursor solutions by converting the water-insoluble photoinitiator TPO into water-dispersible nanoparticles,⁵⁹ which exhibited a high efficiency and high speed of polymerization upon irradiation.⁶⁰ The reaction rate also depends on the light intensity of the projector. In other words, the processing speed of the precursors is

related to the intensity of light and the efficiency of photoinitiators. For practical applications, the selection of photoinitiators should also consider the stability of the whole system, which should be ensured after the addition of photoinitiators. The photoinitiators used for DLP printing, as well as the light initiation wavelength and corresponding curing speed, are summarized in Table 1.

Furthermore, photoinitiators and photo-absorbers are particularly important for DLP-based 3D printing. The former determines the time required to initiate the polymerization and/or crosslinking reaction and the cross-linking degree, while the latter is used to control the curing depth of the photopolymer resin and prevent ultraviolet light from penetrating the entire layer.⁶⁴ Photo-inhibitors contribute to the smooth surface of printed building blocks, avoiding the occurrence of excessive cured hydrogel in preset sections. Otherwise, hydrogels normally undergo excessive curing in the absence of a light absorber and displays a poor printing ability.⁶⁵ For a better comparison of the influencing factors on the DLP printing of hydrogel materials, the material composition, printing method, light initiation wavelength, curing speed, mechanical properties, resolution, and relevant applications of printed constructs are summarized in Table 2.

3. DLP 3D printing of hydrogels and their applications

Elaborate architectures of hydrogel materials can be printed by selecting suitable raw materials and adjusting the printing parameters, which greatly broadens the application of hydrogels in diverse fields. In this section, 3D hydrogel constructs fabricated by DLP printing are reviewed with their applications in tissue engineering, biomedical devices, soft actuators/robots, and flexible electronics.

Table 1 Photoinitiators commonly used for DLP printing of hydrogels

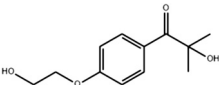
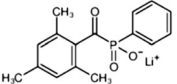
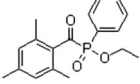
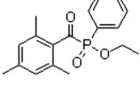
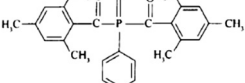
Name	Molecular structure	Solubility	Initiation wavelength (nm)	Ref.
I2959		Water-soluble	365–405	47
LAP		Water-soluble	365–405	61
Water-soluble TPO		Water-soluble	365–405	47
TPO		Oil-soluble	365–405	62
Irgacure 819		Oil-soluble	365–405	63

Table 2 Various DLP printed hydrogels, including the material system, photoinitiator, photo-absorber, printing approach, initiation wavelength, curing time, Young's modulus, resolution, and relevant applications

Material system	Photoinitiator	Photo-absorber	Printing method	Initiation wavelength (nm)	Curing speed	Young's modulus (kPa)	Resolution (μm)	Applications	Ref.
PEGDA/GelMA	LAP	Brilliant blue	Bottom-up	365	4.9 s/50 μm	~500	10	Cell culture	66
AAm	Water-soluble TPO	Sudan I/food dye	Top-down	405	7.5–32 s/140 μm	7–260	7	Stretchable electronics	67
ACMO/PEGDA/Aac	Oil-soluble TPO	Sudan III	Top-down	405	8 s/100 μm	—	500	Self-weldability	62
AAm/Aac	Water-soluble TPO	Tartrazine	Bottom-up	—	2.4 s/50 μm	42	100	Tissue engineering	68
PVA/Aac/PEGDA	Water-soluble TPO	Methyl red and brilliant green	Bottom-up	385	5 s/200 μm	~60	1000	—	53
Aac	Irgacure 819	Sudan I	Top-down	385	3–10 s/100 μm	—	—	—	69
AAm/Aac	Irgacure 819	Sudan I	Bottom-up	405	3 s/100 μm	~110	—	Sensor	48

Note: PEGDA, GelMA, AAm, ACMO, PVA, and Aac are the abbreviations of poly(ethylene glycol) diacrylate, gelatin methacrylate, acrylamide, 4-acryloylmorpholine, polyvinyl alcohol, and acrylic acid, respectively.

3.1. Tissue engineering and biomedical devices

Hydrogels are an ideal candidate for tissue engineering and biomedical devices due to their special characteristics such as flexibility, biocompatibility, and sensitivity to physiological environments.^{70–73} DLP-based 3D printing offers a fascinating manufacturing method to fabricate sophisticated constructs with self-defined microstructures, which can greatly widen the application of hydrogels or their hybrids in these areas. For example, Yang and coworkers have fabricated a heterogeneous structure with the shape of a human heart valve derived from computed tomography (CT) data.⁶⁸ This hybrid hydrogel construct consisted of a hydrogel skeleton produced by DLP-based 3D printing with the “bottom-up” projection approach and another hydrogel matrix prepared by casting (Fig. 2a). The artificial heart valve exhibited excellent fatigue resistance during cyclic experiments, much better than that of comparative homogeneous hydrogel constructs. This work will inspire the creation of artificial organs with tailored mechanical performances and good biocompatibility based on the DLP printing technology. In addition, Zhang *et al.* printed high-resolution and high-fidelity stretchable hydrogel tissues such as the ear, nose, and blood vessels by using the DLP-based 3D printing technology.⁶⁷ The raw materials used for printing included acrylamide, poly(ethylene glycol) diacrylate, and a self-made water-soluble photoinitiator, which showed excellent biocompatibility. In addition, Xue *et al.* printed cell-seeding hydrogel scaffolds by DLP-based 3D printing of precursors containing poly(ethylene glycol) diacrylate (PEGDA) and a home-made photoinitiator, which exhibited regionally varied stiffness by adjusting the exposure time (Fig. 2b).²⁴ 3T3 fibroblasts were evenly distributed on the printed scaffold and proliferated well during cell culture, indicating the excellent biocompatibility and physical support of the hydrogel scaffolds. The approach provides a solution to constructing heterogeneous cell-seeding hydrogel scaffolds with different regional stiffness by changing the exposure time to adjust the mechanical properties. Moreover, Wang *et al.* have developed complex hydrogel constructs at a high resolution by using a gradient DLP 3D printing system with a combination of a digital micromirror device-based bioprinter and a microfluidic chaotic mixer-linked vat (Fig. 2c).⁷⁴ The approach can achieve functional (bio)printing by controlling the (bio)ink gradients with various cell densities, substrate stiffness, and growth factor concentration, as well as porosity and pore size, and endow the recapitulation of the gradient properties of natural tissues with complex architectures and at high resolution. Furthermore, Ge *et al.* printed a cardiovascular shape memory polymer stent with a self-built multi-material DLP printer by integrating a hydrogel inside it, which can be used to load drugs at the designated hydrogel sites.⁷⁵ The working principle of the printed stent was demonstrated using artificial blood vessels (Fig. 2d). The stent contracted prior to use and expanded gradually after being held at the desired site accompanied by drug release.

