4D-printed light-responsive structures

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Introduction

Additive manufacturing, also popularly known as three-dimensional (3D) printing, possesses the great and advantageous features of high efficiency, materials saving, and individuation in the fabrication of complex structures and components in areas ranging from industry to daily life (Ligon et al., 2017; Ngo et al., 2018). The increase in various applications, including prototyping (Hanisch et al., 2020; Saggiomo & Velders, 2015), education (Clifton & Damon, 2020; Hansen et al., 2020), construction (Boumaraf & İnceoğlu, 2020; Saggiomo & Velders, 2015), medical engineering (Feng et al., 2017; Oladapo et al., 2021), and others has led to the fast development of 3D printing. Therefore, 3D printing, which involves various methods, materials, and equipment, has evolved over the years and now enables us to build samples with multimaterial properties (Fang et al., 2020; Ge et al., 2021; Hensleigh et al., 2020; Skylar-Scott et al., 2019; Zhang, Jonhson, et al., 2020), multiscale properties (Skliutas et al., 2020; Zhu, Zhang, et al., 2020), ultrafast printed speed (Kelly et al., 2019; Liashenko et al., 2020; Saha et al., 2019), and particular function (Han, Morde, et al., 2020; Jiang, Ji, et al., 2020; Yuk & Zhao, 2018). Moreover, the dynamic changes in the structural and functional properties of 3D-printed samples have extended the capabilities of 3D-printed materials by giving rise to the fourth dimension of time, which has created a new concept, that is, 4D printing (Lin et al., 2020; Tibbits, 2016).

In February 2013, Tibbits from MIT first presented the concept of 4D printing at a TED (Technology, Entertainment, Design) Talk, and displayed the programmable shape change of "MIT" once the rope-like sample was stimulated by water (Tibbits, 2014, 2016). With the merit of allowing objects to self-transform in shape or other functional properties under external stimuli, emerging 4D printing has attracted much attention. It is expected to achieve a breakthrough in the technical plateau of smart materials and structures in various fields, including self-construction structures, medical devices, and soft robotics (Chu et al., 2020; Hann et al., 2020; Joshi et al., 2020; Ma et al., 2020; Moradi et al., 2020). In addition, the market for 4D printing could be worth $555.60 million in 2025 based on the end-user industries in aerospace, automotive, clothing, construction, defense and military, healthcare, and utility (MarketsandMarkets, 2015). As a very active topic, 4D printing has been recognized

Smart Materials in Additive Manufacturing, Volume 1: 4D Printing Principles and Fabrication
https://doi.org/10.1016/B978-0-12-824082-3.00017-9

in academia and the market and will generate further hype and interest in the years to come.

Compared with 3D printing, the fundamental building blocks of 4D printing are composed of a 3D printing facility, an external stimulus, stimuli-responsive material, an interaction mechanism, and mathematical modeling (Momeni et al., 2017). Among these elements, the external stimuli that triggers the alterations of shape/property/functionality of a 3D-printed structure generally include humidity, light, heat, pH, chemical, magnetic, electro, and combinations (Falahati et al., 2020; Ji, Yan, Yu, et al., 2019; Zhou, Ye, et al., 2020). Corresponding to the external stimulus, the stimulus-responsive material with special performance can be commonly classified as a hydrogel (Hu et al., 2020), shape memory polymer (Subash & Kandasubramanian, 2020; Zhang et al., 2021), shape memory alloy (Farber et al., 2020; Yao, Wang, et al., 2020), polyurethane (Chen et al., 2021; Zhang, Yin, et al., 2019), and so forth. The integration of the external stimulus and stimulus-responsive material, the dominating design principle, and the interaction mechanism enable the creation of on-demand dynamically controllable shapes by integrating the dimension of time.

Recently, taking advantage of the achievements in synthetic smart materials, novel printers, deformation mechanisms, and mathematical modeling, the feasibility of 4D printing has been greatly expanded (Zhang, Demir, & Gu, 2019). Especially, the activated mode of light exhibits a flexible feature to realize the complex shape-changing ability, including bending, elongating, twisting, and corrugating. Correspondingly, the light-responsive 4D printing has also attracted much attention due to its excellent properties as an abundant source of energy, noncontact mode, clean and easy control of intrinsic characteristics such as wavelength, and a tunable intensity (Lahikainen, Zeng, & Priimagi, 2018; Leist & Zhou, 2016; Zhu, Gao, Han, Zhang, & Sun, 2019). The number of publications on topics of "light-responsive" and "3D printing and light" has rapidly increased, as shown in Fig. 3.1. In fact, light-induced shape changes have recently been conducted widely, such as the photochemical reaction with ultraviolet (UV) light-induced bending of composite structures (Mu et al., 2015); the hydrogel-based biomimetic robot capable of multimodal locomotion fueled and steered by light irradiation (Skliutas et al., 2020; Zhu, Zhang, et al., 2020); the

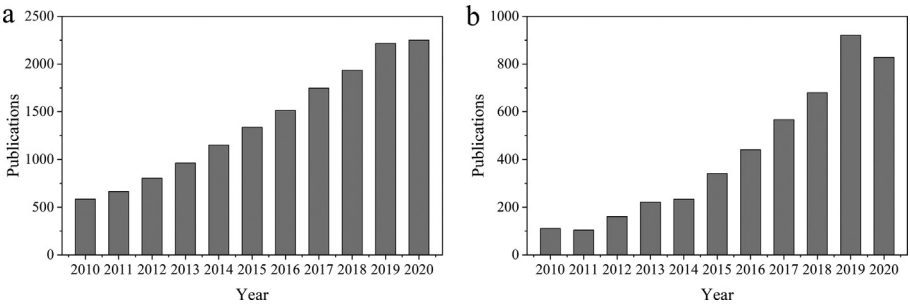

Fig. 3.1 Dates collected from Web of Science. The statistics of publications on: (A) light-responsive and (B) 3D printing and light, from Web of Science. Dates collected were the past 11 years (2010 – 2020).

photo-responsive liquid crystal gels used for locomotion, including crawling, walking, jumping, and swimming by localized and time-varying illumination (Shahsavan et al., 2020); the multistimuli-responsive liquid crystal elastomer soft actuator that had both multidirectional movement and different shape morphing modes (Zuo et al., 2019); and some others (Yanlei Hu et al., 2020).

It should also be noted that light-responsive 4D printing still has some intrinsic defects, such as the limitation of optical penetration depth, especially for opaque samples. Furthermore, it is challenging to directly transform light energy into mechanical energy to induce shape changes. Usually, the light response is expressed by a photochemical or photothermal nature, and then the photochemical or photothermal nature triggers photomechanical behavior such as shape deformation on the macroscopic scale (Stoychev et al., 2019; Zeng et al., 2018; Zolfagharian et al., 2018). The photochemical effect is based on photoisomerization and photodimerization, which result from photoreactions of the light-responsive group, such as the azobenzene undergoes *trans* → *cis* isomerization (Bandara & Burdette, 2012) while the anthracene and its derivatives are used to photodimerize under UV irradiation (Bouas-Laurent et al., 2000). In these cases, the chemical reactions would convert the energy into mechanical motions. For the photothermal effect, it is actually light-to-heat conversion, then leading to mechanical change behavior. For example, Fe_3O_4 nanoparticles (Du et al., 2018; Ji, Yan, Yu, et al., 2019) and carbon nanotubes (CNTs) (Han, Zhang, Chen, & Sun, 2018; J. Li et al., 2019; Zhou, Chen, Yao, Weng, & Zhang, 2018) usually exhibit the typical photothermogenesis effect and are used for light-responsive actuators. Accordingly, light-responsive 4D printing is dependent on the conversion of photochemical or photothermal effects and then results in mechanical behaviors.

There are many publications on 3D/4D printing with different focuses (Browne et al., 2020; Hassan et al., 2020; Ngo et al., 2018; Yan et al., 2020; Zhou, Fu, & He, 2020). Herein, we review the major advances in light-responsive 4D-printed structures, including innovative design principles, activation mechanisms, light-activated smart materials, and some typical/emerging applications; see Fig. 3.2. Within this framework, this chapter delivers a comprehensive review from mechanisms to applications. More importantly, the future research opportunities and interests of 3D-printed light-responsive structures are emphasized.

4D printing is the evolution of traditional 3D printing with the fourth dimension of time. Thus, the fabrication methods used in 4D printing are the same as 3D printing, such as digital light processing (DLP), fused deposition modeling (FDM), direct ink writing (DIW), stereolithography (SLA), and so on. The processing, mechanism, and equipment of these methods is briefly summarized as follows.

Design principles and activation mechanisms

Shape changes, actuation, and other functional property changes of smart materials can be performed under light stimuli. The light stimuli can be divided into many kinds, such as visible light, ultraviolet light, near-infrared light, infrared light, and even the manipulation of light intensity, light wavelength, light spot radius, and light exposure

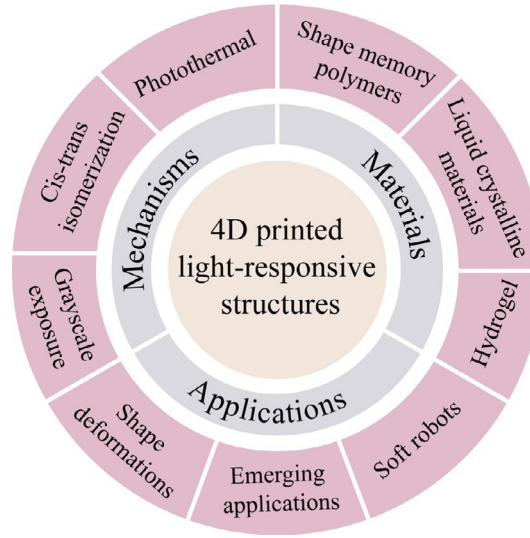

Fig. 3.2 The framework of this chapter. Schematic overview of 4D-printed light-responsive structures, including the design mechanisms, functional materials, and applications.

duration. On this basis, the principles of various design and activation mechanisms for light-responsive 4D printing were developed. Generally, the *cis-trans* isomerization of the azobenzene-based molecule, inorganic nanoparticles, carbon materials, and discrepant exposure induce special physical and optical properties that are employed as active elements, resulting in the printed objects exhibiting these smart behaviors. Therefore, the dominant design principles and activation mechanisms stimulated by light for 4D printing, described from the point of view of designing advanced materials and developing novel methods (Fig. 3.3), are briefly discussed in the following.

Photothermal effect

Among various light-responsive strategies, the photothermal behavior has evolved as an appealing manner for 4D printing due to its unique features such as the expansion of volume, desorption of molecules, phase change, and surface tension effect. In addition, compared with other light-responsive methods, the photothermal effect has the advantages of simple design principles, outstanding performance, controllable reconfiguration, and good stability (Han et al., 2018). For example, the blending method combined with polymer and photothermogenesis ingredients is a very generic and versatile yet simple approach that endows the printed architectures with multiple functions. With regard to the photothermal materials, high light absorption and excellent thermal conductivity are required so that the light energy can be effectively converted into heat energy, then leading to the programmed mechanical deformations (Kuenstler et al., 2020; Lim et al., 2017; Wu et al., 2020). To date, the typical photothermal materials are carbon-based nanomaterials such as CNTs, graphene (GR), and their derivatives. Moreover, inorganic nanoparticles such as gold nanorods/nanoparticles (Au NRs or Au NPs), ferromagnetic nanoparticles (Fe NPs or

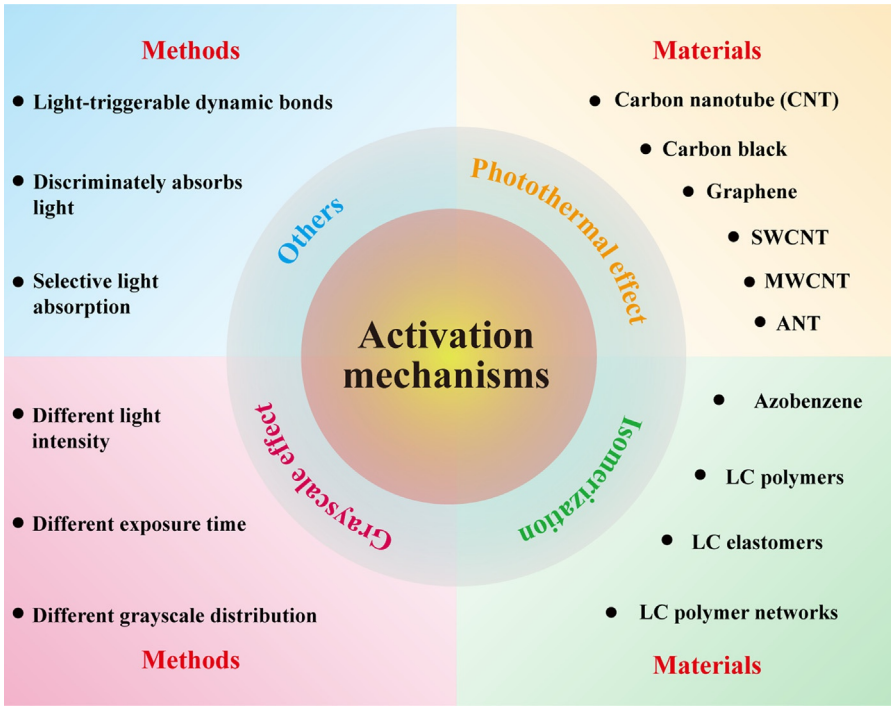

Fig. 3.3 Guide map of the activation mechanisms, including the advanced materials and novel methods.

Fe_3O_4 NPs), and polypyrrole nanoparticles also exhibited an excellent photothermogenesis performance; usually, they are used in photothermal therapy instead of light-responsive structures for 4D printing (Dong et al., 2018; Gelebart et al., 2017; Hu et al., 2019; Park et al., 2016; Rogóż et al., 2019; Stoychev et al., 2019; Wu, Li, et al., 2020; Yang, Zhang, & Sun, 2020; Yang, Chang, Hu, et al., 2020).

For carbon-based nanomaterials, the different carbon allotropes present different physical and optical properties; these differences are summarized in Table 3.1 (Han et al., 2018). It can be seen that both CNTs and GR possess outstanding properties as photothermogenesis active materials. Thus, most studies concerned with 4D-printed light-responsive structures would focus on CNTs, GR, or their derivatives, especially as related to the photothermal effect. As Fig. 3.4A shows, Hua et al. prepared a flexible paper-based actuator composed of polylactic acid (PLA) and multiwalled carbon nanotube (MWCNTs) composites by fused deposition modeling (FDM) 3D printing technology (Hua et al., 2018). PLA, as one of the most versatile inks of FDM 3D printing, combined with the photomechanical performance of MWCNTs, would endow the 3D printable actuators with photoresponsiveness. According to a predetermined sequence, the flexible actuator exhibited a shape-changing behavior triggered by infrared irradiation. Once the irradiation is turned off, the printed actuators would gradually recover and be completely restored to their

Table 3.1 Typical carbon allotropes and their physical/optical properties.

