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Advances in 4D printed shape memory composites and structures: Actuation and application

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Shape memory polymer composites (SMPCs) are a type of smart material that can change shapes under the stimulation of the external environment, and they have great potential in aerospace, biomedical, robotics, and electronic devices due to their advantages of high strength and toughness, lightweight, impact resistance, corrosion resistance, and aging resistance. 4D printing technology has provided new opportunities for the further development of smart materials. The addition of various fillers enriches the variety of printable materials and provides composites with different properties and functions. The combination of SMPCs and printing technologies realizes the structure-function integration. This paper introduces the emergence and development of 4D printing technologies, the preparation methods and properties of SMPCs for 4D printing; as well as the research progress and potential application of 4D printable SMPCs in recent years in terms of thermal, electrical, magnetic, and optical driving. Finally, the existing problems and future development of 4D printable SMPCs are discussed.

shape memory polymer composites, 4D printing, deformable structures, actuation modes, applications

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1 Introduction

Shape memory polymers (SMPs) are polymer materials that can return to their original shapes from temporary shapes under external stimulus conditions and realize the function of deformation. They are an important branch of smart materials [1–6]. SMPs have the advantages of low density, large deformation, ease of processing, and inexpensive raw materials. The degree of response to external stimuli can be adjusted by chemical methods to achieve the multi-functionalization of SMPs. Therefore, SMPs are considered as new smart materials, and they have potential applications in many fields [7–11]. 3D printing technology originated in the mid-1980s and is a new manufacturing technology for realizing the rapid processing of objects [12]. The printable materials are accumulated layer-by-layer through computer control, and finally, a three-dimensional object is obtained. 3D printing is a cumulative manufacturing technology that is often used to make models in the fields of mold manufacturing and industrial design, and is then gradually used for the direct manufacturing of some products. At present, this technology has been applied in jewelry, clothing and footwear, industrial design, construction, automotive, aerospace, dental and medical industries, education, civil engineering, and other fields.

In February 2013, Skylar Tibbits from the Massachusetts Institute of Technology in the United States first proposed the concept of 4D printing at the Technology Entertainment Design Conference and showed the research results of 4D printing. A piece of a rope-like object was put into the water, and the object was automatically folded into the pre-designed "MIT" shape. Thereafter, Ge et al. [13] published the first paper on 4D printing in Applied Physics Letters. 2D sheets were obtained through inkjet printing and transformed

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into 3D complex structures via thermodynamic programming. Since then, 4D printing has attracted widespread attention from the media and researchers. Initially, people defined 4D printing as "3D printing + time" adding a time dimension to 3D printing. Recently, the concept of 4D printing has been continuously updated and improved. When a 3D printing structure is given a specific stimulus (such as electricity, heat, light, magnetism, and force), its shape, properties, or functions can change over time, which is the most common definition of 4D printing. Currently, the research on 4D printing is still in its infancy. The rapid development of 4D printing depends on the interdisciplinary research of 3D printers, smart materials, and design. It has become an important branch of additive manufacturing, attracting significant interest from academia and industry.

Research on 4D printing of SMPCs mainly includes three aspects, 3D printing technologies, driving methods and applications, as shown in Figure 1. 3D printing technologies of SMPCs mainly include fused deposition modeling (FDM), direct ink writing (DIW), digital light processing (DLP), stereo lithography appearance (SLA), inkjet printing, and selective laser sintering (SLS). The printing technologies of nanofibers, nanoparticles, and chopped-fiber-reinforced SMPCs are essentially the same as those of SMPs. Currently, the main printing technology for continuous fiber-reinforced composites is FDM printing, and the printer has two delivery pipes: One for SMPs and one for continuous fiber [14–16]. Thermal drive is the main driving mode of SMPs, and the addition of fillers enriches the driving mode of the SMPs. The SMPCs can also be driven by electricity, magnetism, and light. The addition of fillers endows the SMPCs with more excellent properties and multi-functions, and they have more