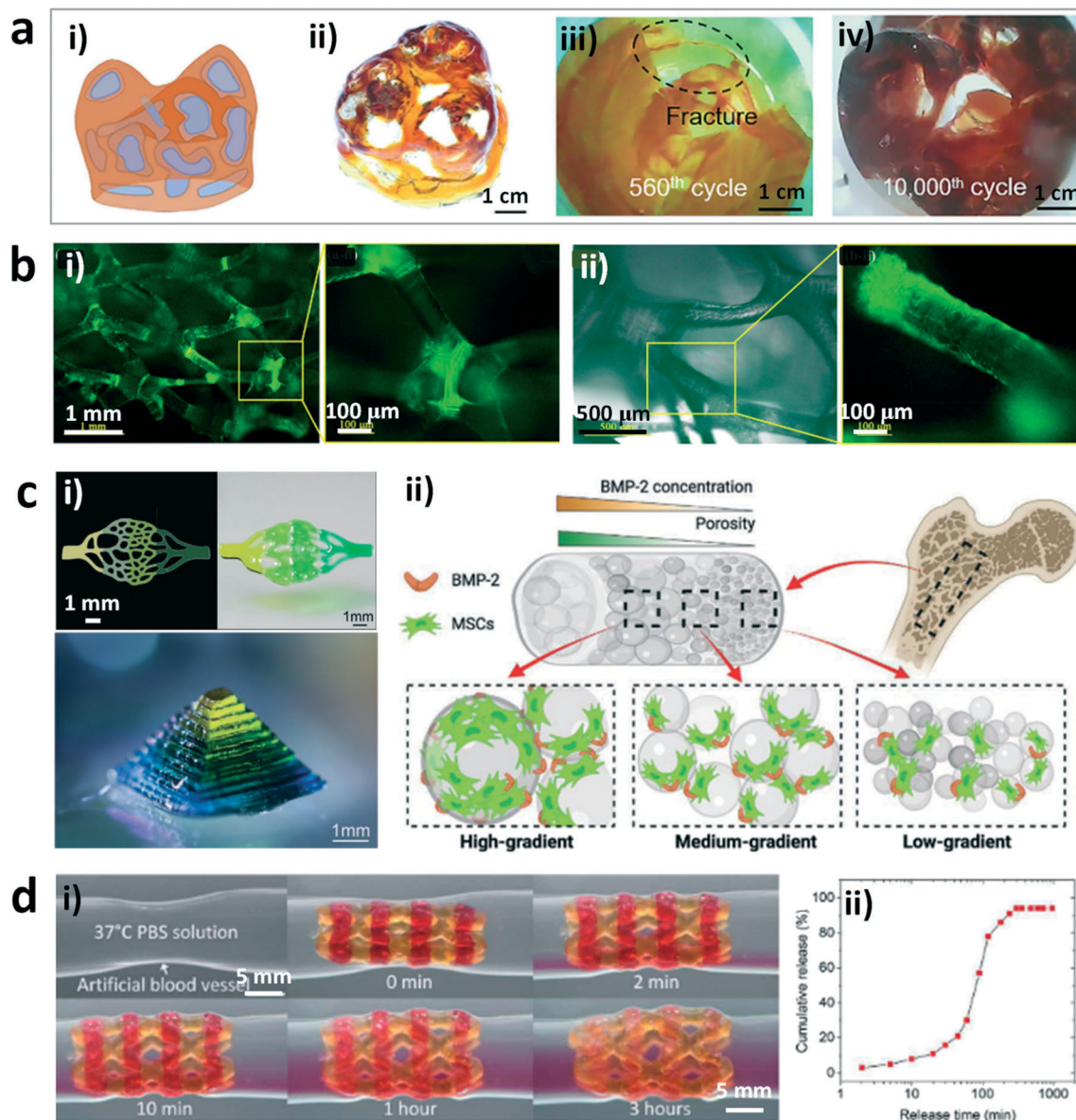


Fig. 2 DLP printed hydrogels and their applications in tissue engineering and biomedical devices. (a) Schematic (i) and image (ii) of the heterogeneous hydrogel, and endoscopy images of the homogeneous (iii) and heterogeneous (iv) hydrogel heart valves after cyclic experiments.⁶⁸ Reprinted from ref. 68, copyright 2021, Elsevier. (b) Fluorescence microscopy images of the 3T3 fibroblast distribution in the printed hydrogel scaffold (i) and interaction of 3T3 fibroblasts with the joint of the scaffold (ii).²⁴ Reprinted from ref. 24, copyright 2019, American Chemical Society. (c) 2D capillary-like network structure and 3D pyramid structure printed by the gradient DLP printing technique (i) and a schematic to show the printed 3D object encapsulated with MSCs for the investigation of osteogenic effects of the dual gradients of porosity and BMP-2 (ii).⁷⁴ Reprinted from ref. 74, copyright 2022, Wiley-VCH. (d) Illustrations of drug release from the printed stent in the artificial blood vessel (i) and the quantification of drug release from the printed stent (ii).⁴⁷ Reprinted from ref. 47, copyright 2021, American Association for the Advancement of Science.

The release rate of loaded drugs can reach 90% within 3 hours. This work provides a new way to realize the fabrication of soft devices with multiple materials by bonding hydrogels with other polymers in 3D architectures.

3.2. DLP 4D printing of hydrogels

4D printing is an emerging technology, in which the 3D-printed structure can self-transform in shape, properties, and

functions in response to stimuli.^{69,76,77} Inspired by the biological deformations of natural systems, abundant bionic morphing hydrogels have been developed by creating heterogeneous network structures and/or imparting inhomogeneous stimulations.^{78–81} Recently, there have been several programmed shape-morphing systems developed by using DLP-based 3D printing technologies to fabricate hydrogels or hydrogel-polymer hybrids. For example, Ji *et al.* explored a one-step method to fabricate complex 3D