Material	Absorption characteristics	Thermal conductivity ($W\ m^{-1}\ K^{-1}$)	Mechanical strength (TPa)	Specific surface area ($m^2\ g^{-1}$)
Carbon nanotube	–	1000–6000	0.063	50–1315
SWCNT	Chirality related	Up to 6000	1	435
MWCNT	–	2000–3000	0.2–4	25–260
ANT	Blackest material (≈99.9%)	99.5	0.016	500
Graphene	Monolayer graphene absorb white light of ≈2.3%	Up to 6000	1	2630
GO	–	1	0.032	705
RGO	–	400–1800	0.042	466–1520
Graphite	–	3000	0.13	0.8–50
Carbon black	–	0.01	–	100

Modified from Han, B., Zhang, Y.-L., Chen, Q.-D., & Sun, H.-B., 2018. Carbon-based photothermal actuators. Adv. Funct. Mater. 28 (40), 1802235. https://doi.org/10.1002/adfm.201802235.

original shape. Similarly, Chen et al. developed high-performance thermoset materials composed of epoxy and benzoxazine with the addition of CNTs, and the printed products showed excellent shape memory ability under heat stimuli (Chen et al., 2021; Zhang, Yin, et al., 2019). Bi and coworkers reported shape memory polymer composites combined with dopamine-modified MWCNTs for light-responsive 4D printing (Bi et al., 2020), as Fig. 3.4B shows. To solve the problem of weak interaction between the MWCNTs and the polymer matrix (such as thermoplastic polyurethane and polycaprolactone blends), dopamine (DA) was used as an effective surface modifier that enhanced the filler/matrix interface interaction. Simultaneously, the MWCNTs acting as the photothermal conversion fillers make 3D-printed samples with shape memory property under near-infrared light irradiation.

Besides CNTs, GR or its derivatives not only has photothermal property but also several unique advantages, including: (i) excellent mechanical strength, (ii) high light absorption ability, (iii) high thermal conductivity, (iv) distinctively negative coefficient of thermal expansion, and (v) ultralight weight (Han et al., 2018). Fortunately, most of them can be employed for designing light-responsive 4D printing, and thus extensive literature on this topic has been reported. For example, to prepare a printable hydrogel composite with light- and thermoresponsive properties, Jin et al. utilized Laponite nanoclay as an effective additive to improve the free-standing poly (*N*-isopropyl acrylamide) (pNIPAAm), and utilized graphene oxide (GO) as a

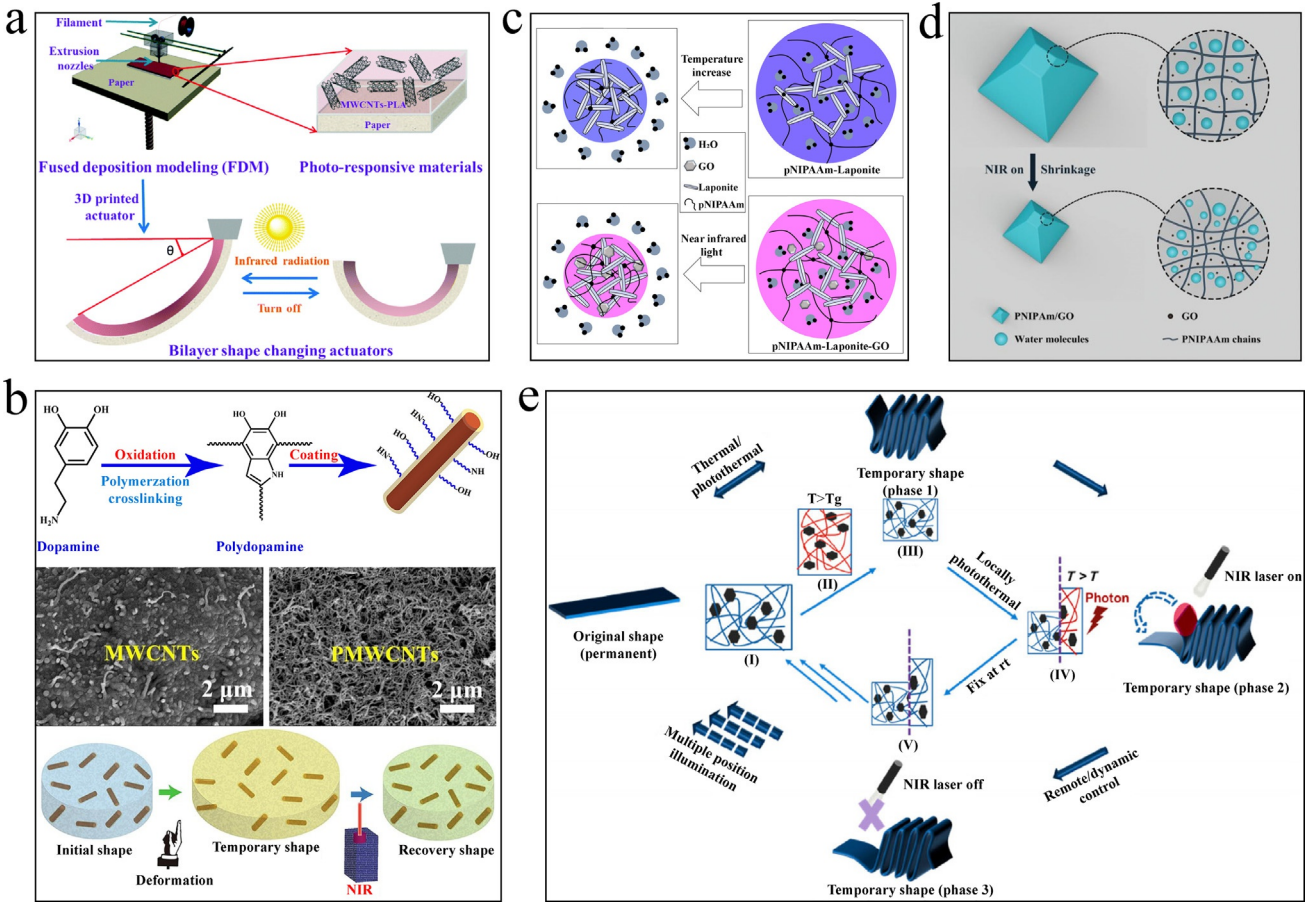

Fig. 3.4 Photothermal effect with various polymers. (A) Fabrication process of 3D-printed light-responsive actuator and its shape change mechanism; (B) schematic of the modification of MWCNTs by DA (above) and the shape memory behaviors stimulated by NIR light (below); (C) Shape deformation mechanism of nanocomposite; (D) Schematic illustration of swelling and shape change behaviors of 3D-printed pNIPAAm/GO hydrogel structure under NIR laser irradiation; (E) Schematic of 4D transformation of the printed object under NIR light irradiation.
From Bi, H., Ye, G., Yang, H., Sun, H., Ren, Z., Guo, R., et al., 2020. Near infrared-induced shape memory polymer composites with dopamine-modified multiwall carbon nanotubes via 3D-printing. Eur. Polym. J. 136, 109920. https://doi.org/10.1016/j.eurpolymj.2020.109920

nanoscale heater responsive to near-infrared radiation (NIR) (Jin et al., 2018). Similarly, Zhang et al. fabricated the pNIPAAm/GO composite hydrogel through self-assembly 3D printing under the assistance of UV light (Zhang, Zhang, et al., 2020). Their shape deformation mechanisms are illustrated in Fig. 3.4C and D. As one of the most famous thermoresponsive hydrogel precursors, pNIPAAm has been extensively investigated for shape deformation and actuator design (Lanzalaco et al., 2020; Lin, Ma, Yu, Cai, et al., 2019; Lin, Ma, Yu, Pei, et al., 2019; Ma et al., 2019; Shin, Choi, Na, & Kim, 2021). When the temperature is lower than the lower critical solution temperature (LCST), the pNIPAAm hydrogel displays a swollen hydrated state due to the presence of hydrogen bonds between the pNIPAAm molecular amide bond and water molecules. As the temperature increases (larger than the LCST), the pNIPAAm hydrogel would reduce the volume significantly due to the hydrophobic groups becoming active. Corresponding directly to the temperature rise, the GO would function as an NIR-responsive heater, leading to a rapid photothermal conversion. Once the temperature is higher than the LCST, a similar hydration-dehydration behavior appears, which results in a volume change of the hydrogel. Fig. 3.4E displays the shape memory polymers (SMPs) combined with GR used for shape transformation under NIR irradiation (Cui et al., 2019). When the printed SMP architecture was exposed to NIR illumination for heating (a photothermal-triggered process) until the temperature arrived the glass transition temperature (T_g), an external force was applied at this atmosphere and changed its initial shape. After that, the changed shape (defined as the temporary shape) was fixed at room temperature and removed the external force. Finally, once reheating to T_g through NIR exposure, the temporary shape gradually returns to its original shape (III $\rightarrow$ IV $\rightarrow$ V $\rightarrow$ I).

In fact, some other carbon-based materials, inorganic nanoparticles, and other polymers also can be used for light-responsive structures of 4D printing in some cases due to their excellent stability, low cost, easy accessibility, and ease of processing. Zolfagharian et al. reported a 3D-printed photothermal self-folding actuator based on active hinges that was composed of chitosan hydrogel and carbon black ink (Zolfagharian et al., 2017). Yang et al. utilized the excellent photothermal conversion efficiency of carbon black and added it to SMPs of polyurethane to endow 3D printable shape memory devices with photoresponsivity (Yang, Leow, et al., 2017). This ink integrates with the FDM technique to enable fabricating smart devices with shape memory and photoresponsive properties through layer-by-layer deposition (Fig. 3.5A). Liu et al. prepared a composite film by dispersing magnetic iron microparticles into the SMP matrix, and thus the film can respond to magnetic fields and light, which was used for shape reconfiguring and remote actuation (Liu et al., 2020 ; Wang, Li, et al., 2018 ; Wang, Ma, et al., 2018 ; Yang, Yang, et al., 2017 ; Zeng et al., 2021). Nishiguchi et al. developed a light-driven soft actuator composed of thermoresponsive pNIPAAm and AuNRs by 3D printing technology (Nishiguchi et al., 2020). With the ingenious design of printing density with a dynamic layer and ultrafast conversion from light energy to the heat of AuNRs, the nanocomposite gels undergo nonequilibrium actuation comprising a distinct forward and reverse stroke, which can realize the remotely controlled energy uptake (Fig. 3.5B). As a representative of thermoresponsive shape memory polymers, polystyrene (PS) also can

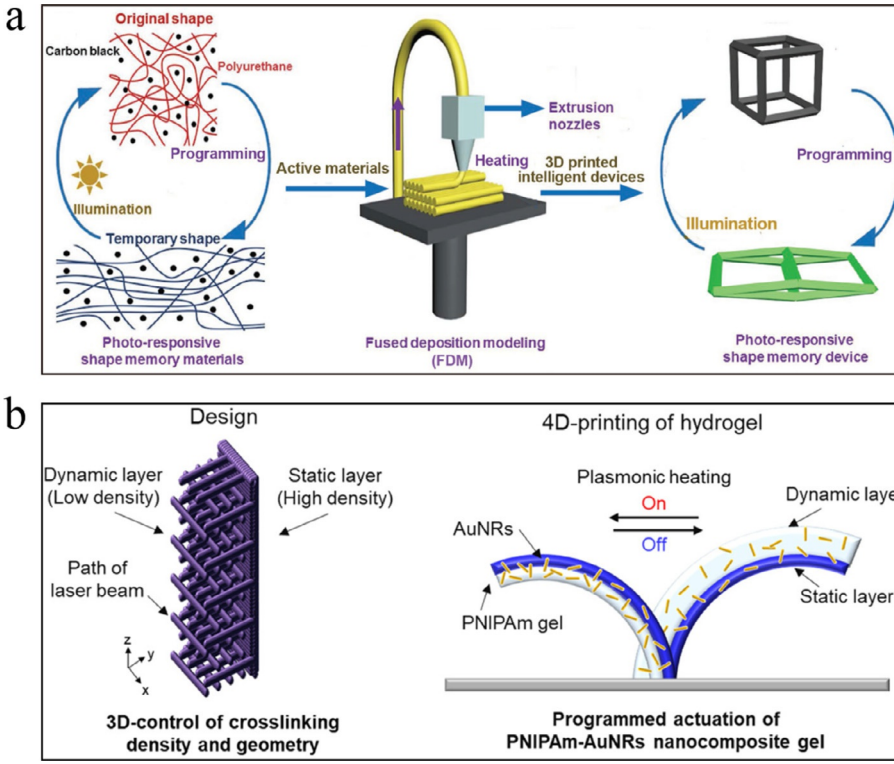

Fig. 3.5 The photothermal nature of carbon black and AuNRs. (A) Schematic of 3D-printed materials composed of carbon black and polyurethane, the printed device fabricated by FDM, and the shape deformation behaviors stimulated by light; (B) the designed hydrogel structure (left) and the light-induced actuation mechanism through plasmonic heating of AuNRs (right). From Yang, H., Leow, W.R., Wang, T., Wang, J., Yu, J., He, K., et al., 2017. 3D printed photoresponsive devices based on shape memory composites. Adv. Mater. 29 (33), 1701627. https://doi.org/10.1002/adma.201701627

be used as the main material to be remotely stimulated via light emission, and then a self-folding actuator is realized by 3D printing technology (Zolfagharian et al., 2018).

cis-trans *isomerization of azobenzene*

Azobenzene is a derivative of diazene (HN=NH) where phenyl groups replaced the hydrogens (Hartley, 1937; Rau, 2003), and it possesses the extended (*trans*) or compact (*cis*) conformation. The *trans* → *cis* isomerization of azobenzene occurs following irradiation with UV–visible light, mechanical stress, and electrostatic stimulation (Fig. 3.6A) (Bandara & Burdette, 2012). Therefore, the photochromic property has been utilized as a light-triggered switch in a variety of polymers. Based on reversible isomerization, the photoresponsivity can be achieved and is accompanied by a shift in absorbance. In addition, azobenzene has the advantage of facile incorporation with

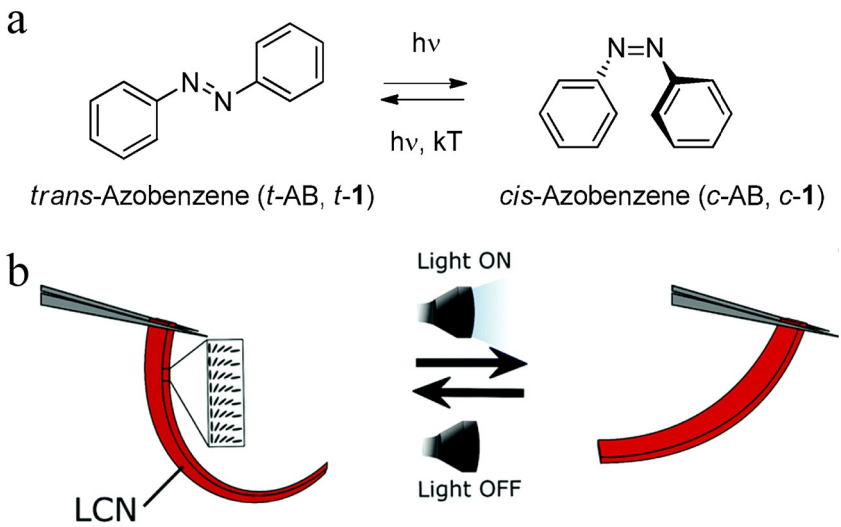

Fig. 3.6 The light-responsive mechanism of azobenzene. (A) Isomerization of azobenzene; (B) bending behavior of LCP film under light stimuli.
From Bandara, H.M.D., Burdette, S.C., 2012. Photoisomerization in different classes of azobenzene. Chem. Soc. Rev. 41 (5), 1809–1825. https://doi.org/10.1039/C1CS15179G

different kinds of polymers, such as liquid crystal polymers (LCPs) (Lahikainen et al., 2020; Pang et al., 2019; Wen et al., 2020), polyethylene (Varghese et al., 2020), and some others (J. Li et al., 2019). Therefore, the photoisomerization of azobenzene in polymer matrices becomes a powerful method to convert light energy into mechanical work. For example, Cunha et al. prepared LCPs that contain low (2 mol%) concentrations of different photoactive azobenzene derivatives (Pilz da Cunha et al., 2019). As Fig. 3.6B shows, the liquid crystal networks (LCN) exhibit a prebent shape at room temperature, and once the film is irradiated by light, it would display the unbending behavior into a flattened geometry. Namely, the illumination would result in the prepared film experiencing an uncurling motion directed toward the light source.