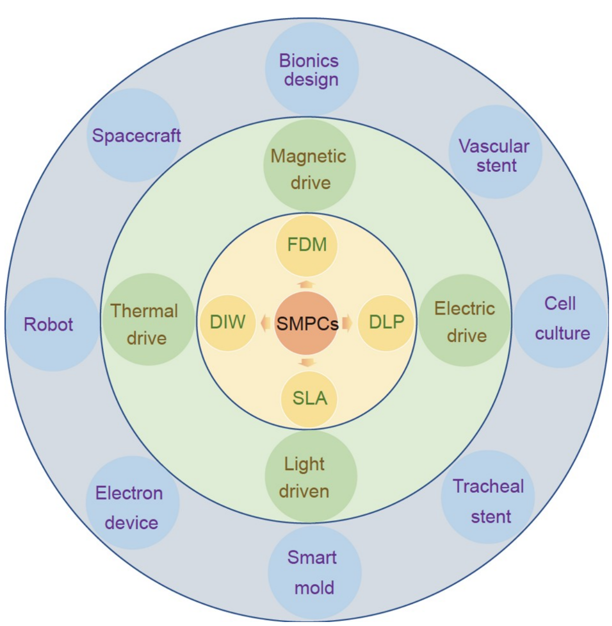

Figure 1 (Color online) Printing technologies, driving methods, and applications of SMPCs.

advantages in various fields.

The 4D printing technology has significant advantages over 3D printing technology. SMPCs can be printed into various smart devices to meet people's different needs and endow the printed structures with different functions by changing the structure's shape, color, transparency, healing, and other properties [17–22]. In addition, the ability of printed objects to change their shape in response to stimuli can effectively save storage and transportation space. To facilitate storage and transportation, SMPCs can be programmed into a flat 2D structure. When a certain stimulus is provided, the printed object is transformed from a flat 2D structure into a 3D structure [23–26]. The combination of SMPCs and 3D printing technology promotes the development of 4D printing technology, which can prepare complex 3D individualized, intelligent, and functional integrated structures. The research status and application development of 4D printable SMPCs are summarized from three aspects: 3D printing technologies, driving modes, and application prospects of SMPCs-based smart structures in various fields.

2 Development of 3D printing technologies

3D printing is a multifunctional technology platform for advanced manufacturing systems. Compared with conventional manufacturing processes, 3D printing is faster, more flexible, and cheaper, particularly in production. It can process complex three-dimensional structures that are difficult to achieve with conventional processing methods, and simultaneously has the advantages of high material utilization, fast processing speed, and personalized customization. With the development of 3D printing technologies, their applications in various fields have become increasingly extensive. Here, the various additive manufacturing technologies for SMPs and their composite materials, as well as the emerging printing technologies that have been researched and reported in recent years are introduced.

2.1 FDM printing technology

FDM is the most commonly used printing technology. The printable filaments are thermoplastic polymers and composites. A heating device is installed near the printer needle. When the needle is heated to a certain temperature (above the melting point of the polymer), the polymer becomes a viscous fluid state and is then squeezed by an external force [27,28]. The needle was moved to a preset position. The polymer is squeezed out of the heated needle. The polymer temperature soon cools below the melting point and the polymer solidifies. The printing technology can print a wide range of materials, and many types of thermoplastic engineering plastics can be printed. Currently, the commercially available filaments include polylactic acid (PLA), acrylonitrile-butadiene-styrene copolymer, polyether ether ketone (PEEK), polyvinyl alcohol (PVA), polyamide (commonly known as nylon), high impact polystyrene, polycaprolactone (PCL), polyurethane (PU), polymethyl methacrylate, polycarbonate (PC), etc., as many as dozens of kinds. In addition to the aforementioned SMPs, FDM can also print their SMPCs. The main types of SMPCs include continuous fiber-, chopped fiber-, nanoparticles-, and nanofiber-reinforced SMPCs. The most significant difference between the FDM printers of the SMPs and continuous fiber-reinforced SMPCs is the number of the delivery pipes. The FDM printer for chopped fibers, nanofibers, and nanoparticle-reinforced SMPCs is the same as that for SMPs. With the rapid development of 4D printing technologies in recent years, many researchers have been working on the research and development of printable filaments based on SMPs and SMPCs.

2.2 Photosensitive resin printing technologies

SLA and DLP are currently the most common printing technologies used for photosensitive resins. SLA uses a laser to focus on the surface of the light-cured material; thus, it is cured sequentially from point to line, from line to surface, and repeats so that layers are superimposed to form a 3D entity. The DLP printer contains a resin tank to hold the photosensitive resin to be printed. The accuracy of DLP printers depends on the projection pixels and is higher than that of other 3D printing equipment; its accuracy can generally reach a few microns.