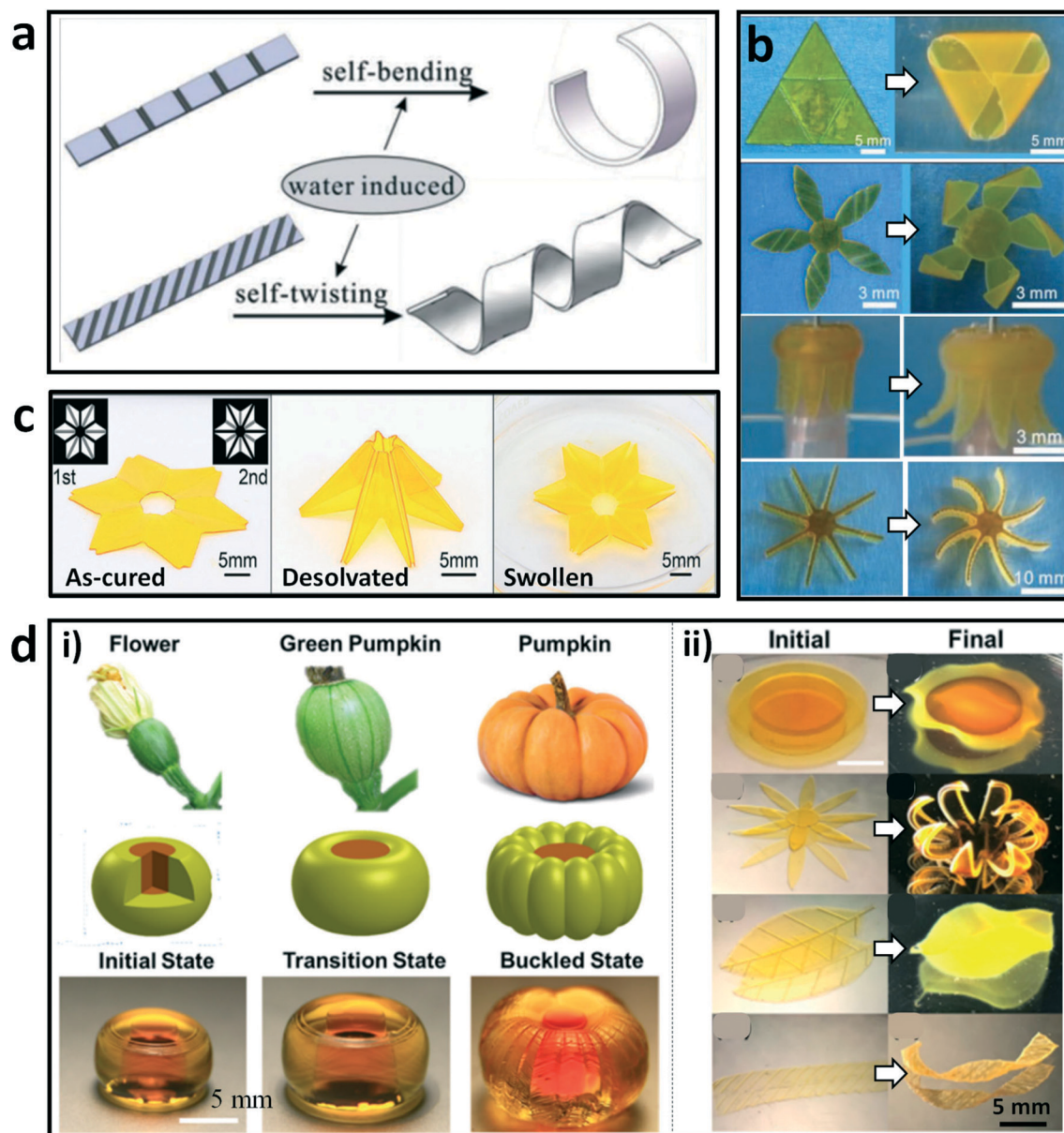


Fig. 3 DLP-based 4D printing of hydrogels. (a) Illustration of the bending and twisting deformations of printed strips with programmed structures. (b) Complex shape morphing of printed constructs triggered by water.⁸² Reprinted from ref. 82, copyright 2019, Wiley-VCH. (c) As-cured flat pattern, desolvated origami shape, and swollen flat shape of the printed six-petal flower with the origami structure. Insets show two grayscale patterns for DLP printing.⁸³ Reprinted from ref. 83, copyright 2017, Wiley-VCH. (d) Images, schematic diagram, and photos of the printed hydrogel (i) that deformed into a pumpkin-like morphology during the swelling process; morphological transformations (ii) of printed biomimetic structures from the initial plain states to their final states after the swelling process.⁶⁹ Reprinted from ref. 69, copyright 2019, American Chemical Society.

architectures that can deform under stimuli from humidity and temperature.⁸² These hydrogel constructs were developed by using a commercial DLP printer with the “bottom-up” projection approach. The principle of shape morphing was related to the asymmetric swelling of the printed hydrogel blocks with programmed secondary microstructures on one surface. The printed architectures showed bending and twisting deformations induced by moisture, and returned to their original shapes by adjusting the environment conditions (Fig. 3a). In particular, various 3D desired morphologies including triangular pyramid, stereo windmill,

“octopus”, and hydroturbine shapes can be obtained by taking advantage of the flexible design and freeform fabrication of this method (Fig. 3b). In addition, Zhao *et al.* printed self-folding origami constructs with environmental responsiveness by DLP printing of a PEGDA based material system.⁸³ As shown in Fig. 3c, different cross-linking degrees existed in the as-printed architecture by controlling the light intensity during the printing, which resulted in self-folding deformation when desolvation in water occurred. Notably, the folded origami recovered its original shape after being incubated in the swelling medium. Moreover, Wu *et al.*

achieved distinct circumferential buckling, visible during the growth of pumpkins, which was reproduced by a core-shell barrel structure developed by 4D printing of responsive hydrogels (Fig. 3d).⁶⁹ The deformation process was triggered by swelling of the hydrogels. Various morphological transformations of biomimetic structures were inspired by real cabbage flowers/leaves, chrysanthemum, leaves of rose, and helix strips of seedpods. These studies have paved the way to fabricating hydrogels with heterogeneous structures, which should broaden the applications of hydrogel materials in bionics and engineering fields.

3.3. DLP printed hydrogels as soft actuators

As one class of intelligent devices, soft actuators and robots can transform external stimuli into programmed deformations and mechanical motions.^{84–87} By using DLP-based 3D printing technologies, a variety of hydrogel actuators and robots have been developed with responsive elements and/or asymmetrical geometries in the constructed blocks.⁸⁸ For example, an eight-arm gripper was printed by incorporating the responsive component with a lower critical solution temperature (LCST) to the system, and showed asymmetric swelling behavior in