Integrating with the advanced technology of 3D printing, 4D printing light-responsive structures induced by azobenzene and its derivative have attracted much attention in recent years (del Barrio & Sánchez-Somolinos, 2019; Fang et al., 2020; Ge & Zhao, 2020; Ge et al., 2021; Hensleigh et al., 2020; Skylar-Scott et al., 2019; Zhang, Jonhson, et al., 2020). For example, Hagaman and coworkers developed a photoactive layer consisting of a poly(siloxane) containing pendant azobenzene groups that were used to fabricate polymeric bilayer actuators via syringe 3D printing (Hagaman et al., 2018). Corresponding to the photoactive layer, the passive layer comprises commercially available Kapton polyimide thin films due to their flexible nature, inertness to most organic solvents, and desirable mechanical properties. Accordingly, when the bilayer actuator is irradiated with the appropriate wavelength light, it would lead to a *trans-cis* isomerization of azobenzene molecules in the active

layer. On the macroscopic view of this, the bilayer actuator exhibits a rapid actuation with full cycles completed within seconds (Fig. 3.7A). Taking advantage of azobenzene dyes that cause shape deformation when included in a liquid-crystal network or liquid-crystal rubber (Camacho-Lopez et al., 2004; Finkelmann et al., 2001; Koerner et al., 2008; White et al., 2008), L. van Oosten et al. employed the dyes of A3MA and DR1A to prepare light-responsive artificial cilia by inkjet printing. These two azobenzene-containing dyes were introduced to the liquid-crystal monomers separately to form different inks with a selective absorbing wavelength of light. With the help of the splay-bend molecular organization through the film's thickness, the sample containing A3MA undergoes *trans-cis* isomerization under UV light irradiation while the other containing DR1A has the same behavior under visible light irradiation. Four positions can be obtained by selecting the color composition of the light, and the actuator exhibits the asymmetric motion of artificial cilia (Fig. 3.7B). Furthermore, the azobenzene-containing liquid crystalline elastomers (LCEs) also can be used for capturing both shape and morphology by photopolymerization in a muscle-like configuration for soft robotic applications (Ceamanos et al., 2020). A fast mechanical response can be observed in these 4D-printed samples once exposed to UV light, and the lift object's behaviors also demonstrate excellent photochemical and photothermal contributions (Fig. 3.7C). In short, the azobenzene and its derivative, especially integrated with liquid crystal materials, play important roles in the light-responsive structures of 4D printing.

Grayscale exposure effect

To develop the gradient crosslinking of polymers, various techniques have been reported, including photochemical reactions with spatially controlled UV irradiation (Nemir et al., 2010; Norris et al., 2016; O'Connell et al., 2018), physical crosslinking (Kim et al., 2015; Oh et al., 2016), and diffusion-based crosslinking (Hadden et al., 2017; Lee et al., 2019). Whereas for light-responsive materials employed to program shape changes, the grayscale exposure becomes one of the most efficient ways. For example, Chen and coworkers realized light-responsive shape deformations by printing patterns with different/gradient grayscale distributions on the actuators (L. Chen et al., 2019). With laser printing technology, the gradient grayscale distribution can be easily obtained by using the "gradient fill" option in Microsoft Office's PowerPoint (Fig. 3.8). It can be concluded that grayscale exposure will result in a variable degree of monomer conversion and crosslinking density, then provide an asymmetric force that is used to program shape changes under the external stimuli.

Grayscale exposure effects integrated with 3D printing have been used for reversible shape changes, graded materials, and some particular functions such as heterogeneous visible light transmittance under external stimuli. Maybe the external stimuli are not the light while the UV exposure with grayscale digital light is used to guide the gradient crosslinking density spatially during the printed process, which thereafter results in the special functions mentioned above. Thus, it is believed that the grayscale pattern of 4D printing is closely related to the 4D-printed light-responsive structures.

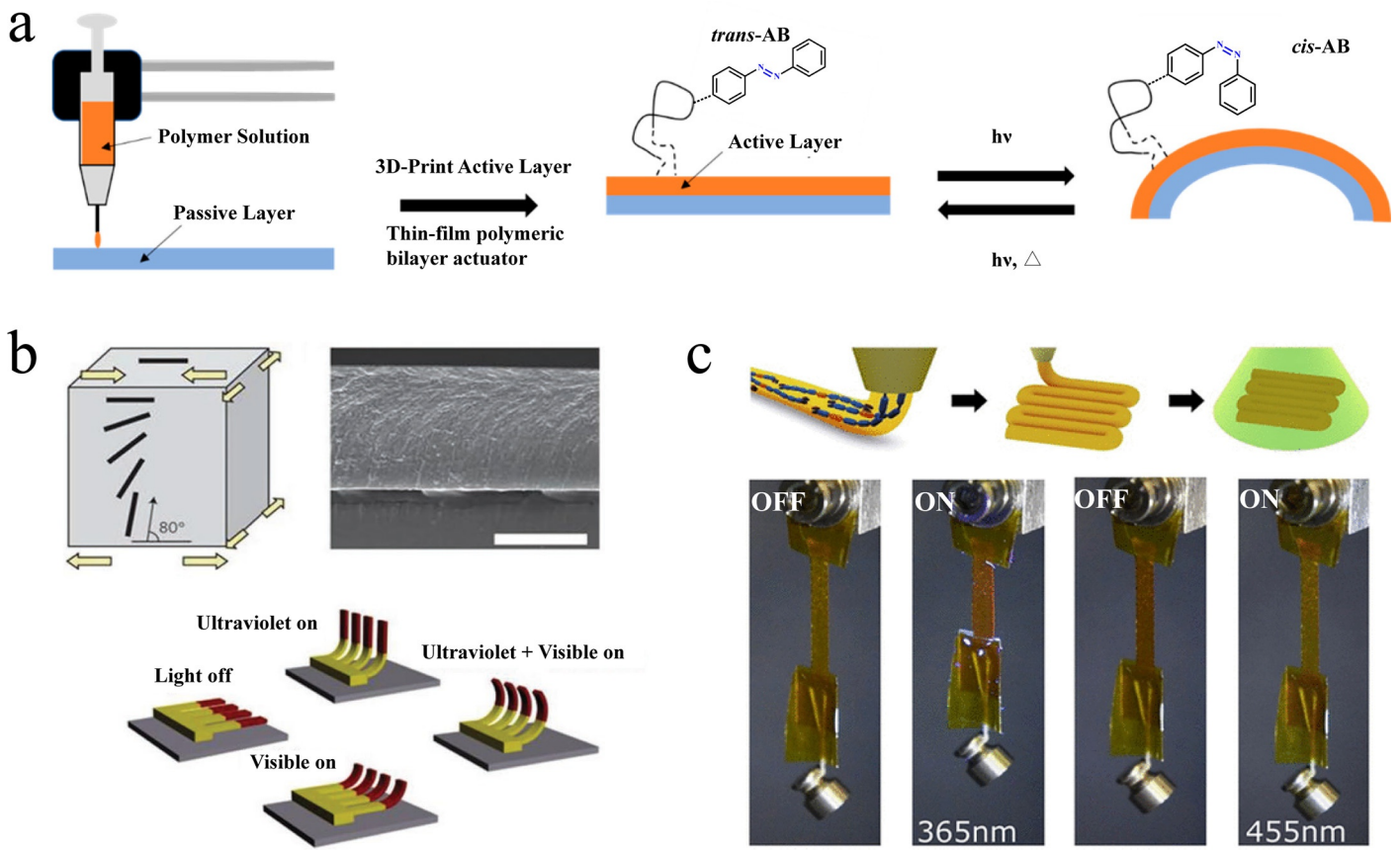

Fig. 3.7 The light-responsive mechanism of azobenzene-based materials. (A) The active bilayer actuator consisting of poly(siloxane) containing a pendant azobenzene group and its fabrication process (left), and a schematic of light-responsive shape deformation (right); (B) schematics of the splay-bend molecular organization through the thickness of the film (top and the scale bar indicates 5 μm) and the four positions of the artificial cilia controlled by the spectral composition of the light (down); (C) 4D-printed azobenzene-containing liquid crystalline elastomers and the lift object behaviors excited with UV light.

From Hagaman, D., Leist, S., Zhou, J., Ji, H.-F., 2018. Photoactivated polymeric bilayer actuators fabricated via 3D printing. ACS Appl. Mater. Interfaces 10 (32), 27308–27315. https://doi.org/10.1021/acsami.8b08503

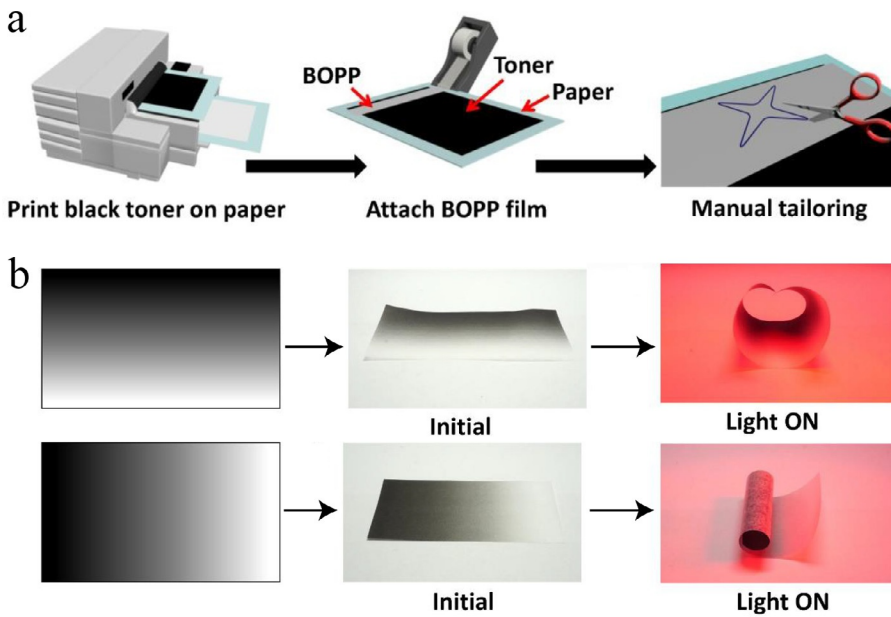

Fig. 3.8 The simple application of grayscale exposure. (A) Fabrication process of the toner-coated paper (TCP)/biaxially oriented polypropylene (BOPP) actuator and (B) its actuate behavior with the help of NIR light.
From Chen, L., Weng, M., Huang, F., Zhang, W., 2019. Light- and humidity-driven actuators with programmable complex shape-deformations. Sensors Actuators B: Chem. 282, 384–390. https://doi.org/10.1016/j.snb.2018.11.067.

Generally, the grayscale exposure effect is controlled by different exposure times or light intensity. All enable providing different curing degrees and lead to different densities at different locations in the cured sample. For example, Tao Xie's group fabricated a simple reaction cell composed merely of two glass slides separated by a spacer. The hydrogel monomer at the spacer would produce a variable degree of monomer conversion and cross-linking density under the different light exposure time at each pixel level (Fig. 3.9A) (Huang et al., 2017). Taking advantage of the different crosslinking densities, the subsequent immersion in water would result in various complex shape changes from 2D film to 3D object. Based on different light densities, Wu and coworkers proposed a 3D grayscale printing method to create reversible shape change structures (Wu et al., 2018). During the digital light processing (DLP) 3D printing process, the designed grayscale pictures at the different spatial positions were employed to control the light intensity distribution of the UV projector. Namely, the darker light owns lower light intensity and exhibited a cured ink with lower cross-linking density. This way, the printed structure would produce a reversible shape change after leaching the uncured oligomers inside the loosely crosslinked network in the water (Fig. 3.9B). Subsequently, Kuang and coworkers further developed this method and defined single-vat grayscale DLP 3D printing as g-DLP 3D printing

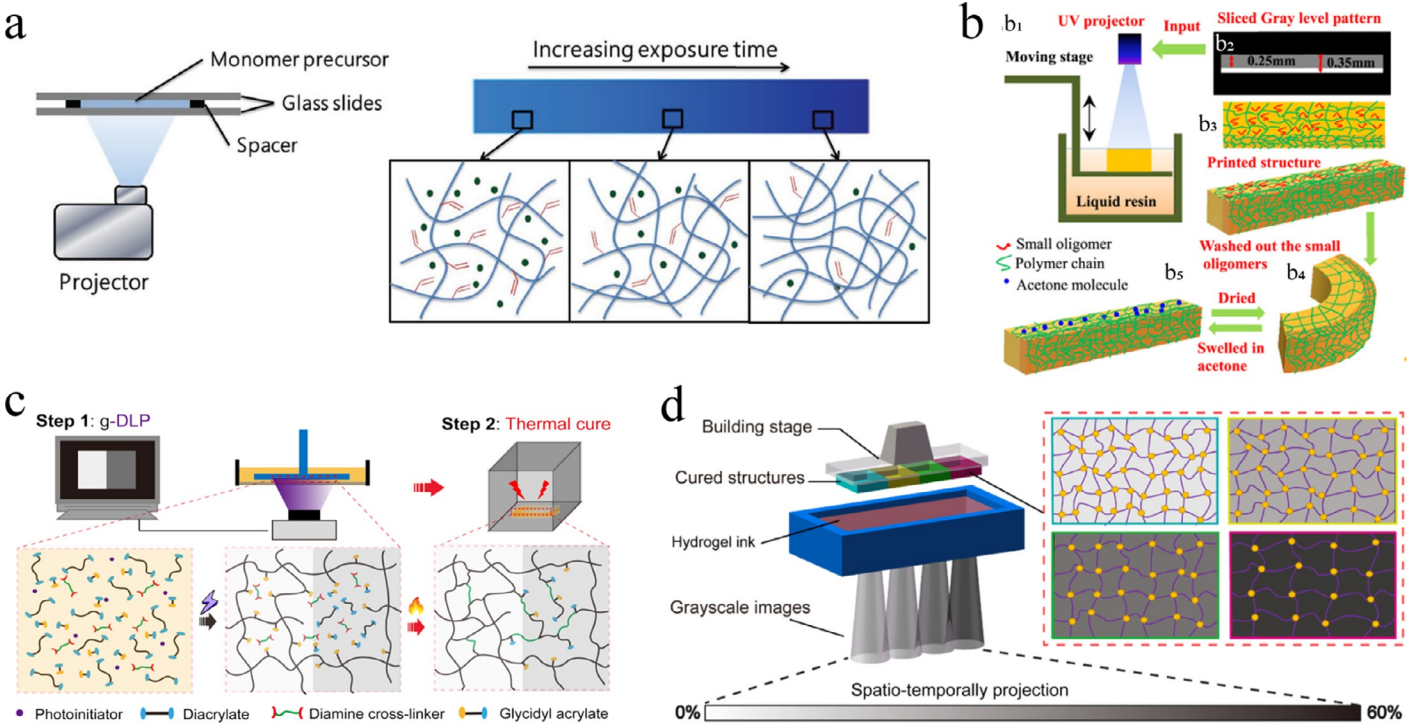

Fig. 3.9 Designed principles of grayscale exposure. (A) Illustrations of the 3D printed set-up (left) and the pixelated control via digital light exposure (right); (B) schematics to show the grayscale 4D printing method and its shape change mechanism; (C) schematics showing the g-DLP printing method used to prepare the graded material via a two-stage curing process; (D) Schematic of the 3D printing of patterning hydrogel by spatially grayscale patterned images.