New printing methods are constantly being developed to solve the problems of some existing printing methods and meet the application requirements. Considering the long printing time of DLP and SLA printing technologies, Kelly et al. [29] developed a novel light-curing integrated printing method called volumetric 3D printing technology. The printing principle is illustrated in Figure 2. Volumetric 3D printing technology breaks the conventional light-curing printing technology in which photosensitive resin is printed layer-by-layer. When the glass container is filled with transparent liquid photosensitive resin, the projector projects a video loop onto the glass container. This loop corresponds to a 2D slice of a printed object. The printer could print objects with a minimum size of 0.3 mm. Moreover, a fast speed of 20–30 s can print out cm-sized objects. Currently, DLP and SLA cannot print continuous fiber-reinforced SMPCs owing to the limitations of the printing method. They can print chopped fiber, nanofiber, and nanoparticle reinforced SMPCs. The light transmittance of composite inks is an important parameter affecting the printing effect. Ren et al. [30] modified a DLP printer (Figure 3(a)) and installed a permanent magnet near the resin tank to print particle or fiber-reinforced composite materials. The magnet could rotate and move freely and the direction of the magnetic field could be changed at will. The DLP printer with magnets prints the photosensitive resin doped with short steel fibers. As shown in Figure 3(b)–(d), the short steel fibers were oriented at a certain angle in the light-cured resin to enhance the mechanical properties. In addition to the aforementioned technologies, photosensitive resins can also be formed by UV-assisted DIW printing.

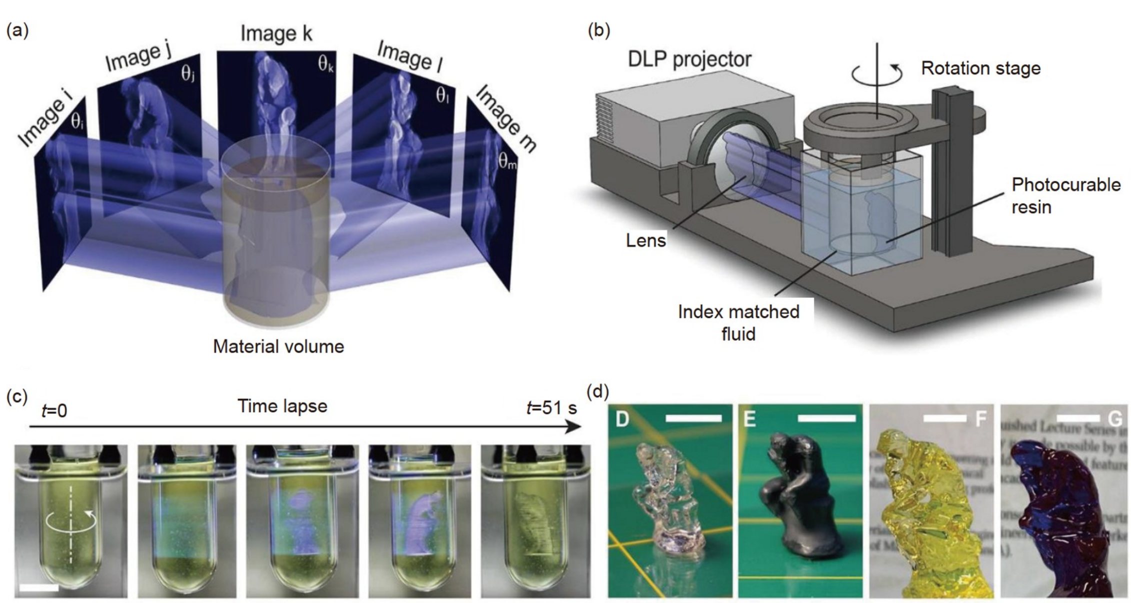

Figure 2 (Color online) Volumetric 3D printing technology [29]. (a) Projecting patterns of printed objects onto the resin container from multiple directions; (b) schematic diagram of the principle of volumetric 3D printing; (c) the forming process of the printed object; (d) the printed object. Ruler = 10 mm. Reproduced with permission of ref. [29]. Copyright©2019, AAAS.

2.3 DIW printing technology

DIW was first proposed by Cesarano et al. [31] at the Sandia National Laboratory in the United States. This technology uses a computer to pre-design structures and controls the rheological properties of suspensions to extrude or eject suspensions from the nozzle. Fine 3D structures of various shapes have been widely used in advanced ceramic materials, sensors, bionic materials, and piezoelectric materials. Compared with other rapid processing methods, the significant advantage of DIW is the diversification of printable inks, including inorganic non-metals, metals, organic polymers, and living cells. Like DLP and SLA, DIW cannot print continuous fiber-reinforced SMPCs; however, it can print short fiber-, nanofiber-, and nanoparticle-reinforced SMPCs. The fillers were mixed with printable inks to create composite inks for DIW printing.