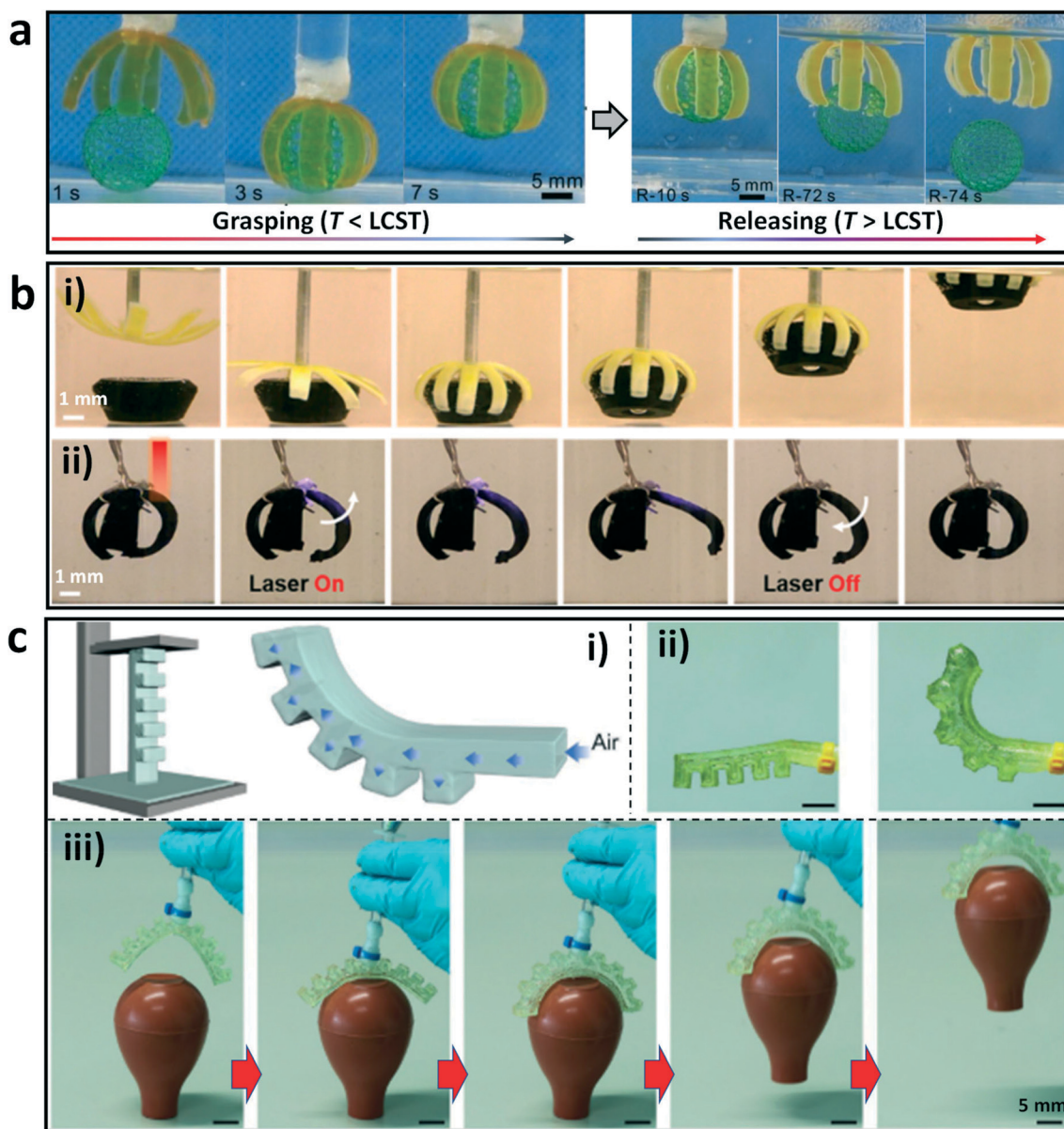


Fig. 4 DLP printed hydrogels as soft actuators. (a) 3D printed thermal-responsive hydrogel actuator for object transportation.⁸² Reprinted from ref. 82, copyright 2019, Wiley-VCH. (b) Grasping of an object with a 3D printed bilayer hydrogel gripper through thermal actuation (i), and infrared laser-mediated remote and selective actuation of the bilayer actuator coated with polypyrrole (ii).⁶¹ Reprinted from ref. 61, copyright 2021, American Chemical Society. (c) Schematic diagram of the soft pneumatic actuator and the deformation after pressurization (i); photos of the printed two-arm hydrogel actuator to capture a soft rubber pipette bulb (iii).⁸⁹ Reprinted from ref. 89, copyright 2022, Wiley-VCH.

response to variation of temperature. The printed gripper can be used to transport objects quickly by controlling the environment temperatures (Fig. 4a).⁸² In addition, Hua *et al.* have devised a bilayer hydrogel actuator with high toughness and actuation force by DLP-based 3D printing with the raw materials *N*-isopropylacrylamide (NIPAm) and poly(vinyl alcohol) (PVA) or

its methacrylate derivatives (PVA-MA).⁶¹ The passive layer was composed of PVA/PVA-MA, while the active layer was composed of PVA/PVA-MA-*g*-PNIPAm with temperature responsiveness. In a hot water bath, the actuator can grasp an object multiple times its own weight. The bilayer actuator was further coated with polypyrrole to enable remote and selective activation by

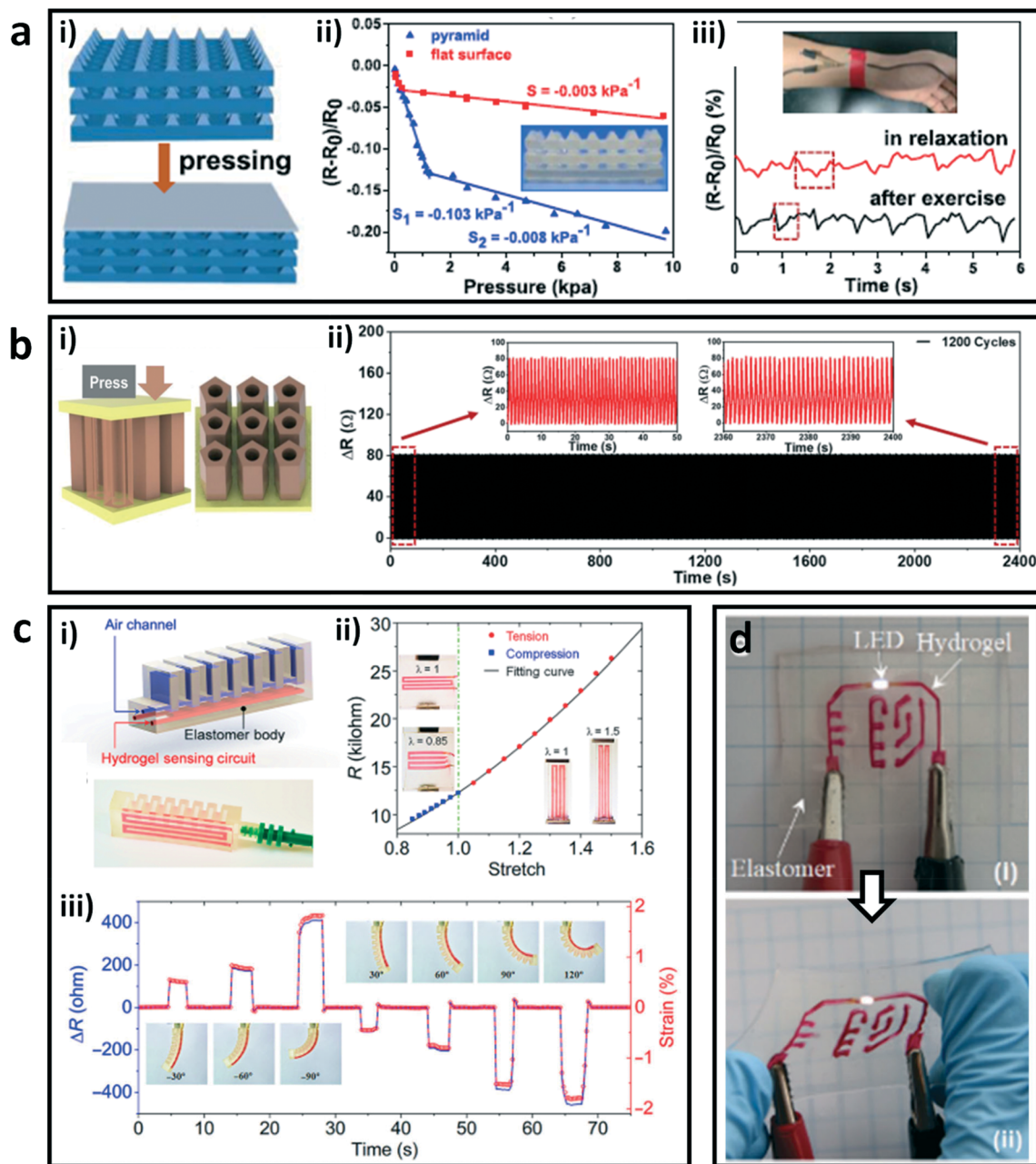


Fig. 5 DLP printed hydrogels and their hybrids as soft electronics. (a) Schematic illustration of the printed three-layer pressure sensors with micrometer-scale pyramids (i); the pressure sensitivities of the printed hydrogel sensor and the planar sensor (ii); usage of the printed sensor to monitor the pulse at the wrist of a volunteer in the relaxation state and after exercise (iii).⁴⁸ Reprinted from ref. 48, copyright 2021, American Chemical Society. (b) Printed pressure-sensitive sensor with the structure of regularly arranged hollow pentagonal prisms (i) and the change of its resistance in a cyclic loading process (ii).⁵⁶ Reprinted from ref. 56, copyright 2021, American Chemical Society. (c) Schematic and illustration of the printed soft pneumatic actuator (SPA) (i); the relationship between the resistance and stretching (ii) and the sensing performance of the printed hydrogel SPA to bending deformations (iii).⁴⁷ Reprinted from ref. 47, copyright 2021, American Association for the Advancement of Science. (d) An electronic panel achieved by printing an ionic hydrogel circuit on an elastomeric substrate in initial state (i) and stretched state (ii).⁶⁷ Reprinted from ref. 67, copyright 2018, Royal Society of Chemistry.

using an infrared laser (Fig. 4b), which makes the actuator easier to use in practical applications.