From Jiang, P., Yan, C., Ji, Z., Guo, Y., Zhang, X., Jia, X., et al., 2019. Drawing high-definition and reversible hydrogel paintings with grayscale exposure. ACS Appl. Mater. Interfaces 11 (45), 42586–42593. https://doi.org/10.1021/acsami.9b14342.

(Kuang, Wu, et al., 2019). The authors prepared a novel two-stage curing hybrid ink system containing acrylates, glycidyl methacrylate (GMA), a diamine cross-linker, and others. During the printed process, each image with desired grayscale distribution was used to cure the acrylate inks by free radical polymerization. Notably, with the increasing grayscale percentage, the crosslinking density and the materials' modulus would decrease. The following thermal curing of GMA monomers and diamine cross-linker make the two-stage curing ink obtains the functionally graded property with the mechanical gradient up to three orders of magnitude (Fig. 3.9C). Jiang et al. combined both factors of spatial grayscale exposure and exposure time into one system for reversible hydrogel paintings (Jiang et al., 2019); the mechanism is shown in Fig. 3.9D. Different from the homogenous light patterns in the traditional DLP printer, the photopolymerization can be manipulated by the grayscale of projected patterns, which results in the cross-linking density of the UV-cured hydrogel being dictated by grayscale light intensity and exposure time. The grayscale hydrogel pattern with high definition, rapid response, reversibility, and integral information can be obtained on this basis.

In short, the grayscale exposure effect that induced by different exposure time and light intensity would result in a heterogeneous distribution of cross-linking density. Integrating with 3D printing and smart materials, the prepared architectures enable to exhibit various functions such as reversible shape changes, functionally graded materials, and others. Among them, most smart materials related to grayscale exposure generally are UV-cured hydrogels due to the great humidity needed to perform the shape change behaviors. This new designed mechanism is believed to open a new avenue of light-responsive 4D-printed structures that has wide versatility, is easy to customize, and has excellent flexibility.

Others

As previously mentioned, light can be classified as NIR, UV, visible light, and others based on the diversity of the wavelength; therefore the design principles and activation mechanisms of 4D-printed light-responsive structures are miscellaneous. Except for the methods stated above, design mechanisms in line with photochemistry and photophysical properties have also been realized that all exhibit great significance for light-responsive 4D printing. Recently, Jennifer *A. Lewis*'s group prepared a 3D-printed ink with light-triggerable dynamic bonds that was used to reconfigure LCE architecture under light stimuli (Davidson et al., 2020). The synthesized LCE-based ink exhibited a fully reversible and programmable shape change upon heating above and below its nematic-to-isotropic transition temperature (T_{NI}) after cross-linking. As Fig. 3.10A shows, when the as-printed network is exposed to UV light, the stress in the dynamic LCE network drives bond exchange without requiring an externally imposed mechanical field. After that, a reconfigured network is formed and into a locked-in state, which enable the programmed shape to be maintained even the atmosphere was cooling to 25°C. The researchers also developed some light-induced smart devices used for complex shape-changing based on discriminate light absorption that were color- and wavelength-dependent. For instance, Jeong et al. developed a multicolor 4D-printed technique and integrated it with selective light absorption and heat in

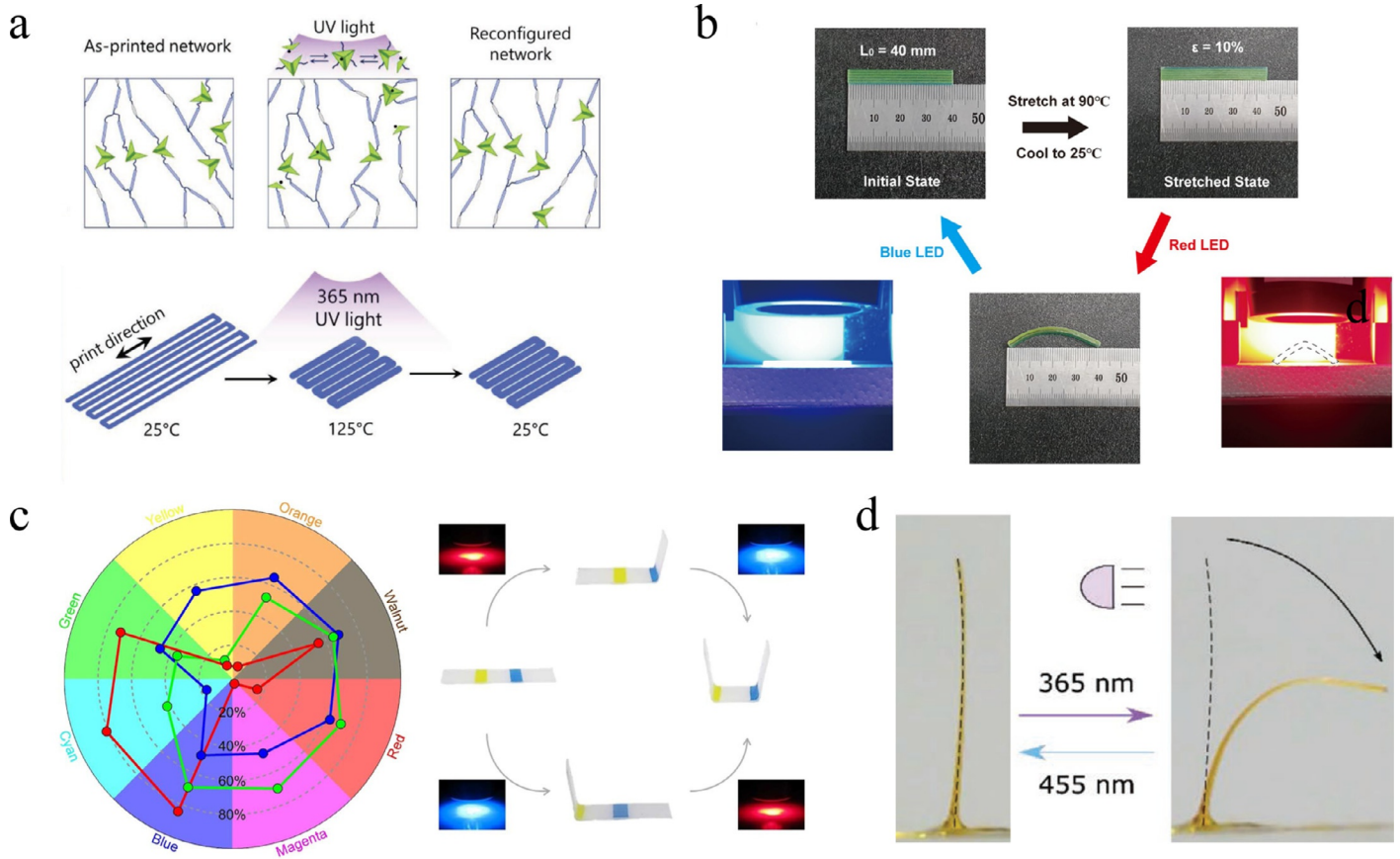

Fig. 3.10 Design principles concerned with photochemistry and photophysical properties. (A) Schematic illustration of LCE reconfiguration under UV light via dynamic covalent bond exchange (above), and the diagram of the LCE sample reconfigured process (bottom); (B) thermomechanical programming and bending behavior; (C) Radar plot in which each wedge corresponds to an ink color from a laserjet printer (left) and the sequential self-folding behavior stimulated by *red* and *blue* LEDs (right); (D) side views of bending and unbending behaviors under the irradiation of UV light and visible light.

From Davidson, E.C., Kotikian, A., Li, S., Aizenberg, J., Lewis, J.A., 2020. 3D printable and reconfigurable liquid crystal elastomers with light-induced shape memory via dynamic bond exchange. Adv. Mater. 32 (1), 1905682. https://doi.org/10.1002/adma.201905682.

multicolor SMP composites; remote actuation under light stimuli can be realized (Jeong et al., 2020). As Fig. 3.10B shows, with the help of structure design, the architecture was stretched with a strain of $\varepsilon = 10\%$ at high-temperature (90°C) and followed cooling in low-temperature (25°C). Then the sample was first illuminated by a red light-emitting diode (LED) that leading to the bent downward behavior, the following illumination of blue LED would make the bent structure reverted to its original flat shape. Furthermore, Liu et al. fabricated a polymer sheet that discriminately absorbs light based on the wavelength of light and the color of printed ink (Y. Liu et al., 2017). As Fig. 3.10C shows, the prestrained polymer sheet that is optically transparent in the visible range was integrated with colored hinges that selectively absorb (or transmit) light of a given wavelength, and then employed them to perform the sequential folding behaviors. The radar plot (Fig. 3.10C, left) highlights the absorption of blue (470 nm), green (530 nm), and red (660 nm) light by different colors of ink printed on the polymer sheet. Take the yellow and cyan inks, as they have an opposite absorption response to red and blue LEDs, respectively. Therefore, when the red LED is switched on, the blue hinge becomes folding; when the blue LED is switched on, the yellow hinge becomes folding (Fig. 3.10C, right). Through regulating the procedure of the switch, the self-folding behaviors were presented in chronological sequence too. Pozo et al. reported a similar work that prepared a functional ink that was used to fabricate the light-responsive underwater liquid crystal actuator (del Pozo et al., 2020). When the prepared fiber was exposed to UV light, it would bend away from the light source; when illuminating with visible light, it would recover to the unbent state (Fig. 3.10D). This behavior provides a new strategy for controlling the bending direction.

In summary, universal principles and activation mechanisms for light-responsive 4D-printed structures, such as the photothermal effect, *cis-trans* -isomerization, grayscale exposure, discriminate light absorption, light-triggerable dynamic bond exchange, etc., have been widely introduced to create a variety of smart behaviors, including bending, spirals, self-folding, and other complex shape deformations. It should be noted that the shape memory effect of light-responsive 4D printing is usually dependent on the photothermal effect. Taking advantage of the effect, the increased heat would make SMPs recover to their initial state. Hence, we classified the light-triggered shape memory effect as part of the photothermal effect. In addition, even though the diverse actuation mechanisms have different capabilities related to programmed shape change, the design principles may overlap and crisscross sometimes. All the design principles and actuation mechanisms exhibit powerful potential in programming shape changes integrated with 3D printing.

Light-responsive materials used for 4D printing

In recent years, 4D printing of light-responsive structures has been achieved by different functional materials, including liquid crystalline polymeric materials, hydrogels, and SMPs, which can be either semicrystalline or amorphous. Significantly, a polymer-based composition with light-responsive additives is one of the most critical

Table 3.2 Summary of different 3D printing technologies and their corresponded light-responsive materials, activation mechanisms, and applications.

3D printing technologies	Light-responsive materials	Activation mechanisms	4D applications
Fused Deposition Modelling (FDM)	Composite with particles; Bisphenol A-based epoxy	Photo-thermal	Actuator; Shape deformation
Digital Light Processing (DLP)	PCL-based polymer, Methacrylate-based polymer, Hydrogel	Grayscale exposure	Smart device; Shape deformation, Anti-counterfeiting
Direct Ink Writing (DIW)	Hydrogel, Composite with particles, SMPs, Hybrid ink, Nanocellulose composites; Liquid crystal polymer	Photo-thermal; Photo-degradation; Dynamic bond exchange	Intelligent Switch; Grab and transformation; Sensor; Soft robots
Inkjet Printing	Polystyrene and polystyrene-based composite; SMPs; Liquid-crystal network	Discriminately absorbs light; Photothermal; color dependent light absorption; Trans-cis isomerization	Self-folding; Remote actuation
Multiphoton Lithography (MPL)	Hydrogel, Methacrylamide chitosan	Photothermal	Actuator; Shape deformation

materials for 4D printing light-responsive structures. In fact, the dominant 4D printing light-responsive flexible materials, activation mechanisms, and applications are summarized in Table 3.2 based on the different 3D printing technologies. Therefore, this section briefly introduced recent advances in 3D printing of typical polymers and polymer-based composites, including SMPs, liquid crystalline materials, and functional hydrogels.

SMPs

Shape memory materials are ideal ingredients for integrated intelligent systems as they can morph and transform the shape over time under an external stimulus. In fact, there are a number of types of shape memory materials that have been developed so far, such as SMPs, shape memory alloys (SMAs), shape memory ceramics (SMCrs), shape memory composites (SMCs), shape memory gels (SMGs), and shape memory

hybrids (SMHs) (Ryan et al., 2021; Sun et al., 2012). Among them, SMPs with large deformation, high sensing, excellent processing capabilities, and easy design properties have become significant and have attracted great attention in the development of smart devices (Bodaghi, Damanpack, & Liao, 2016; Ge et al., 2016; Kuang, Wu, et al., 2019; Liu, Gillen, Mishra, Evans, & Tracy, 2019). The SMPs respond through physical and chemical crosslinks related to temperature transitions such as the glass transition temperature (T_g). When the temperature is lower than T_g, the SMPs are in the glass state with high stiffness. In this state, the SMP sample exhibits its "stable and original shape" due to the soft segment in SMPs being frozen in place. While when the temperature is larger than T_g, the soft segment is easy to maneuver/deform, and therefore the SMPs are in the rubber state and are flexible (Huang et al., 2017; Huang, Yang, Zhao, & Ding, 2010). At this time, the SMPs are usually processable and shaping can create a new morphology. Finally, the deformed shape memory architecture cooled down to its T_g and fixed the changes. Once increasing the temperature to its T_g again, the deformed sample would recover to its original shape; this process is summarized in Fig. 3.11 (Ohki, Ni, Ohsako, & Iwamoto, 2004). Accordingly, 4D-printed shape memory structures enable preparing complex architectures and dynamic control of the shape change under external stimuli. Here, we focus on the state-of-the-art advancements in the field of light-responsive SMPs, especially for light-responsive 4D-printed SMPs.