It is difficult for common thermosetting polymers to be cured quickly during DIW printing, and the manufacturing technology for thermosetting polymers is limited. Chen et al. [32] designed a UV-light-assisted DIW printing technology to effectively print epoxy resin effectively. A photosensitive mixed ink of acrylic and epoxy resins was prepared. UV-light curing was performed after printing one layer until the entire structure was printed, as shown in Figure 4. Common DIW printers usually operate with only one printing needle. One printing needle can print only one type of ink, not a multi-material structure. Skylar-Scott et al. [33] combined inkjet printing and DIW printing to solve the above problem, and they developed multi-material multi-nozzle 3D printing (MM3D). The operating principle of this technology is illustrated. The squeezing force (P1, P2, P3, and P4) of the print head was controlled by the corresponding voltage waveforms (V1, V2, V3, and V4), and the pressure was applied to the four materials of the print head. It is a cubic element structure of the four materials that were successfully printed. In addition, MM3D printing can also converge multiple viscoelastic materials at a connection point, and use the

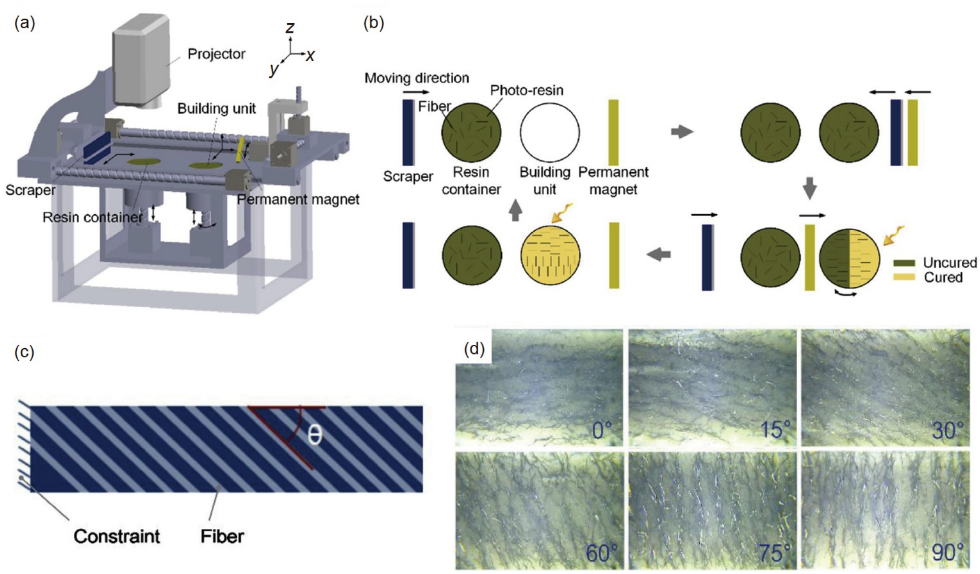

Figure 3 (Color online) Magnetic assisted DLP printing technology [30]. (a) Magnetic assisted DLP printer; (b) working principle diagram of the magnetic field; (c) schematic diagram of fiber arrangement angle; (d) fiber arrangement in different angles in resin. Reproduced with permission of ref. [30]. Copyright©2019, Elsevier.

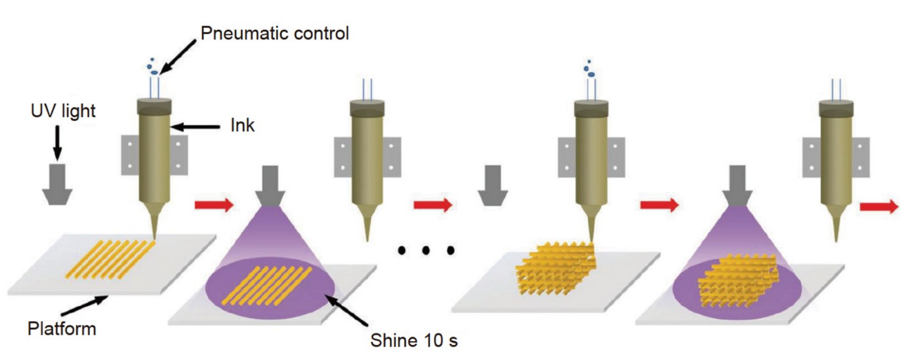

Figure 4 (Color online) Schematic diagram of UV-assisted DIW printing [32]. Reproduced with permission of ref. [32]. Copyright©2018, RSC.

diode-like behavior to achieve seamless and high-frequency switching between up to eight different materials. A cubic voxel with a volume close to the diameter of the nozzle successfully solved the problem of multi-material printing.