Moreover, Wang *et al.* developed a special polymer gel (PEGgel) system by polymerizing hydroxyethyl methacrylate and acrylic acid in poly(ethylene glycol) (PEG) medium.⁸⁹ A pneumatic soft actuator with an asymmetric hollow structure was printed by DLP 3D printing with the PEG gel precursor (Fig. 4c). When pressurized, the serrated portion expanded and the printed gel deformed toward the non-serrated side, resulting in a directional force that acted as an actuator. A two-arm actuator was further fabricated, which can realize the capture of a rubber pipette bulb successfully. This work avoids the complex and multi-step molding or casting manufacturing processes for the fabrication of soft actuators, and enables geometric complexity and functionality for the design of soft robots.

3.4. DLP printed hydrogels as soft electronics

The network structure of hydrogels is conducive to the rapid movement of ions and endows them good conductivity, which gives the application possibility of conductive hydrogels in soft electronics.^{90–92} However, conventional fabrication methods such as molding lead to simple structures and insufficient dimensional accuracy of constructs, which are crucial for the reliability and functionality of hydrogel devices.^{93,94} The DLP-based 3D printing technology can provide a solution to address this conundrum. For example, He and coworkers prepared composite hydrogels through DLP 3D printing with a synthesized microemulsion and common hydrophobic photoinitiator.⁴⁸ The composite hydrogel possessed high mechanical strength (22.9 MPa) and ionic conductivity (9.64 S m⁻¹). Pressure sensors with micrometer-scale pyramids were printed, and showed a high absolute value of pressure sensitivity of 0.103 kPa⁻¹ below 1.25 kPa. Compared to a planar hydrogel sensor with the same material, the printed three-layer pyramid sensor had a higher sensitivity due to the larger deformation under the same pressure. On account of the excellent sensitivity, the obtained hydrogel sensors were used to monitor real-time large and subtle human motions (Fig. 5a). In addition, Wang *et al.* synthesized a water-soluble photoinitiator through a simple and straightforward one-pot method.⁵⁶ They printed a pressure sensor with a structure of regularly arranged hollow pentagonal prisms by DLP-based 3D printing. The obtained sensor showed fast responsiveness and excellent durability under cyclic loading–unloading due to its special geometry structure (Fig. 5b). These special geometry structures can increase the sensitivities and stabilities of these strain sensors by increasing the deformation capacity under external force, which is informative for the design of high-performance sensors.

Besides, Ge and coworkers printed a soft pneumatic actuator (SPA) with a strain sensor by using a self-built DLP-based 3D printer with multiple hydrogel and elastomer materials.⁴⁷ The relationships between resistance and tension

and compression of the composite sensor were constructed by longitudinal and transverse tensile respectively, which exhibited nonlinear resistance–deformation behaviors. The constructed strain sensor can detect the actuations of the SPA with both positive and negative bending by transforming the measured resistance variations to the strains of the printed SPA (Fig. 5c). Moreover, they also printed a flexible electronic board with an ion conductive hydrogel circuit on an elastomer sheet with high resolution and high fidelity, which maintained electrical functionality under large deformation due to the strong interface bonding between different materials (Fig. 5d).⁶⁷ These studies greatly broadened the functionality and performance of hydrogel–polymer hybrid devices and machines.

4. Conclusions and perspectives

Among all the additive manufacturing technologies, DLP-based 3D printing exhibits many advantages such as high printing speed and high resolution, and thereby has been recognized as an ideal fabrication strategy to develop sophisticated architectures with applications in tissue engineering, soft actuators, and flexible electronics.^{95–100} This review summarizes recent progress in relevant fields with the focus on DLP printing of hydrogel materials.

In recent years, hydrogels have been developed rapidly and widely used in diverse fields.^{101–106} However, hydrogel systems suitable for DLP printing are still very limited because of the lack of high-efficiency water-soluble photoinitiators. In addition, most of photocurable hydrogels have the problems of cumbersome polymerization rate and inferior solidification capacity, leading to fundamental shortcomings such as a low Young's modulus of the printed hydrogels. It remains a grand challenge to achieve high-resolution printing of tough hydrogels.^{47,67} It is highly desired to expand hydrogel systems suitable for DLP printing in terms of developing high-efficiency water-soluble photoinitiators and designing tough hydrogels with unique network structures and energy dissipation mechanisms.^{101–104} Besides, DLP-based multi-material 3D printing is another way to expand the application of hydrogels, in which the problem of interface bonding between different materials should be well addressed. In this way, materials with different functions can be integrated to afford versatile printed structures.^{107–109}

DLP printing has the advantages of high printing accuracy and smooth product surface, and it is mainly used for manufacturing small volume items such as jewelry casts and dental molds. This is because the light source in the printing process is flat exposure, and the exposure area is limited. Due to the limited resolution of the digital light mirror (DMD) of the printing equipment, it is still challenging to print large sized products. Therefore, future efforts should be devoted to improving the resolution of DMDs by enhancing the number of microscopes inside the DMD chips for the fabrication of large-sized products.

As described above, the DLP printing technology has enabled the engineering hydrogels with sophisticated architectures and/or heterogeneous structures in a high-efficiency way, which greatly improves the applications of gel materials in the biomedical and engineering fields. We believe that this review will broaden research interest and inspire innovative ideas for the fabrication and application of hydrogel constructs. The DLP-based 3D printing technologies will provide stronger power for people from all walks of life in the future.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51973189, 52173012) and the Excellent Youth Foundation of Zhejiang Province of China (LR19E030002).