In fact, SMPs respond to various external stimuli, including heat, light, electricity, magnetism, solution, and others (Meng & Li, 2013; Xia et al., 2021). Even though thermoresponsive SMPs are among the most common studies, light-triggering SMPs have unique features, such as remote and target control. For example, Leng et al. prepared a thermoresponsive thermoset styrene-based SMP and heated it by having it absorb laser energy (Leng et al., 2010). Taking advantage of the remote-controlled

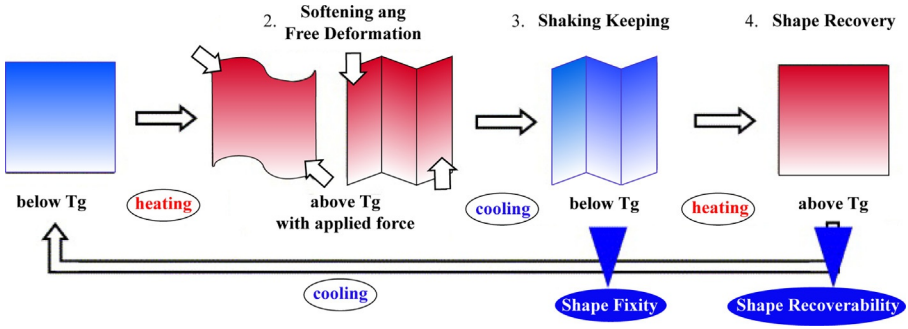

Fig. 3.11 Shape memory mechanism of typical SMPs. Schematic representation of the shape memory process under external stimuli.
From Ohki, T., Ni, Q.-Q., Ohsako, N., & Iwamoto, M. (2004). Mechanical and shape memory behavior of composites with shape memory polymer. *Composites Part A: Applied Science and Manufacturing, 35* (9), 1065–1073. https://doi.org/10.1016/j.compositesa.2004.03.001.

actuation, it may be used to remove clots in human blood vessels in the future. Subsequently, Leng's group continues research concerned with light-induced shape recovery behavior and has some new achievements (Herath et al., 2020; Lu et al., 2014; Wan et al., 2020). Recently, light-induced SMPs integrated with 3D printing techniques have led to a series of advanced materials and novel designs. Tao Xie's group introduced material heterogeneity into a well-known thermoplastic SMP (poly(L-lactide), [PLLA]), and utilized a digital photothermal effect to induce spatiocontrolled crystallinity via cold crystallization (Peng et al., 2020). Based on this mechanism, the gradient grayness pattern was printed onto the amorphous film, which led to different temperature increases due to the digital ink's photothermal effect. Consequently, the cold crystallization technique converts the temperature distribution into a crystallinity pattern; it was then used to design 3D permanent shapes and achieve 4D transformation (Fig. 3.12A). Bi et al. prepared shape memory composites consisting of MWCNTs and thermoplastic polyurethane (TPU)/polycaprolactone (PCL) blends (Bi et al., 2020). Composite preparation is shown in Fig. 3.12B. It is composed of mixture solutions of TPU, PCL, cellulose nanocrystal (CNC), and dimethylformamide (DMF) after stirring and dispersing. Among them, PCL was the typical SMP to program dynamic shape change behaviors, and the MWCNTs mentioned above were used as photothermal conversion fillers. Under these circumstances, NIR-induced shape memory composites were obtained. Zhang and coworkers synthesized thermoreversible shape memory polyurethanes (PDAPUs) that were used for precise self-healing and targeted shape memory under the stimuli of light control (Zhang, Yin, et al., 2019). The synthetic routes of PDAPUs are displayed in Fig. 3.12C. The aniline trimer (AT) shows a well-defined molecular structure and high-efficiency photothermal effect, and the amino groups in the AT molecule provide ideal reaction sites to the NCO- of the DA-reactive shape memory PU (SMPU) to obtain photothermal DA-reactive SMPU inks. With direct ink writing (DIW) printing technology, the printed samples exhibit light-induced programmable shape memory and precise self-healing properties. In addition, the typical epoxy-based SMP, bisphenol A diglycidyl ether (DGEBA), integrated with the thermoset resin of bisphenol A-aniline-type benzoxazine (BA-a), and CNTs were able to formulate FDM inks and were used for 4D printing (Chen et al., 2020). The chemical structures of DGEBA and BA-a are shown in Fig. 3.13A, and the experimental procedures are shown in Fig. 3.13B. The DGEBA gel and BA-a were followed by the addition of CNTs under twin-screw melt extrusion to prepare the shape memory and light-responsive FDM inks. In this way, the 3D-printed samples would exhibit excellent shape memory performance with a fast recovery rate and large recovery degree.

We should note that there are various types of SMPs, including PLA (Leonés, Sonseca, López, Fiori, & Peponi, 2019; Wang, Wang, et al., 2019), PCL (Zarek et al., 2016), epoxy (Amornkitbamrung et al., 2020; Rousseau & Xie, 2010), polyurethane (Gorbunova, Anokhin, & Badamshina, 2020; Li et al., 2020), hydrogel (Maiti et al., 2020; Yang, Zhang, Wang, Sun, & Tong, 2020), and others (Xie et al., 2019). They can be classified as two mechanisms under light stimuli, that is, photoresponsive SMPs and photothermal shape memory polymer composites. Compared with photoresponsive SMPs, we believe the photothermal nanoparticles

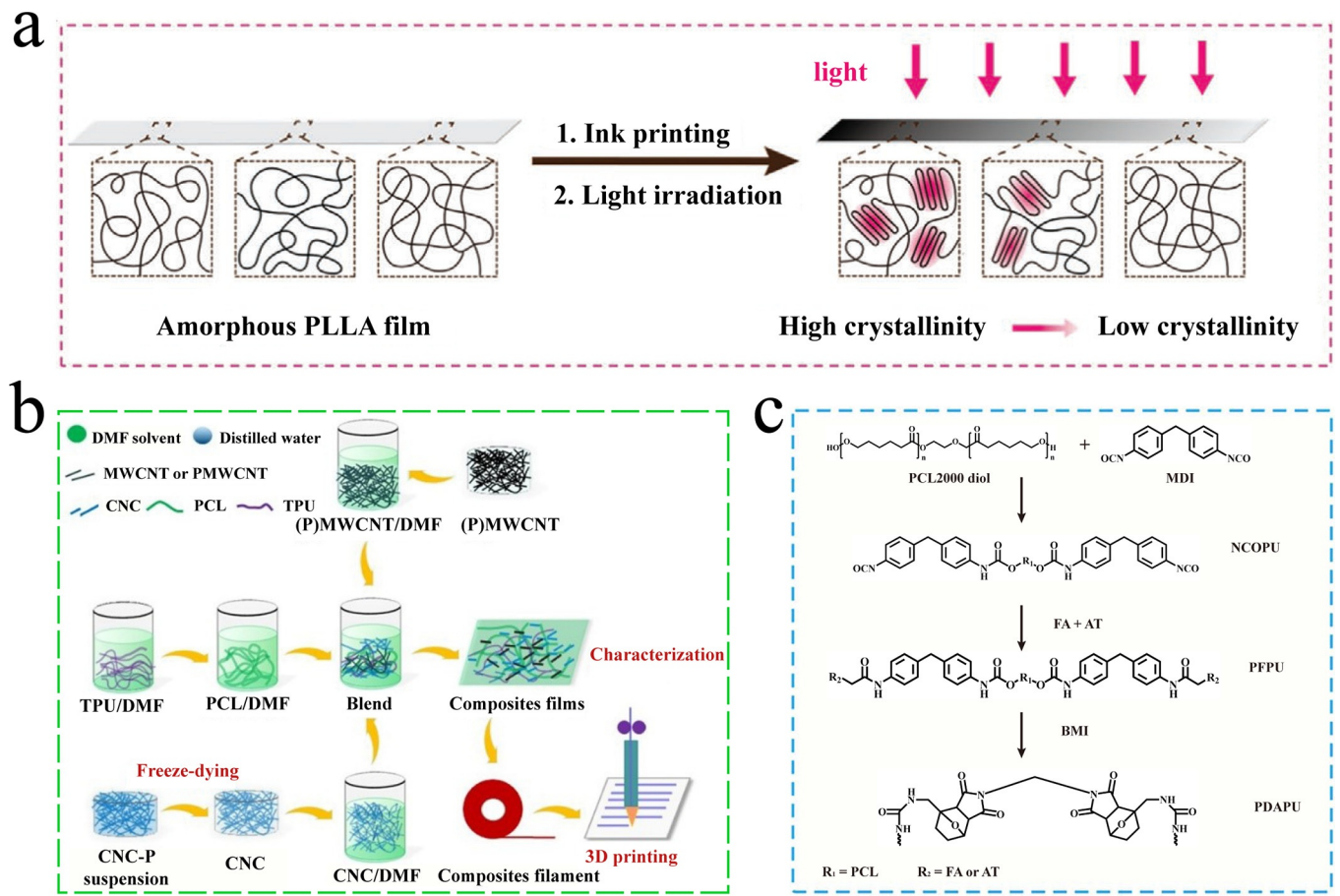

Fig. 3.12 Light-responsive SMPs. (A) The design principle of forming the crystallinity pattern via cold crystallization induced by a digital photothermal effect; (B) schematic diagram of the preparation of 3D-printed shape memory inks; and (C) schematic showing the synthetic routes of PDAPUs.

From Peng, W., Zhang, G., Liu, J., Nie, S., Wu, Y., Deng, S., et al., 2020. Light-coded digital crystallinity patterns toward bioinspired 4D transformation of shape-memory polymers. Adv. Funct. Mater. 30 (19), 2000522. https://doi.org/10.1002/adfm.202000522.

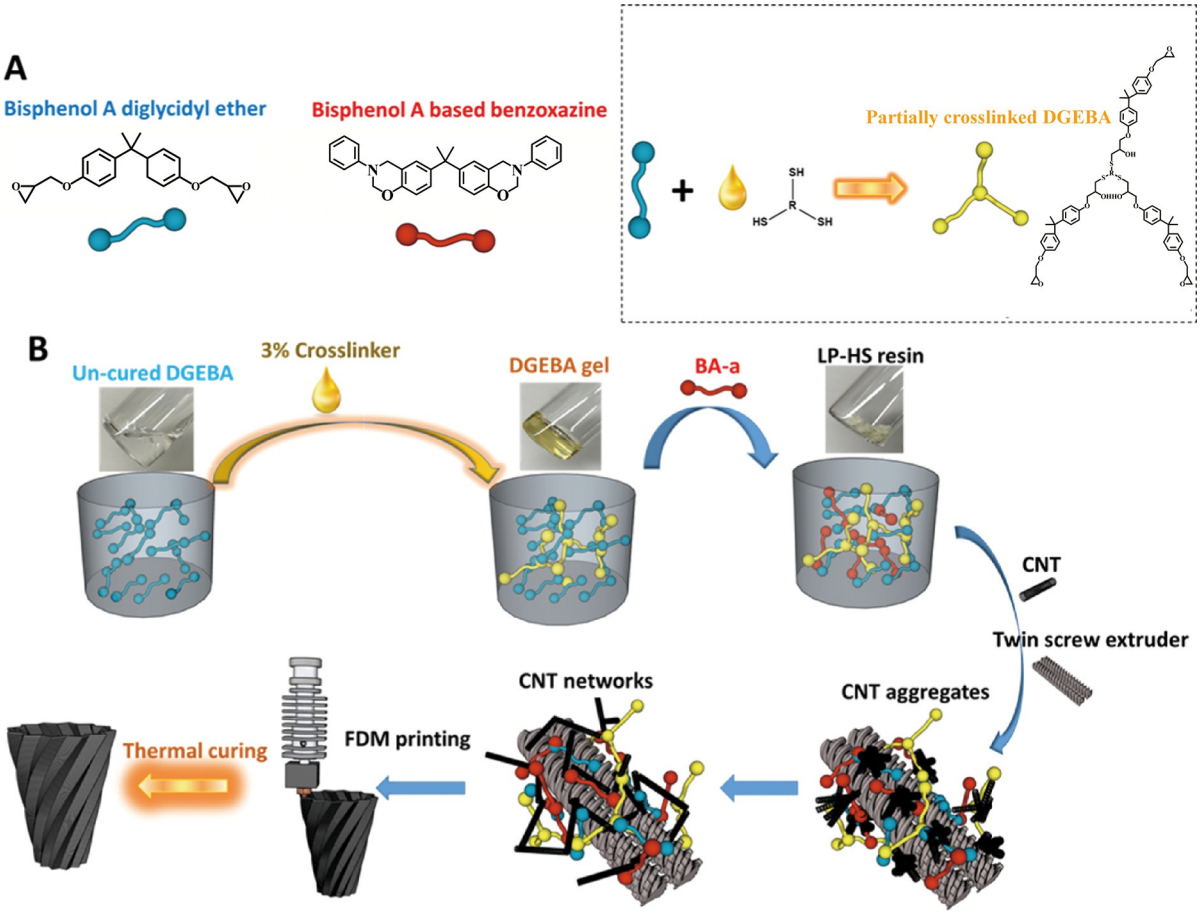

Fig. 3.13 Light-responsiveness of printable epoxy-based SMPs. (A) The chemical structures of DGEBA and BA-a, and a mixture of a branched oligomer with unreacted DGEBA; and (B) schematic illustration of the experimental procedures.
From Chen, Q., Han, L., Ren, J., Rong, L., Cao, P., Advincula, R.C., 2020. 4D printing via an unconventional fused deposition modeling route to high-performance thermosets. ACS Appl. Mater. Interfaces 12 (44), 50052–50060. https://doi.org/10.1021/acsami.0c13976.

and integration with SMP composites have larger potential and faster development due to the free design and easy manipulation properties.

Liquid crystalline materials

Liquid crystalline (LC) materials, which possess photoresponsive capabilities, have been used for diverse applications due to the coexistence of order and mobility that makes LCs functional soft materials. Recently, the polymeric materials that integrate the characteristics of the polymers with the LC materials into one single system have become particularly attractive candidates for polymeric actuators and shape deformations, especially integrated with 3D printing techniques (Ren et al., 2020; Roach et al., 2018; Wang, Jiang, et al., 2020). They have been referred to by several names, including liquid crystal polymers (LCPs), liquid crystal polymer networks (LCNs), or LCEs, and the differences between these classes are shown in Fig. 3.14 (Stoychev et al., 2019; White, 2018). The LCPs are generally described as linear main-chain or *comb*-like polymers. They are typically uncrosslinked macromolecules (such as Vectran) and can organize into liquid crystalline phases through stiff rod-like molecular conformation and intramolecular interactions (White & Broer, 2015). The distinguishing feature of LCNs from LCPs is that the former possess crosslinked network architectures and maintain some of the high-performance properties of LCPs. The LCNs can be glassy or elastomeric, where elastomeric LCNs are most often referred to as LCEs. LCEs are generally used for large and reversible shape deformations due to their flexible polymer backbone and lower crosslinking density (Ula et al., 2018; White & Broer, 2015). In addition, they also exhibit different T_g, elastic moduli (E), and change in order (Δs) when subjected to appropriate stimuli.