References

- 1 R. L. Truby and J. A. Lewis, Printing soft matter in three dimensions, *Nature*, 2016, **540**(7633), 371–378.
- 2 A. Ambrosi and M. Pumera, 3D-printing technologies for electrochemical applications, *Chem. Soc. Rev.*, 2016, **45**(10), 2740–2755.
- 3 W. T. Nugroho, Y. Dong and A. Pramanik, *et al.*, Smart polyurethane composites for 3D or 4D printing: General-purpose use, sustainability and shape memory effect, *Composites, Part B*, 2021, **223**, 109104.
- 4 E. MacDonald and R. Wicker, Multiprocess 3D printing for increasing component functionality, *Science*, 2016, **353**(6307), aaf2093.
- 5 G. Ge, Q. Wang and Y. Z. Zhang, *et al.*, 3D printing of hydrogels for stretchable ionotronic devices, *Adv. Funct. Mater.*, 2021, **31**(52), 2107437.
- 6 T. J. Wallin, J. Pikul and R. F. Shepherd, 3D printing of soft robotic systems, *Nat. Rev. Mater.*, 2018, **3**(6), 84–100.
- 7 J. Li and M. Pumera, 3D printing of functional microrobots, *Chem. Soc. Rev.*, 2021, **50**(4), 2794–2838.
- 8 F. Zhu, J. Lin and Z. L. Wu, *et al.*, Tough and conductive hybrid hydrogels enabling facile patterning, *ACS Appl. Mater. Interfaces*, 2018, **10**(16), 13685–13692.
- 9 S. C. Daminabo, S. Goel and S. A. Grammatikos, *et al.*, Fused deposition modeling-based additive manufacturing (3D printing): techniques for polymer material systems, *Mater. Today Chem.*, 2020, **16**, 100248.
- 10 M. A. Caminero, J. M. Chacón and I. García-Moreno, *et al.*, Impact damage resistance of 3D printed continuous fibre reinforced thermoplastic composites using fused deposition modelling, *Composites, Part B*, 2018, **148**, 93–103.
- 11 S. Y. Zheng, Y. Shen and F. Zhu, *et al.*, Programmed deformations of 3D-printed tough physical hydrogels with high response speed and large output force, *Adv. Funct. Mater.*, 2018, **28**(37), 1803366.
- 12 C. Du, J. Hu and X. Wu, *et al.*, 3D printing of a tough double-network hydrogel and its use as a scaffold to construct a tissue-like hydrogel composite, *J. Mater. Chem. B*, 2022, **10**(3), 468–476.
- 13 S. H. Kim, Y. K. Yeon and J. M. Lee, *et al.*, Precisely printable and biocompatible silk fibroin bioink for digital light processing 3D printing, *Nat. Commun.*, 2018, **9**(1), 1620.
- 14 B. Li, N. Hu and Y. Su, *et al.*, Direct inkjet printing of aqueous inks to flexible all-solid-state graphene hybrid micro-supercapacitors, *ACS Appl. Mater. Interfaces*, 2019, **11**(49), 46044–46053.
- 15 Z. Zhu, H. Ning and W. Cai, *et al.*, Morphology modulation of direct inkjet printing by incorporating polymers and surfactants into a sol-gel ink system, *Langmuir*, 2018, **34**(22), 6413–6419.
- 16 F. Sillani, R. G. Kleijnen and M. Vetterli, *et al.*, Selective laser sintering and multi jet fusion: Process-induced modification of the raw materials and analyses of parts performance, *Addit. Manuf.*, 2019, **27**, 32–41.
- 17 R. Ajdary, N. Kretschmar and H. Baniasadi, *et al.*, Selective laser sintering of lignin-based composites, *ACS Sustainable Chem. Eng.*, 2021, **9**(7), 2727–2735.
- 18 B. Y. Yu, K. Son and K. B. Lee, Evaluation of intaglio surface trueness and margin quality of interim crowns in accordance with the build angle of stereolithography apparatus 3-dimensional printing, *J. Prosthet. Dent.*, 2021, **126**(2), 231–237.
- 19 D. K. Patel, A. H. Sakhaei and M. Layani, *et al.*, Highly stretchable and UV curable elastomers for digital light processing based 3D printing, *Adv. Mater.*, 2017, **29**(15), 1606000.
- 20 J. R. Tumbleston, D. Shirvanyants and N. Ermoshkin, *et al.*, Continuous liquid interface production of 3D objects, *Science*, 2015, **347**(6228), 1349–1352.
- 21 A. J. Capel, R. P. Rimington and M. P. Lewis, *et al.*, 3D printing for chemical, pharmaceutical and biological applications, *Nat. Rev. Chem.*, 2018, **2**(12), 422–436.
- 22 E. Sachyani Keneth, A. Kamysny and M. Totaro, *et al.*, 3D printing materials for soft robotics, *Adv. Mater.*, 2021, **33**(19), e2003387.
- 23 X. Kuang, J. Wu and K. Chen, *et al.*, Grayscale digital light processing 3D printing for highly functionally graded materials, *Sci. Adv.*, 2019, **5**(5), eaav5790.
- 24 D. Xue, J. Zhang and Y. Wang, *et al.*, Digital light processing-based 3D printing of cell-seeding hydrogel scaffolds with regionally varied stiffness, *ACS Biomater. Sci. Eng.*, 2019, **5**(9), 4825–4833.
- 25 L. Y. Zhou, J. Fu and Y. He, A review of 3D printing technologies for soft polymer materials, *Adv. Funct. Mater.*, 2020, **30**(28), 2000187.
- 26 X. Li, R. Yu and Y. He, *et al.*, Self-healing polyurethane elastomers based on a disulfide bond by digital light processing 3D printing, *ACS Macro Lett.*, 2019, **8**(11), 1511–1516.

- 27 M. Layani, X. Wang and S. Magdassi, Novel materials for 3D printing by photopolymerization, *Adv. Mater.*, 2018, **30**(41), e1706344.
- 28 B. Zhang, K. Kowsari and A. Serjouei, *et al.*, Reprocessable thermosets for sustainable three-dimensional printing, *Nat. Commun.*, 2018, **9**(1), 1831.
- 29 J. Wu, J. Guo and C. Linghu, *et al.*, Rapid digital light 3D printing enabled by a soft and deformable hydrogel separation interface, *Nat. Commun.*, 2021, **12**(1), 6070.
- 30 F. Kotz, K. Arnold and W. Bauer, *et al.*, Three-dimensional printing of transparent fused silica glass, *Nature*, 2017, **544**(7650), 337–339.
- 31 B. Zhang, H. Li and J. Cheng, *et al.*, Mechanically robust and UV-curable shape-memory polymers for digital light processing based 4D printing, *Adv. Mater.*, 2021, **33**(27), e2101298.
- 32 M. Zarek, M. Layani and I. Cooperstein, *et al.*, 3D printing of shape memory polymers for flexible electronic devices, *Adv. Mater.*, 2016, **28**(22), 4449–4454.
- 33 N. A. Traugutt, D. Mistry and C. Luo, *et al.*, Liquid-crystal-elastomer-based dissipative structures by digital light processing 3D printing, *Adv. Mater.*, 2020, **32**(28), e2000797.
- 34 S. Deng, J. Wu and M. D. Dickey, *et al.*, Rapid open-air digital light 3D printing of thermoplastic polymer, *Adv. Mater.*, 2019, **31**(39), e1903970.
- 35 Y. F. Zhang, N. Zhang and H. Hingorani, *et al.*, Fast-response, stiffness-tunable soft actuator by hybrid multimaterial 3D printing, *Adv. Funct. Mater.*, 2019, **29**(15), 1806698.
- 36 S. Peng, Y. Li and L. Wu, *et al.*, 3D printing mechanically robust and transparent polyurethane elastomers for stretchable electronic sensors, *ACS Appl. Mater. Interfaces*, 2020, **12**(5), 6479–6488.
- 37 Q. Lv, X. Hu and X. Zhang, *et al.*, Highly efficient removal of trace metal ions by using poly(acrylic acid) hydrogel adsorbent, *Mater. Des.*, 2019, **181**, 107934.
- 38 X. N. Zhang, Q. Zheng and Z. L. Wu, Recent advances in 3D printing of tough hydrogels: A review, *Composites, Part B*, 2022, **238**, 109895.
- 39 X. P. Hao, Z. Xu and C. Y. Li, *et al.*, Kirigami-design-enabled hydrogel multimorphs with application as a multistate switch, *Adv. Mater.*, 2020, **32**(22), e2000781.
- 40 F. Zhu, L. Wang and B. Demir, *et al.*, Accelerating solar desalination in brine through ion activated hierarchically porous polyion complex hydrogels, *Mater. Horiz.*, 2020, **7**(12), 3187–3195.
- 41 L. X. Hou, H. Ding and X. P. Hao, *et al.*, Multi-level encryption of information in morphing hydrogels with patterned fluorescence, *Soft Matter*, 2022, **18**(11), 2149–2156.
- 42 Y. Zhao, C. Xuan and X. Qian, *et al.*, Soft phototactic swimmer based on self-sustained hydrogel oscillator, *Sci. Robot.*, 2019, **4**(33), eaax7112.
- 43 M. Kurdtabar, S. Saif Heris and M. Dezfulian, Characterization of a multi-responsive magnetic graphene oxide nanocomposite hydrogel and its application for DOX delivery, *Chin. J. Polym. Sci.*, 2021, **39**(12), 1597–1608.
- 44 C. N. Zhu, T. Bai and H. Wang, *et al.*, Dual-encryption in a shape-memory hydrogel with tunable fluorescence and reconfigurable architecture, *Adv. Mater.*, 2021, **33**(29), e2102023.
- 45 J. Ren, X. Shu and Y. Wang, *et al.*, Key progresses of MOE key laboratory of macromolecular synthesis and functionalization in 2020, *Chin. Chem. Lett.*, 2022, **33**, 1650–1658.
- 46 S. Jung, J. L. Kaar and M. P. Stoykovich, Design and functionalization of responsive hydrogels for photonic crystal biosensors, *Mol. Syst. Des. Eng.*, 2016, **1**(3), 225–241.
- 47 Qi Ge, Z. Chen and J. Cheng, *et al.*, 3D printing of highly stretchable hydrogel with diverse UV curable polymers, *Sci. Adv.*, 2021, **7**(2), eaba4261.
- 48 Y. He, R. Yu and X. Li, *et al.*, Digital light processing 4D printing of transparent, strong, highly conductive hydrogels, *ACS Appl. Mater. Interfaces*, 2021, **13**(30), 36286–36294.
- 49 Y. He, F. Wang and X. Wang, *et al.*, A photocurable hybrid chitosan/acrylamide bioink for DLP based 3D bioprinting, *Mater. Des.*, 2021, **202**, 109588.
- 50 B. Grigoryan, S. J. Paulsen and D. C. Corbett, *et al.*, Multivascular networks and functional intravascular topologies within biocompatible hydrogels, *Science*, 2019, **364**(6439), 458–464.
- 51 H. Quan, T. Zhang and H. Xu, *et al.*, Photo-curing 3D printing technique and its challenges, *Bioact. Mater.*, 2020, **5**(1), 110–115.
- 52 O. Santoliquido, P. Colombo and A. Ortona, Additive Manufacturing of ceramic components by Digital Light Processing: A comparison between the “bottom-up” and the “top-down” approaches, *J. Eur. Ceram. Soc.*, 2019, **39**(6), 2140–2148.
- 53 M. Caprioli, I. Roppolo and A. Chiappone, *et al.*, 3D-printed self-healing hydrogels via Digital Light Processing, *Nat. Commun.*, 2021, **12**(1), 2462.
- 54 Y. Luo, C. K. Dolder and J. M. Walker, *et al.*, Synthesis and biological evaluation of well-defined poly(propylene fumarate) oligomers and their use in 3D printed scaffolds, *Biomacromolecules*, 2016, **17**(2), 690–697.
- 55 Z. Liu, W. Pan and K. Wang, *et al.*, Acoustophoretic liquefaction for 3D printing ultrahigh-viscosity nanoparticle suspensions, *Adv. Mater.*, 2022, **34**(7), e2106183.
- 56 H. Wang, B. Zhang and J. Zhang, *et al.*, General one-pot method for preparing highly water-soluble and biocompatible photoinitiators for digital light processing-based 3D printing of hydrogels, *ACS Appl. Mater. Interfaces*, 2021, **13**(46), 55507–55516.
- 57 Y. Shen, H. Tang and X. Huang, *et al.*, DLP printing photocurable chitosan to build bio-constructs for tissue engineering, *Carbohydr. Polym.*, 2020, **235**, 115970.
- 58 B. D. Fairbanks, M. P. Schwartz and C. N. Bowman, *et al.*, Photoinitiated polymerization of PEG-diacrylate with lithium phenyl-2,4,6-trimethylbenzoylphosphinate: polymerization rate and cytocompatibility, *Biomaterials*, 2009, **30**(35), 6702–6707.

- 59 A. A. Pawar, G. Saada and I. Cooperstein, *et al.*, High-performance 3D printing of hydrogels by water-dispersible photoinitiator nanoparticles, *Sci. Adv.*, 2016, **2**(4), e1501381.
- 60 R. Cao, X. Pu and X. Du, *et al.*, Screen-printed washable electronic textiles as self-powered touch/gesture tribo-sensors for intelligent human-machine interaction, *ACS Nano*, 2018, **12**(6), 5190–5196.
- 61 M. Hua, D. Wu and S. Wu, *et al.*, 4D printable tough and thermoresponsive hydrogels, *ACS Appl. Mater. Interfaces*, 2021, **13**(11), 12689–12697.
- 62 Z. Sun, Y. Lu and Q. Zhao, *et al.*, A new stereolithographic 3D printing strategy for hydrogels with a large mechanical tunability and self-weldability, *Addit. Manuf.*, 2022, **50**, 102563.
- 63 L. Huang, R. Jiang and J. Wu, *et al.*, Ultrafast digital printing toward 4D shape changing materials, *Adv. Mater.*, 2017, **29**(7), 1605390.
- 64 M. P. de Beer, H. L. van der Laan and M. A. Cole, *et al.*, Rapid, continuous additive manufacturing by volumetric polymerization inhibition patterning, *Sci. Adv.*, 2019, **5**(1), eaau8723.
- 65 C. Zhang, H. Zheng and J. Sun, *et al.*, 3D printed, solid-state conductive ionoelastomer as a generic building block for tactile applications, *Adv. Mater.*, 2022, **34**(2), e2105996.
- 66 Y. Li, Q. Mao and X. Li, *et al.*, High-fidelity and high-efficiency additive manufacturing using tunable pre-curing digital light processing, *Addit. Manuf.*, 2019, **30**, 100889.
- 67 B. Zhang, S. Li and H. Hingorani, *et al.*, Highly stretchable hydrogels for UV curing based high-resolution multimaterial 3D printing, *J. Mater. Chem. B*, 2018, **6**(20), 3246–3253.
- 68 H. Yang, M. Ji and M. Yang, *et al.*, Fabricating hydrogels to mimic biological tissues of complex shapes and high fatigue resistance, *Matter*, 2021, **4**(6), 1935–1946.
- 69 D. Wu, J. Song and Z. Zhai, *et al.*, Visualizing morphogenesis through instability formation in 4D printing, *ACS Appl. Mater. Interfaces*, 2019, **11**(50), 47468–47475.
- 70 J. L. Drury and D. J. Mooney, Hydrogels for tissue engineering: scaffold design variables and applications, *Biomaterials*, 2003, **24**(24), 4337–4351.
- 71 X. Xue, Y. Hu and Y. Deng, *et al.*, Recent advances in design of functional biocompatible hydrogels for bone tissue engineering, *Adv. Funct. Mater.*, 2021, **31**(19), 2009432.
- 72 Y. J. Wang, X. N. Zhang and Y. Song, *et al.*, Ultrastiff and tough supramolecular hydrogels with a dense and robust hydrogen bond network, *Chem. Mater.*, 2019, **31**, 1430–1440.
- 73 H. Ding, X. N. Zhang and S. Y. Zheng, *et al.*, Hydrogen bond reinforced poly(1-vinylimidazole-co-acrylic acid) hydrogels with high toughness, fast self-recovery, and dual pH-responsiveness, *Polymer*, 2017, **131**, 95–103.
- 74 M. Wang, W. Li and L. S. Mille, *et al.*, Digital light processing based bioprinting with composable gradients, *Adv. Mater.*, 2022, **34**(1), e2107038.
- 75 Q. Ge, Z. Chen and J. Cheng, *et al.*, 3D printing of highly stretchable hydrogel with diverse UV curable polymers, *Sci. Adv.*, 2021, **7**(2), eaba4261.
- 76 A. S. Gladman, E. A. Matsumoto and R. G. Nuzzo, *et al.*, Biomimetic 4D printing, *Nat. Mater.*, 2016, **15**(4), 413–418.
- 77 X. Xin, L. Liu and Y. Liu, *et al.*, 4D printing auxetic metamaterials with tunable, programmable, and reconfigurable mechanical properties, *Adv. Funct. Mater.*, 2020, **30**(43), 2004226.
- 78 Z. J. Wang, C. N. Zhu and W. Hong, *et al.*, Cooperative deformations of periodically patterned hydrogels, *Sci. Adv.*, 2017, **3**, e1700348.
- 79 Z. J. Wang, W. Hong and Z. L. Wu, *et al.*, Site-specific pre-swelling-directed morphing structures of patterned hydrogels, *Angew. Chem., Int. Ed.*, 2017, **56**(50), 15974–15978.
- 80 B. P. Lee and S. Konst, Novel hydrogel actuator inspired by reversible mussel adhesive protein chemistry, *Adv. Mater.*, 2014, **26**(21), 3415–3419.
- 81 Z. J. Wang, C. Y. Li and X. Y. Zhao, *et al.*, Thermo- and photo-responsive composite hydrogels with programmed deformations, *J. Mater. Chem. B*, 2019, **7**(10), 1674–1678.
- 82 Z. Ji, C. Yan and B. Yu, *et al.*, 3D printing of hydrogel architectures with complex and controllable shape deformation, *Adv. Mater. Technol.*, 2019, **4**(4), 1800713.
- 83 Z. Zhao, J. Wu and X. Mu, *et al.*, Desolvation induced origami of photocurable polymers by digit light processing, *Macromol. Rapid Commun.*, 2017, **38**(13), 1600625.
- 84 Q. L. Zhu, C. Du and Y. Dai, *et al.*, Light-steered locomotion of muscle-like hydrogel by self-coordinated shape change and friction modulation, *Nat. Commun.*, 2020, **11**(1), 5166.
- 85 S. Y. Zheng, Y. Tian and X. N. Zhang, *et al.*, Spin-coating-assisted fabrication of ultrathin physical hydrogel films with high toughness and fast response, *Soft Matter*, 2018, **14**(28), 5888–5897.
- 86 S. Y. Zheng, C. Y. Li and M. Du, *et al.*, Programmable deformations of biomimetic composite hydrogels embedded with printed fibers, *ACS Appl. Mater. Interfaces*, 2020, **12**(51), 57497–57504.
- 87 C. Y. Li, S. Y. Zheng and X. P. Hao, *et al.*, Spontaneous and rapid electro-actuated snapping of constrained polyelectrolyte hydrogels, *Sci. Adv.*, 2022, **8**(15), eabm9608.
- 88 Y. Dong, S. Wang and Y. Ke, *et al.*, 4D printed hydrogels: fabrication, materials, and applications, *Adv. Mater. Technol.*, 2020, **5**(6), 2000034.
- 89 Z. Wang, H. Cui and M. Liu, *et al.*, Tough, transparent, 3D-printable, and self-healing poly(ethylene glycol)-gel (PEGgel), *Adv. Mater.*, 2022, **34**(11), e2107791.
- 90 C.-C. Kim, H.-H. Lee and K. H. Oh, *et al.*, Highly stretchable, transparent ionic touch panel, *Science*, 2016, **353**(6300), 682–687.
- 91 M. Kaltenbrunner, T. Sekitani and J. Reeder, *et al.*, An ultra-lightweight design for imperceptible plastic electronics, *Nature*, 2013, **499**(7459), 458–463.
- 92 X. P. Hao, C. Y. Li and C. W. Zhang, *et al.*, Self-shaping soft electronics based on patterned hydrogel with stencil-