Light-induced liquid crystal materials have been reported for fabricating 3D-printed soft actuators or shape-changing devices, especially for LCEs (Ambulo et al., 2017; Yang, Full, et al., 2019). To date, most liquid crystal materials are printed by the DIW technique due to their outstanding compatibility. While the LC-based materials with photoresponsive property as the DIW inks, they need to fulfill the two critical performances, i.e., excellent free-standing property and incorporated with a reactive azobenzene molecule (Pilz da Cunha et al., 2019). To meet these requirements, Pozo et al. prepared inks for fabricating the liquid crystal actuator with light-responsive and underwater properties (del Pozo et al., 2020). The chemical composition of the ink, as Fig. 3.15A shows, consists of: (1) reactive mesogens, (2) photoresponsive moiety of azobenzene, (3) isotropic chain extender of 3,6-dioxa-1,8-octanedithiol, and (4) photoinitiator. After chain extension and mixing with each other, the inks can be obtained. Similarly, Cunha and coworkers reported acrylate-based LCNs used for light-induced actuation as previously described (Pilz da Cunha et al., 2019), and the LCNs are composed of two liquid crystal mesogens (Fig. 3.15B) and 2 mol% of an azobenzene derivative. Finally, LCEs, as one of the most promising 4D-printed systems (Ambulo et al., 2017; Camacho-Lopez et al., 2004; Davidson et al., 2020; Ren et al., 2020), can also provide light-induced shape morphing and reconfiguration. For example, Ceamanos and coworkers prepared inks comprising a reactive LC oligomer bearing an acrylate end group at the chain

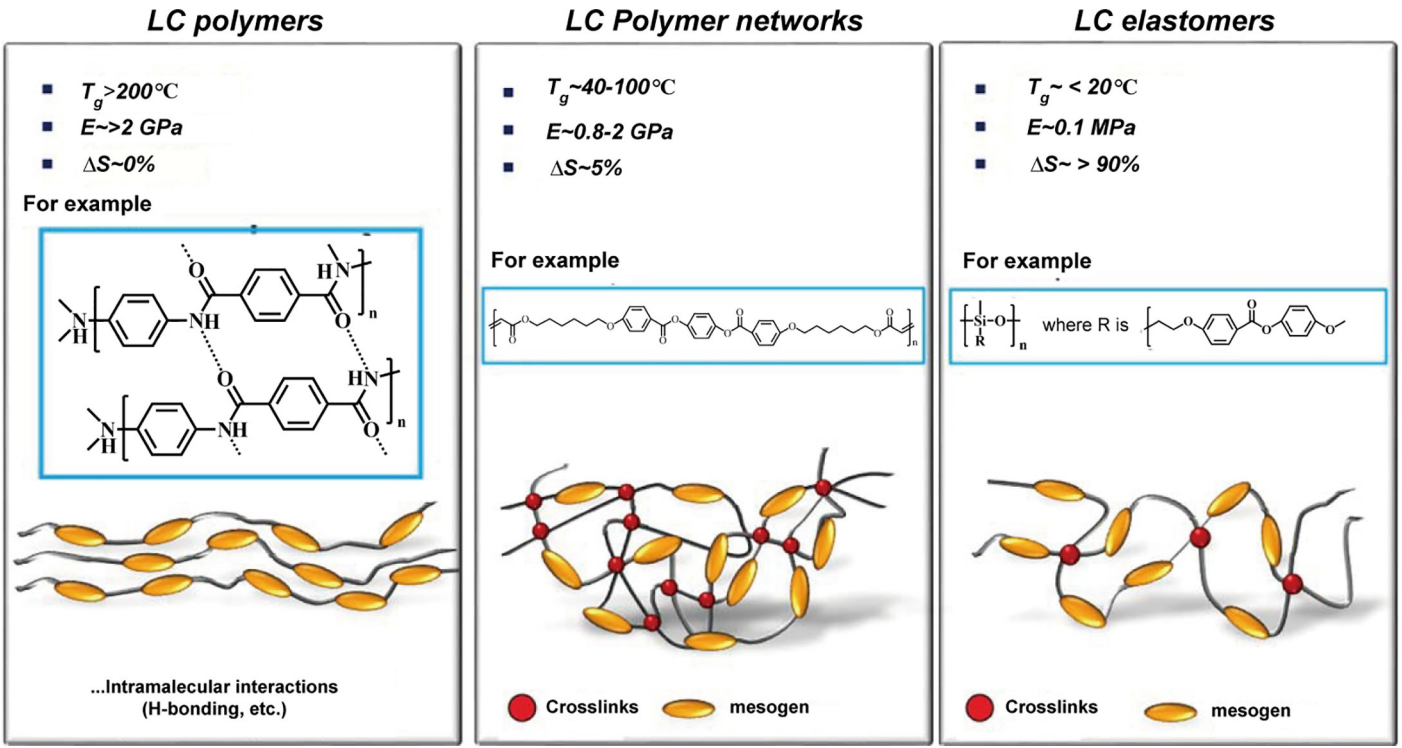

Fig. 3.14 Differences between LCPs, LCNs, and LCEs. Properties and molecular configurations of LCPs (left), LCNs (middle), and LCEs (right). From Stoychev, G., Kirillova, A., Ionov, L., 2019. Light-responsive shape-changing polymers. Adv. Opt. Mater. 7 (16), 1900067. https://doi.org/10.1002/adom.201900067.

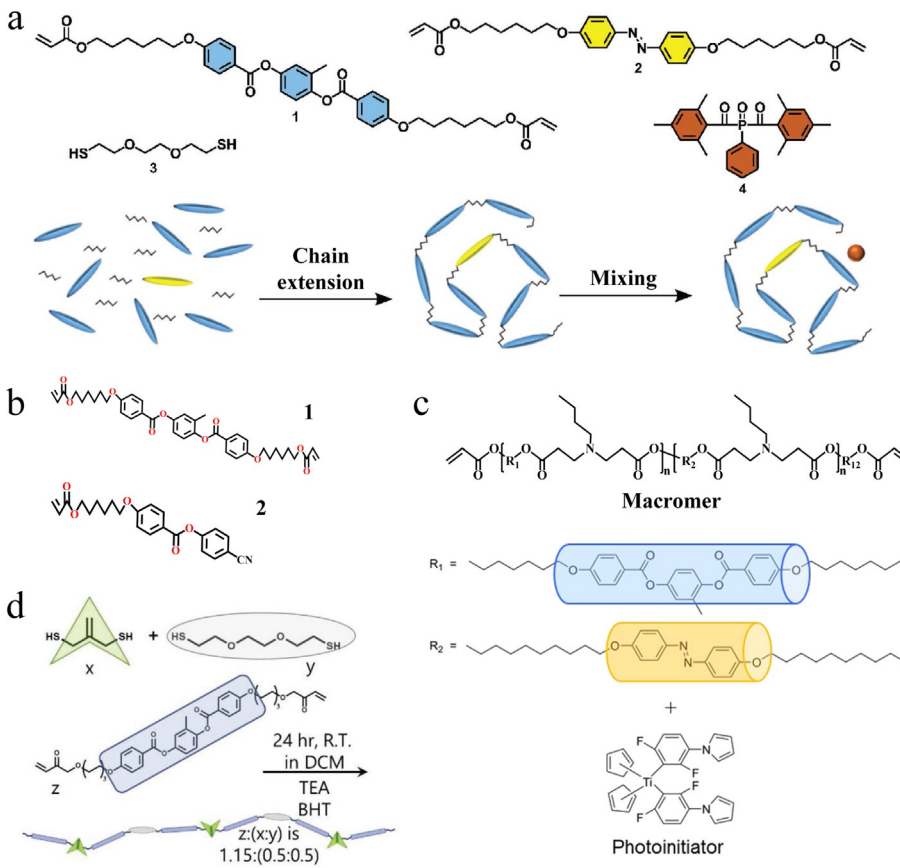

Fig. 3.15 Light-responsiveness of printable and liquid crystal materials. (A) Preparation of the ink and its chemical composition; (B) the molecular structure of the liquid crystalline mesogens comprising the LCN; (C) molecular structure of the LCE ink components; and (D) synthesized photopolymerizable LCE ink composed of the exchangeable spacer (*green*), inert spacer (*gray*), and mesogen (*blue*).
From del Pozo, M., Liu, L., Pilz da Cunha, M., Broer, D. J., Schenning, A.P.H.J., 2020. Direct ink writing of a light-responsive underwater liquid crystal actuator with atypical temperature-dependent shape changes. Adv. Funct. Mater. 30 (50), 2005560. https://doi.org/10.1002/adfm.202005560.

extremes together with a visible light photoinitiator; their molecular structures are shown in Fig. 3.15C (Ceamanos et al., 2020). Very recently, Jennifer A. Lewis's group synthesized a printable LCE-based ink composed of liquid crystal mesogens polymerized with an allyl dithiol chain extender (Fig. 3.15D); this was employed for complex shape reconfiguration via dynamic bond exchange (Davidson et al., 2020).

To sum up, photoresponsive LC materials usually take the azobenzene and its derivative for light absorption, which then results in generating mechanical stresses. In addition, the LC materials generally have intrinsic inferiority, such as the low/insufficient photoreactive property to UV light, and thus can't be printed by light curing of the DLP or SLA technique. Therefore, the most-used rapid prototyping technique of LC materials is the DIW technique due to its great compatibility with the extruded agent. Correspondingly, the resolution of printed LC architectures generally exhibits a coarse surface, which needs to be optimized in the future.

Functional hydrogels

In the past few years, there has been increased interest in hydrogel development and applications, specifically as stimuli-responsive functional materials. With the 3D hydrophilic polymer network and excellent absorbing water property (the amount of water can approach up to 99 wt% of the hydrogel mass without dissolving) (Ionov, 2014), hydrogels are able to considerably swell and shrink when the amount of water in the polymer network changes induced by stimuli such as pH, temperature, light, magnet, and ionic strength, among others (Goudu et al., 2020; Ha et al., 2020; Han, Wang, et al., 2020; Maiti et al., 2020; Zhou, Wang, et al., 2020; Zhou, Wu, et al., 2020; Zou et al., 2021). On this basis, the hydrogel's smart behaviors, including twisting, bending, and other shape deformations, have attracted much attention by changing the amount of water under the external stimuli (Champeau et al., 2020; Farber et al., 2020; Le, Lu, Zhang, & Chen, 2019; Yao, Wang, et al., 2020). Generally, the hydrogels used for shape morphing can be divided into three categories: (1) external nonuniform stimuli such as electric/magnetic field or local light irradiation onto isotropic hydrogel; (2) preparation of internal anisotropic hydrogel, and (3) combining with other nonresponsive materials to form the hydrate/dehydrate layers. Integrating with 3D printing technology, the light-responsive hydrogels involve a change of shape and/or functionality of the printed architecture over time while researchers mainly focused on creating shape morphing devices, as follows.

As a noninvasive stimulation, light-induced shape deformation enables specific and localized reconfigurations by irradiating the specific regions of the sample at any moment. In addition, the light-sensitive particles, such as CNTs, Fe_3O_4, Au, and graphene-based particles, can be dispersed into the hydrogel matrix for the typical photothermogenesis effect as described above. Most of the light-responsive hydrogels used for 4D printing belong to this category. For example, integrating with the typical thermoresponsive hydrogel precursor of NIPAAm, Jin and coworkers introduced GO as the nanoscale heater that responds to near-infrared radiation to prepare an actuator (Jin et al., 2018). The hydrogels are mainly composed of Laponite nanoclay, NIPPAm, GO, deionized water, and other additives, and the deposited process and composition of hydrogel are illustrated in Fig. 3.16A and B. Similarly, Nishiguchi et al. synthesized a newly multiarmed and thermoresponsive macro crosslinker of bi-, tri, and tetra-allyl-functional pNIPAAm (Nishiguchi et al., 2020), as Fig. 3.16C

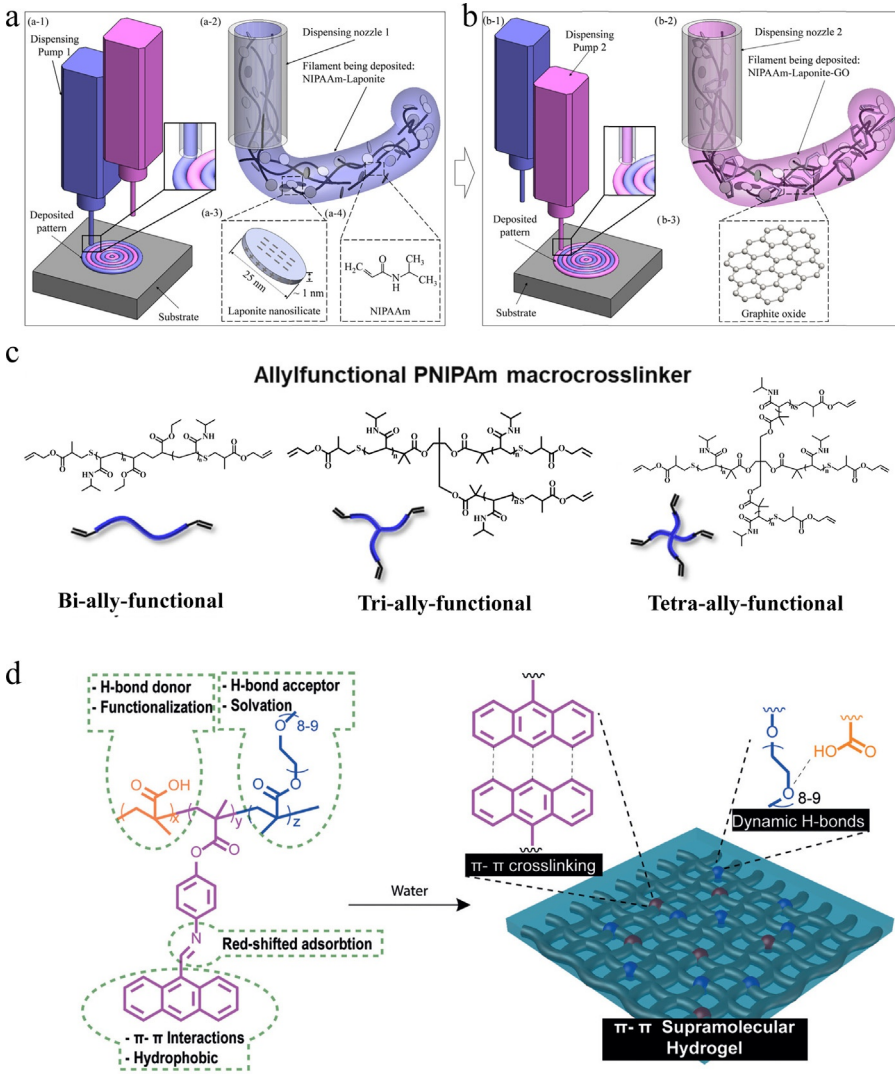

Fig. 3.16 Light-responsiveness of printable functional hydrogels. The printing process of (A) NIPAAm-Laponite nanocomposite hydrogel precursor and (B) NIPAAm-Laponite-GO nanocomposite hydrogel precursor; (C) the chemical structure of multiarmed ally-functional pNIPAAm macro crosslinker; (D) chemical structure of supramolecular hydrogel (left) and functions of each rationally designed chemical group (right).
From Jin, Y., Shen, Y., Yin, J., Qian, J., Huang, Y., 2018. Nanoclay-based self-supporting responsive nanocomposite hydrogels for printing applications. ACS Appl. Mater. Interfaces 10 (12), 10461–10470. https://doi.org/10.1021/acsami.8b00806.

shows. Each macro crosslinker was composed of pNIPAAm as the main chain and a terminating crosslinkable allyl group. With the aid of AuNRs that convert light energy into heat, the 4D printing of a light-driven soft actuator can be obtained.

It should be noted that in addition to the macromolecular hydrogel crosslinked by covalent bonds, the light-responsive supramolecular hydrogels such as cyclodextrins and their derivatives have also attracted a great deal of attention recently (Zhao & Stoddart, 2009). For example, Jiang et al. reported a simple yet efficient molecular design strategy to prepare the photoactive and dynamic polymeric network based on supramolecular motifs (Han, Morde, et al., 2020; Jiang, Ji, et al., 2020; Yuk & Zhao, 2018). The design and fabrication of the supramolecular photoresponsive hydrogel are displayed in Fig. 3.16D. The authors selected anthracene to impart photoresponsiveness into the hydrogel networks (Bai et al., 2018; Van Damme & Du Prez, 2018). By covalently incorporating this small anthracene molecule into a soft, flexible, and highly hydrophilic copolymer, the photoresponsive hydrogel can be fabricated. In an aqueous solution, the anthracene group enables forming a stable supramolecular network due to the π-π interaction as a crosslinking point (Fig. 3.16D, right). This double-crosslinked supramolecular hydrogel via simple synthesis exhibits fast, visible, driven shape morphing both in the wet and dry states.