- printed liquid metal, *Adv. Funct. Mater.*, 2021, **31**(47), 2105481.
- 93 Q. Peng, J. Chen and T. Wang, *et al.*, Recent advances in designing conductive hydrogels for flexible electronics, *InfoMat*, 2020, **2**(5), 843–865.
 - 94 H. Yuk, B. Lu and S. Lin, *et al.*, 3D printing of conducting polymers, *Nat. Commun.*, 2020, **11**(1), 1604.
 - 95 D. Jiao, Q. L. Zhu and C. Y. Li, *et al.*, Programmable morphing hydrogels for soft actuators and robots: from structure designs to active functions, *Acc. Chem. Res.*, 2022, **55**(11), 1533–1545.
 - 96 J. Nie, Q. Gao and Y. Wang, *et al.*, Vessel-on-a-chip with hydrogel-based microfluidics, *Small*, 2018, **14**(45), 1802368.
 - 97 Z. Jin, Y. Li and K. Yu, *et al.*, 3D printing of physical organ models: recent developments and challenges, *Adv. Sci.*, 2021, **8**(17), 2101394.
 - 98 H.-Y. Wu, L. Yang and J.-S. Tu, *et al.*, Hydrogels with dynamically controllable mechanics and biochemistry for 3D cell culture platforms, *Chin. J. Polym. Sci.*, 2022, **40**, 38–46.
 - 99 G. Chen, X. Liang and P. Zhang, *et al.*, Bioinspired 3D printing of functional materials by harnessing enzyme-induced biomineralization, *Adv. Funct. Mater.*, 2022, 2113262.
 - 100 Y. Li, Q. Mao and J. Yin, *et al.*, Theoretical prediction and experimental validation of the digital light processing (DLP) working curve for photocurable materials, *Addit. Manuf.*, 2021, **37**, 101716.
 - 101 J. P. Gong, Materials both tough and soft, *Science*, 2014, **344**(6180), 161–162.
 - 102 T. L. Sun, T. Kurokawa and S. Kuroda, *et al.*, Physical hydrogels composed of polyampholytes demonstrate high toughness and viscoelasticity, *Nat. Mater.*, 2013, **12**(10), 932–937.
 - 103 S. Y. Zheng, H. Ding and J. Qian, *et al.*, Metal-coordination complexes mediated physical hydrogels with high toughness, stick-slip tearing behavior, and good processability, *Macromolecules*, 2016, **49**(24), 9637–9646.
 - 104 X. Dai, Y. Zhang and L. Gao, *et al.*, A mechanically strong, highly stable, thermoplastic, and self-healable supramolecular polymer hydrogel, *Adv. Mater.*, 2015, **27**(23), 3566–3571.
 - 105 M. Wu, Q.-Y. Peng, L.-B. Han and H.-B. Zeng, Self-healing hydrogels and underlying reversible intermolecular interactions, *Chin. J. Polym. Sci.*, 2021, **39**, 1246–1261.
 - 106 J. Kim, G. Zhang and M. Shi, *et al.*, Fracture, fatigue, and friction of polymers in which entanglements greatly outnumber cross-links, *Science*, 2021, **374**(6564), 212–216.
 - 107 H. Wei, M. Lei, P. Zhang, J. Leng, Z. Zheng and Y. Yu, Orthogonal photochemistry-assisted printing of 3D tough and stretchable conductive hydrogels, *Nat. Commun.*, 2021, **12**, 2082.
 - 108 G. Guo, Q. Wu and F. Liu, *et al.*, Solvent-cast-assisted printing of biomimetic morphing hydrogel structures with solvent evaporation-induced swelling mismatch, *Adv. Funct. Mater.*, 2022, **32**, 2108548.
 - 109 S. Hou, D. Sycks and H. F. Chan, *et al.*, 3D printing of highly stretchable and tough hydrogels into complex, cellularized structures, *Adv. Mater.*, 2015, **27**(27), 4035–4040.