The classical way of light-induced hydrogels generally incorporates temperature-responsive (lower than LCST or higher than LCST) and photothermogenesis nanoparticles. Recently, the incorporation of photoswitchable molecules (azobenzenes, spiropyrans, donor-acceptor Stenhouse adduct (DASAs), etc.) as side groups into polymer chains has emerged (Eelkema & Pich, 2020; Phua et al., 2016). To the best of our knowledge, there are few reports in the area of 4D-printed photoresponsive hydrogels directly, and most of the stimuli-responsive hydrogels are stimulated by temperature, pH, and humidity.

In short, compared with metal and ceramic, polymers are considered universal materials in 3D printing areas due to their diversity and ease of adoption to different 3D printing processes (Ngo et al., 2018). In addition, employed with DLP or SLA prototyping, polymers usually have the advantages of low melting point, low weight, low cost, and processing flexibility, thus enabling build the complex architectures by 3D printing techniques (Wang, Jiang, Zhou, Gou, & Hui, 2017). Especially for 4D printing, these features provide enormous benefits for programming shape deformations under external stimuli. Thus, most of the inks used for light-induced 4D printing are polymers or composites. Notably, we also should pay attention to the challenges of polymers and composites, such as the poor mechanical strength and functionality. Therefore, high-performance polymers such as printable polyimide (Guo et al., 2017; Hegde et al., 2017), bismaleimide (Wu et al., 2019), isocyanate ester (Chandrasekaran et al., 2018; Wu, Jiang, et al., 2020), metamaterials (Bodaghi, Damanpack, Hu, & Liao, 2017; Lei et al., 2019), etc., have been developed, and some of them have been used for 4D printing (Gliozzi et al., 2020; Li, Yang, et al., 2020; Yang, Boorugu, et al., 2019). It is believed there will more novel materials appearing for photoresponsive 4D printing in the near future.

4D-printed light-responsive behaviors and emerging applications

4D printing supports the fabrication of complex and customized geometries with spatial control for diverse physical changes and applications, such as shape deformations, smart actuation, etc. (Choi et al., 2015; Mitchell et al., 2018; Momeni et al., 2017; Zhang et al., 2016; Zhang, Demir, & Gu, 2019). In this section, some typical applications of light-responsive 4D printing that exhibit physical changes of the printed components or structures are briefly summarized. In addition, the emerging applications of this system, such as self-healing, smart anticounterfeiting, and others, are also described.

Shape deformations

Shape-morphing systems can be found in many areas, such as tissue engineering (Lin, Lv, Li, Zhang, et al., 2019; Xin et al., 2020), natural analogs (Burgert & Fratzl, 2009; Hua et al., 2018), biomedical devices (Li, Zhang, Liu, & Leng, 2020), and smart textiles (Hu, Meng, Li, & Ibekwe, 2012; Hu et al., 2020). Integrating with stimuli-responsive materials as mentioned above, researchers have made great efforts to design artificial alternatives with controlled shape deformation, including simple bending, twisting, and folding. Also, some complex shape deformations such as from two-dimensional (2D) to 3D or 3D to more complex 3D have been realized with the help of 3D printing or other advanced technologies. Herein, the light-responsive behaviors of shape deformation, that is, switching between one-dimensional (1D), 2D, and 3D shapes, are summarized to demonstrate the powerful functionality of light-induced 4D-printed architectures.

Among all the 4D-printed shape change behaviors, the most common and the simplest systems are self-twisting, self-folding, and self-bending behaviors (Fig. 3.17A–C), and the complex shape deformations usually evolve from these three simple shape deformation systems (Bodaghi, Noroozi, Zolfagharian, Fotouhi, & Norouzi, 2019; Ji et al., 2019; Liu, Shaw, Dickey, & Genzer, 2017; Mu et al., 2015; Sydney Gladman, Matsumoto, Nuzzo, Mahadevan, & Lewis, 2016; Zhao, Zou, & Luo, 2016). For example, shape-adaptive metastructures/metamaterials can be prepared by FDM 4D printing and then the transformation of the 2D/3D configuration can be realized by self-folding and self-coiling features (Bodaghi, Damanpack, Hu, & Liao, 2017; Lei et al., 2019). Notably, compared with self-bending and self-twisting samples composed of homogeneous or single active materials, the self-folding should be encoded with localized or anisotropic responsive performance that induced the following shape changes under external stimuli (Fig. 3.17D) (Mao et al., 2015). Recently, preparing architectures with precise and controllable angles to perform self-twisting, self-folding, and self-bending behaviors has become a challenge in this area.

With the help of various and ingenious design mechanisms and different smart responsive materials, researchers have realized complex shape changes to a certain degree. Typically, Kuang and coworkers utilized the grayscale DLP 3D printing

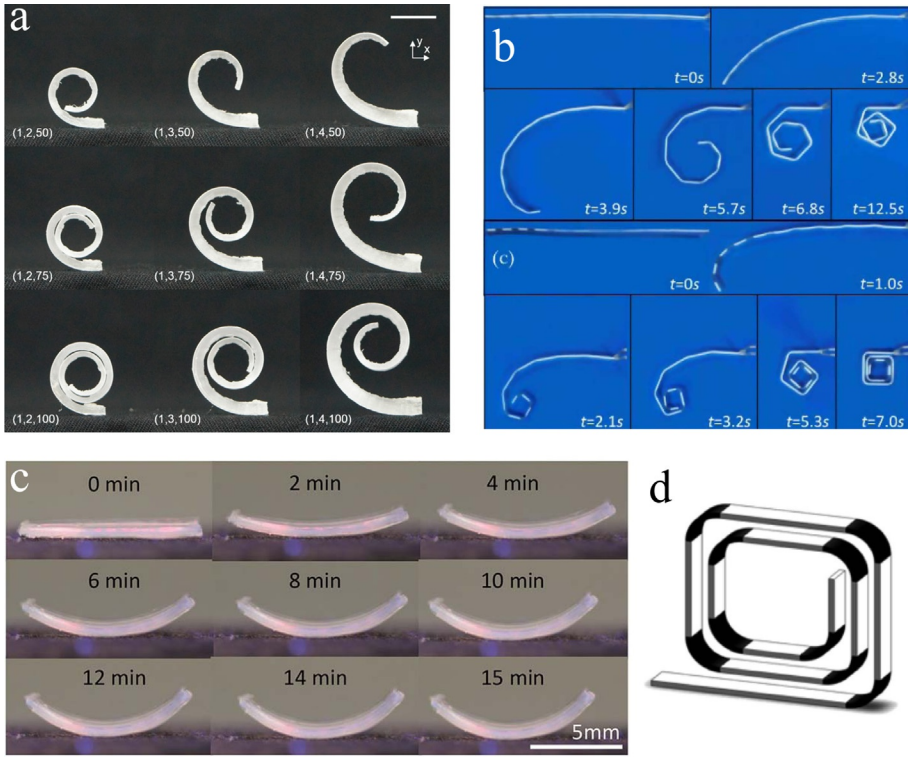

Fig. 3.17 Simple shape deformations. The shape deformation behaviors of: (A) self-twisting, (B) self-folding, (C) self-bending, and (D) schematic illustration of the localized difference. From Mao, Y., Yu, K., Isakov, M.S., Wu, J., Dunn, M.L., Jerry Qi, H., 2015. Sequential self-folding structures by 3D printed digital shape memory polymers. Sci. Rep. 5 (1), 13616. https://doi.org/10.1038/srep13616.

technology to prepare a helical pattern (Kuang, Wu, et al., 2019), whose panel portion was assigned with a grayscale of G20 (G value is the grayscale percentage, from 0% (full intensity) to 100% (full dark)) and whose hinges were assigned different grayscales ranging from G20 to G80. Integrating with SMPs with different T_g s, the helical component enables changing from a straight line to its spiral shape with the hinges folding sequentially under the external stimuli (Fig. 3.18A). In addition, the planar changes from 2D to 2D also exhibit fascinating behaviors. Tao Xie's group prepared a 2D hydrogel pattern with different crosslinking densities (L. Huang et al., 2017). This was able to experience sophisticated shape changes under external stimuli, including transforming to adorable 3D cartoon faces, a dome array with fan style distribution, and a partial cutout 3D structure with honeycomb-shaped domes (Fig. 3.18B). Using a similar principle, Jiang and coworkers used the grayscale exposure technique and a unique patterning mechanism to develop a grayscale image-guided pattern with complex and fine features used for projection (Jiang et al., 2019). This method can reconstitute the famous painting called the *Riverside Scene*

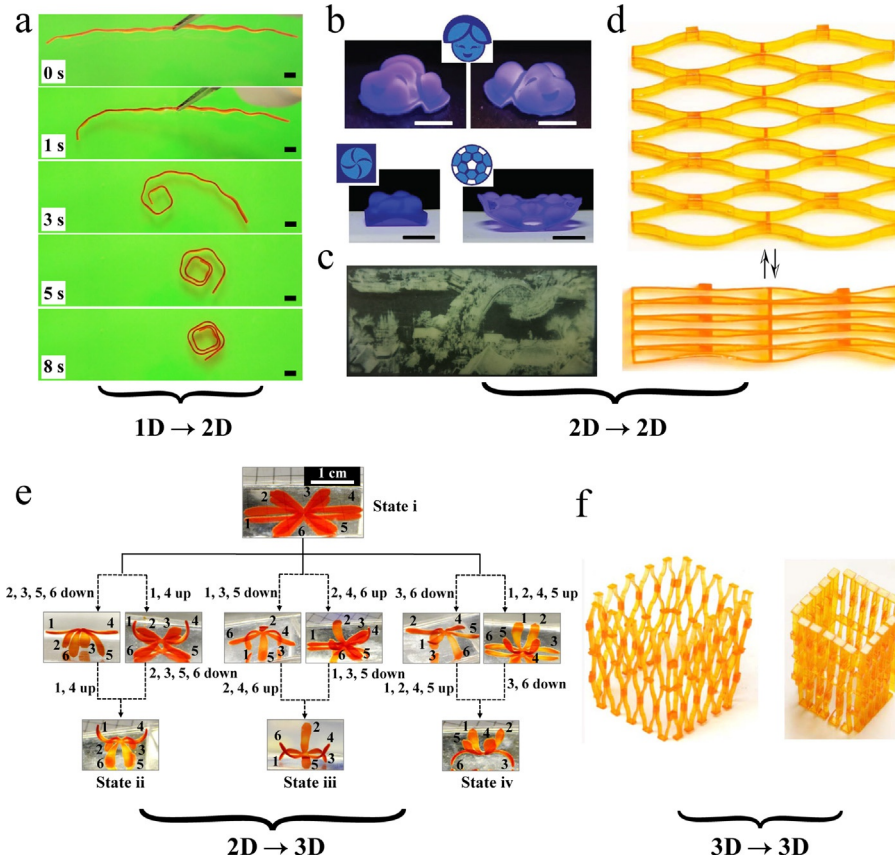

Fig. 3.18 Shape deformation behaviors between 1D, 2D, and 3D. (A) Snapshots showing the sequential shape recovery process of the helical pattern; (B) demonstration of printing versatility including the shape changes of a 3D cartoon face mask (above) and multiscale buckled structures (bottom), all scale bar is 1 cm; (C) GE-DLP of hydrogel with the painting *Riverside Scene at Qing*ming *Festival* from the Chinese Song Dynasty with a lot of fine details; (D) the deformed structure after desolvation (above) and after the swelling process (bottom), respectively; (E) the shape reconfiguration behaviors of a flower-shaped hybrid film by precisely controlling the position and direction of the blue light; (F) the expanded structure (left) and shrunk structure (right) under acetone stimuli.
From Kuang, X., Wu, J., Chen, K., Zhao, Z., Ding, Z., Hu, F., et al., 2019. Grayscale digital light processing 3D printing for highly functionally graded materials. Sci. Adv. 5 (5), eaav5790. https://doi.org/10.1126/sciadv.aav5790.

at Qingming Festival from the Chinese Song Dynasty, where detailed features were contained in the hydrogel patterning, as shown in Fig. 3.18C. The size changes in the 2D plane also can be demonstrated; as Fig. 3.18D shows, the grayscale pattern could expand to two times its original shape in the vertical direction under external stimuli (J. Wu et al., 2018). As one of the most common behaviors, the shape change from

simple 2D plane transforms to complicated 3D architecture is more interesting. Fig. 3.18E shows a prepared hydrogel film with six petals. Under light stimuli, the film could selectively bend any subset of the petals up or down by locally irradiating each one from the top or bottom, respectively (Arumugaperumal et al., 2020; Li, Kim, et al., 2020). Finally, as one of the most difficult projects in the area of shape deformation, the transformation between 3D and 3D seems not very prosperous, especially for the complex shape changes. Some of the cases only realize the shape switching between the very simple 3D structures, such as the expansion and shrinkage of printed 3D architecture under acetone stimuli (Fig. 3.18F) (Wu et al., 2018).

Even though studies have reported the complex shape deformation from 1D to 3D (Ji, Yan, Yu, et al., 2019; Sydney Gladman et al., 2016), the light-induced system is still too difficult to realize the function. Compared with the temperature-responsive and humidity-responsive shape changes, the light-induced system is comparatively rare due to the limitation of light-responsive material. Nevertheless, the emerging microchange in the 2D plane, such as the grayscale hydrogel patterns with visible light transmittance, is developing very fast because of practical applications such as anti-counterfeiting, mechanics, and some others.

Soft robots

There is great attention in developing soft robots that respond to external stimuli to produce mechanical work and activate an autonomous motion. Inspired by biological methods and locomotion systems, various intelligent soft robots inspired by snakes (Kelasidi et al., 2018; Liljebäck et al., 2012), geckos (Wang, Yang, et al., 2020), caterpillars (Li, Du, Yu, van der Gucht, & Zhou, 2015; Rogóż, Zeng, Xuan, Wiersma, & Wasylczyk, 2016; Sun, Chen, Bian, & Zhao, 2020), and cephalopods (Lu et al., 2018) can be prepared with excellent deformability and dexterity under stimulation. In addition, comparing with other stimuli such as heat, pH, and redox reactions, to realize the functions of soft robots, light is particularly attractive given its noninvasive nature, and the possibility of localizing the stimulus would endow the robots with some special functionality. Therefore, light-responsive soft robots exhibit more powerful functions to perform various tasks by mimicking biological behaviors or other locomotion systems.

Integrating with the advanced 3D printing technique, Chuang Li and coworkers designed a hybrid hydrogel used for light-activated mechanical actuation (Li, Iscen, et al., 2020). Following shape change behaviors as mentioned above, the authors created a macroscopic object to convert light to mechanical energy. Fig. 3.19 illustrates the unidirectional motion and rotational movement of a four-arm hydrogel crawler on a ratcheted and transparent PDMS surface upon light exposure from below. Typically, the macroscopic unidirectional crawling is shown in Fig. 3.19A. The front feet of the crawler are immobilized in the ratchet groove, and thus they remain static even though the back feet move forward under light stimuli. When the flattening process begins, the back feet stop moving while the front ones move forward due to the asymmetry in friction or gravity. Based on this mechanism

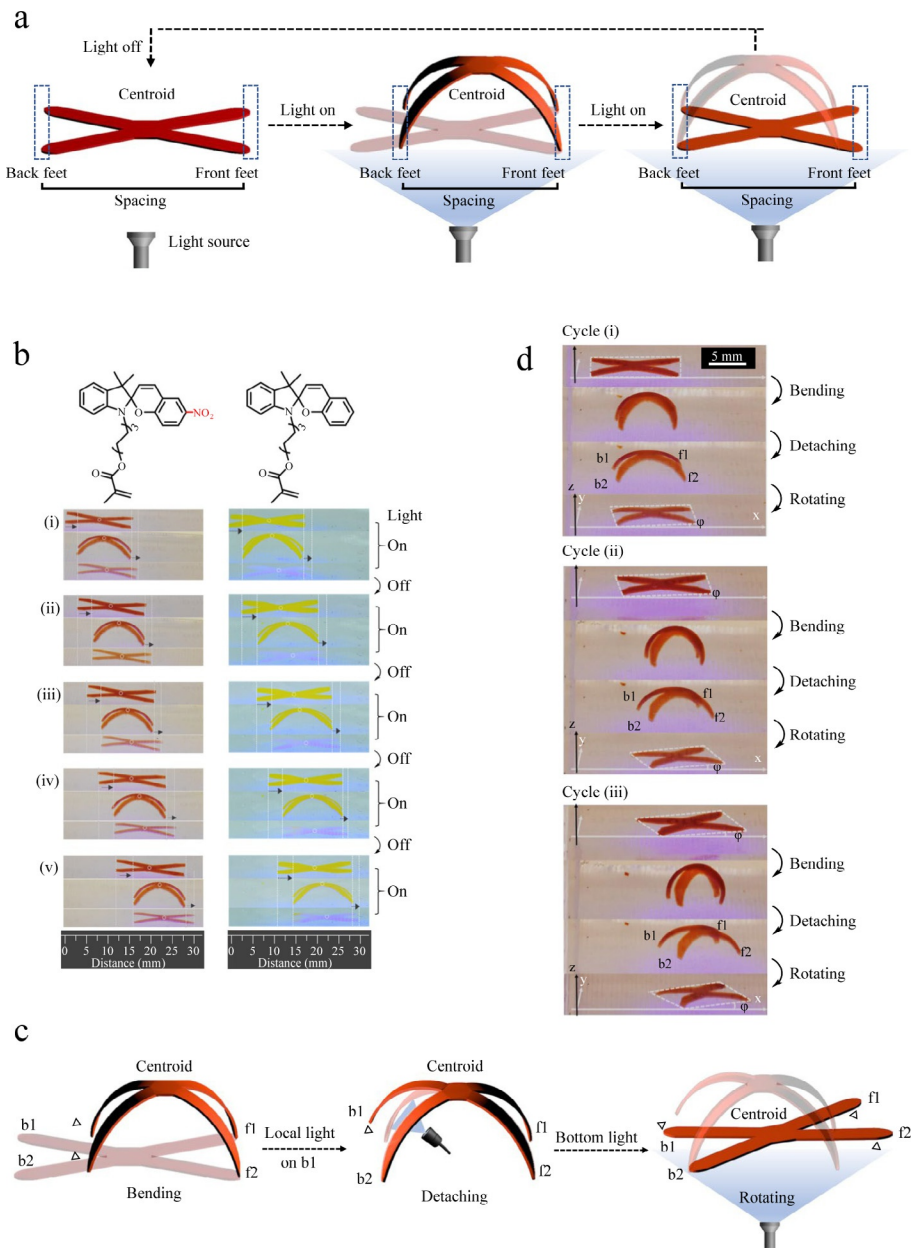

Fig. 3.19 The locomotion behaviors of light-responsive devices. Schematic representation of (A) crawling motion through a bending and flattening process and (C) rotational motion on ratcheted PDMS surface controlled by localized light; Snapshots of (B) five steps and (D) three cycles of the crawler after alternating periods of light on and off.
From Li, C., Iscen, A., Sai, H., Sato, K., Sather, N.A., Chin, S. M., et al., 2020. Supramolecular–covalent hybrid polymers for light-activated mechanical actuation. Nat. Mater. 19 (8), 900–909. https://doi.org/10.1038/s41563-020-0707-7.

and light stimulation being on and off, snapshots of the bending-flattening process associated with each step are shown in Fig. 3.19B. After five steps by alternating light periods on and off, the device eventually advanced 12.5 mm. Besides the unidirectional translation, the soft robot can also perform more complicated movements, such as rotation. As shown in Fig. 3.19C, the localized light induced the irradiated foot (b1) to start flattening, and the results in the foot are released from the ratcheted PDMS surface so it steps back. Once the whole crawler was irradiated from the bottom, three feet anchored and one detached (b1) leads to an unbalanced force, and the object rotates in an anticlockwise way. The snapshots of rotational movement further demonstrate this effect with multiple cycles by light control (Fig. 3.19D). After alternating periods of light on (30 min) and light off (10 h), the final rotational angle about the z-axis over three cycles changed from 0 degrees to 10 degrees. In short, the smart hydrogel crawler is able to realize functions, including macroscopic unidirectional crawling and rotational movement under light stimuli, exhibiting great potential applications in the fields of soft actuators, artificial muscles, and others.

Future challenges in this field require novel and smart materials to achieve a fast response and excellent adaptability of soft robots. In addition, we should also note that although the reported soft robots can perform various difficult functions such as crawling, jumping, climbing, and even crossing an obstacle, most of the tasks were performed on a rough or asymmetric ratcheted surface. The special surfaces would provide the anisotropic friction or mechanical interlocking, which plays a crucial role during the driving process (Baum, Kovalev, Michels, & Gorb, 2014; Ji, Yan, Yu, et al., 2019). Therefore, the light-responsive soft robots driving on a flat and smooth surface may be a potential research field in the future.

Emerging applications

With advancements in 4D-printed light-responsive structures, more and more smart devices are appearing with comprehensive properties. As mentioned above, light is one of the most promising stimuli for smart systems; it has many merits, such as noncontact, selective, and precise illumination as wella s high-resolution temporal and spatial control (Göstl et al., 2014). Thus, integrating with various intelligent materials and advanced 3D printing technology, the applications of light-responsive structures have gradually expanded to some emerging areas with particular functions.

For grayscale 3D printing, the unique patterning mechanism of gradient crosslinking density, which can be introduced for generating patterns, displays potential for encryption and anticounterfeiting. For example, Jiang et al. and Kuang et al. incorporated a quick response (QR) code into a thin film using the grayscale pattern for printing (Jiang et al., 2019; Kuang, Wu, et al., 2019). Under visible light, the film is ordinary; while being stimulated by external stimuli, the QR code of the author's group and the name card would appear, making it recognizable by the smartphone (Fig. 3.20A–C). The heat-triggered self-healing ability has received increasing attention due to the unavoidable degradation and unpredictable damage of printed samples for the photothermal effect. Zhang and coworkers introduced high-efficiency photothermal agent aniline trimers (AT) into printed inks. Under the irradiation of

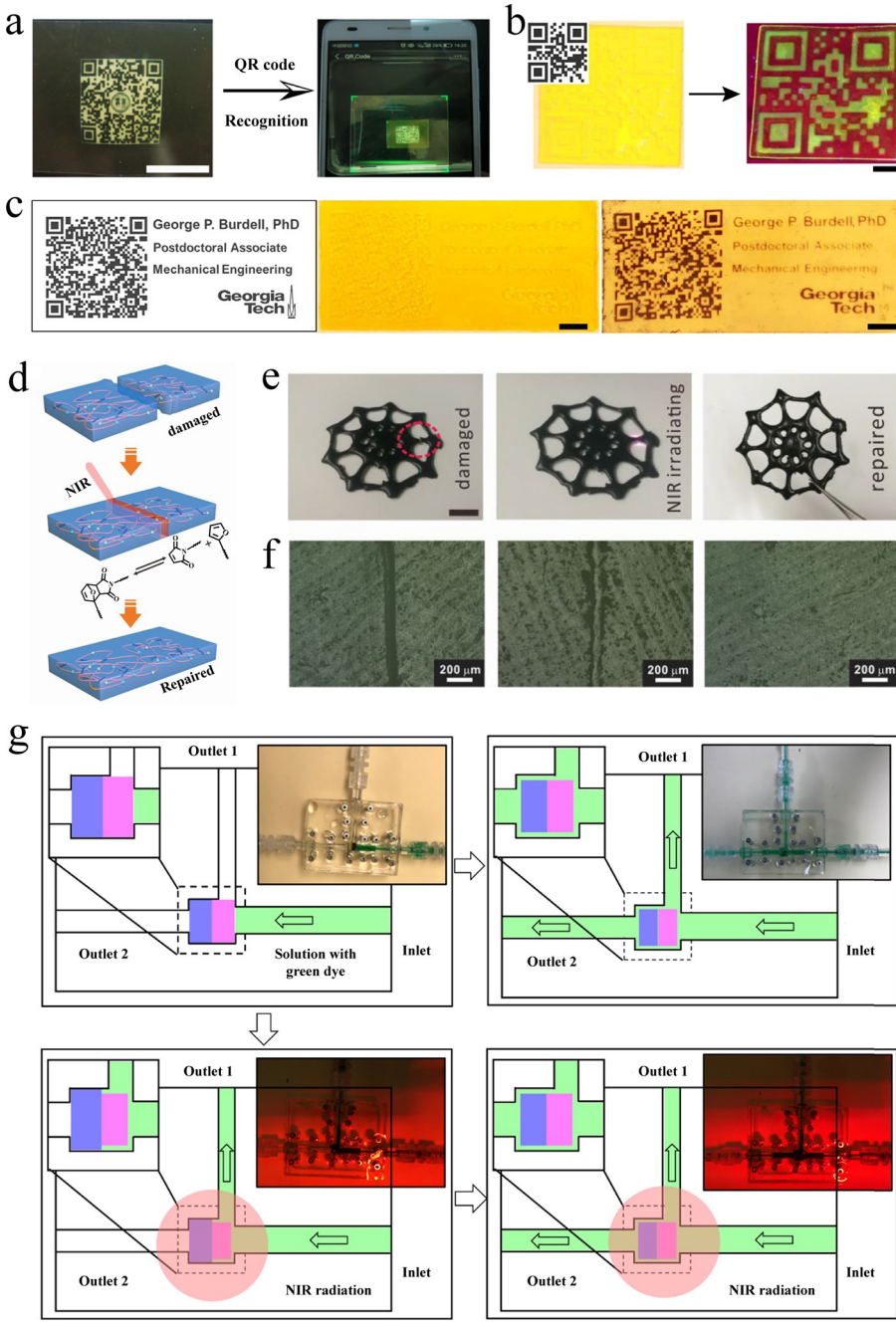

Fig. 3.20 Emerging applications of light-responsive devices. (A and B) Design of a grayscale pattern for QR code and the QR code was recognized by a smartphone under the external stimuli; (C) design of a grayscale pattern for a name card, and recognized by a smartphone; (D) schematic illustration of in situ self-healing property triggered by NIR light;

(Continued)

NIR light, the printed sample would effectively generate large amounts of heat, and such a light-to-heat conversion would provide a remote self-healing property (Fig. 3.20D) (Zhang, Yin, et al., 2019). Fig. 3.20E shows a specimen of a spider-like structure with an opening crack that was irradiated by NIR light (with a power of 0.8 W and an irradiation time at the same location of less than 10 s). The crack closed gradually, and the fracture was finally repaired. The optical microscope photographs of a damaged specimen before and after NIR-triggered self-healing further show that the deep cracks disappeared in the healing process without affecting the surrounding areas (Fig. 3.20F). For a light-responsive hydrogel, smart 3D microfluidic valves were designed to effectively control the flow directions in response to heat and light (Jin et al., 2018). As Fig. 3.20G shows, the microfluidic system is assembled by cured control valves loaded in the valve chamber in the center of the PDMS chip, and the valves are composed of pNIPAAm-Laponite and pNIPAAm-Laponite-GO hydrogel. Therefore, the fully swollen pNIPAAm-based valves would dehydrate almost simultaneously once the microfluidic system was submerged in a hot water bath. As a result, the volume of the valves shrinks, leading to open-flow channels from the inlet to both outlet channels (Fig. 3.20G, top). Correspondingly, the NIR light irradiation makes the pNIPAAm-Laponite-GO valve dehydrate first due to the excellent NIR absorption ability of GO and opens the valve while the pNIPAAm-Laponite valve stays closed. Consequently, this only allows an open-flow channel from the inlet to the first outlet channels (Fig. 3.20G, bottom).

Besides the applications of anticounterfeiting, self-repairing, and microfluidics, there are still many emerging application fields, including biomedicine (Bozuyuk et al., 2018; Cui et al., 2019), lab-on-a-chip (van Oosten et al., 2009), biomimetic devices (Bi et al., 2020), wearable sensors (Deng et al., 2019), Braille-like actuators (Lu et al., 2021) and so forth (Gillono et al., 2020; Gliozzi et al., 2020). Although these applications have not yet matured, we expect that they have great potential to promote further development of 3D printing and light-controlled devices.

Conclusion

This chapter focused on the essential components of 4D-printed light-responsive structures systems: mechanisms, materials, and applications. Recent advances in light-responsive structures were surveyed, first by a primer on the design mechanisms associated with 3D printing. Through exploring novel strategies and new techniques, the researchers developed various principles to support the field as it evolves.

Fig. 3.20, cont'd (E) photographs of the self-repairing process of the spider-like structure; (F) Optical microscopic images of the damaged specimen before and after being repaired; (G) diagrammatic sketch and photographs (the insert images) of the multistimuli-controlled microfluidic valves.
From Kuang, X., Wu, J., Chen, K., Zhao, Z., Ding, Z., Hu, F., et al., 2019. Grayscale digital light processing 3D printing for highly functionally graded materials. Sci. Adv. 5 (5), eaav5790. https://doi.org/10.1126/sciadv.aav5790.

Furthermore, the typical materials used for light-responsive structures such as SMPs, liquid crystalline materials, and hydrogels, were summarized systematically, and the unique strengths and weaknesses of each were given. Finally, by integrating with design mechanisms and smart materials, the precise and complex shape deformation, soft robots, and other emerging applications have been broadened. Notably, some smart materials will involve multiple design mechanisms to perform complicated behaviors. A typical example is a work from Tao Xie's group where the light-responsive structure integrates the mechanisms of shape memory effect, photothermal effect, and grayscale exposure to perform the shape-morphing behaviors. Thus, we believe this system is an interdiscipline, which is the future interest in this field.

It can be concluded that compared with other stimuli, light has many merits, including acting as a source of energy, being a control signal carrier, traveling long distances in a vacuum, the ability to focus onto a certain area, safety for human tissues, and the ability to be dispersed through optical fibers (Herath et al., 2020). These have resulted in light-responsive devices responding to different wavelengths from UV to NIR, triggered directly (photochemical) or indirectly (photothermal). Different from whole exposure, selective or sequential irradiation will lead to localized actuation or stepwise deformation (Wang, Li, et al., 2019). In addition, with the help of the strong penetration and remote control properties of the light, the self-repairing/actuation behaviors of the devices can be realized not only in the air but underwater in some cases (Pilz da Cunha et al., 2019; Yin et al., 2017). The photothermal self-healing method is a distinct way compared with other self-repairing systems. Finally, future light-responsive structures should focus on novel materials and advanced optical technology. Of course, some unique strategies such as surface modification or postprocessing (Bi et al., 2020) also need to be valued. Most importantly, new knowledge will be the foundation for developing this field with improved functionalities essential to develop innovative applications, and these future applications will be grand and limitless.

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