3 Research progress of 4D printing SMPs and their composite materials

SMPs can be divided into two types according to their nature: Thermoplastic and thermosetting. The printing technology of thermoplastic SMPs is mainly of the extrusion type, mainly including FDM and DIW. Their common point is that the structure is constructed through line-line and layer-layer accumulations. The difference is that FDM printing uses thermoplastic solid wires as the raw material, whereas DIW printing uses viscous liquid inks. Shape memory epoxy resin is a commonly used thermosetting resin. It has been widely used because of its excellent properties such as high mechanical strength, good thermal stability, and low shrinkage [34–37]. However, its brittleness limits its application, particularly when large strains are required. The introduction of flexible groups, such as ethoxy groups, propoxy groups, and polyether chains, toughens the molecular structure of epoxy resin [38–41]. Additionally, the molecular chain structure can be changed through chemical modification, such as using polyetheramine curing agents with flexible segments [42–45]. In addition to epoxy resins, acrylic resins are also a common type of thermosetting resins. DLP and SLA are the two most commonly used additive manufacturing techniques for the printing of acrylic resins. The principle is that allyl groups will quickly cross-link when they are exposed to UV radiation.

In general, SMP deformation can be divided into passive and active deformations. It is necessary to apply stress to SMPs that store the strain energy. The deformation achieved in this manner is known as passive deformation. Deformation can occur directly through environmental stimuli without applying stress; this is called autonomous deformation. Common autonomous deformation behaviors include self-bending, self-folding, and self-curling. Researchers have realized the autonomous deformation of simple structures through the design of geometric figures and adjustable deformation behavior, which can provide new opportunities for the development of smart devices. More research focused on the design of multi-material structures, using different response methods of materials to stimulus factors, such as different thermal expansion coefficients or different response factors of different materials [18,46–51]. The emergence of 4D printing technology has accelerated the development of autonomous deformation SMPs. SMPs have the advantages of an ultra-high shape recovery rate, easy adjustment of the shape memory transition temperature, ease of deformation, low density, and low cost. However, their application is significantly restricted owing to their poor mechanical properties and single response mode. The addition of functional fillers can effectively improve the mechanical properties, shape memory properties, electrical and thermal conductivities, and response modes of SMPs to meet application requirements. The drive modes of SMPCs can be divided into thermo-, electro-, magneto-, and photo-induced, depending on the external stimulus conditions.

3.1 4D printed thermal drive SMPCs

In general, SMPs are thermally responsive, and the addition of fillers does not change the response mode of the SMPs; therefore, many types of fillers can be added to SMPs. According to the different functional fillers, SMPCs can be divided into particle-, fiber-, nano-paper-, and mixed-filled types. Fiber-reinforced SMPCs have significantly low density, high strength, and high modulus advantages. Wang et al. [52] synthesized photosensitive epoxy inks and prepared carbon nanotubes (CNTs)- and short carbon fibers (CFs)-doped black inks for printing shape-memory capture devices. CNTs significantly reduce the light-curing ability of inks in the DLP printing process and the thermal radiation effect of CNTs is greater than that of CFs in shape recovery performance. The shape recovery time (T) of the CNTs-reinforced capture device is approximately 100 s and the shortest among them, followed by the CFs-reinforced device, as shown in Figure 5(a). The CNTs and short CFs increased the thermal conductivity and shape-recovery rate of the resin. Cellulose fibers from plants are also fiber fillers and have the characteristics of natural hydrophilicity, high strength, and high modulus. They are typically added to biomedical materials. Mulakkal et al. [53] developed a cellulose-added hydrogel composite ink and studied the physical properties of cellulose-hydrogel composite materials, including stability, swelling potential, and rheology, to determine their suitability for printers. The printed structure can be deformed according to the pre-designed rules after dehydration and hydration as shown in Figure 5(b).

The physical properties of the ink can be adjusted by the addition of particulate fillers, and the strength and functionality of the resin can be increased. Choong et al. [54] proposed a method for improving the light-curing speed of acrylic inks. They established that SiO_2 nanoparticles could change the scattering characteristics of ultraviolet light in the ink and act as a “super catalyst”. The curing time of each layer during printing is significantly reduced from 4 to 0.7 s, which significantly improves the curing speed. As shown in Figure 5(c), there was an interaction between the particles and the polymer because of the large number of nucleation points on the surface of the SiO_2 nanoparticles. Therefore, the mechanical properties of SiO_2 nanoparticles reinforced

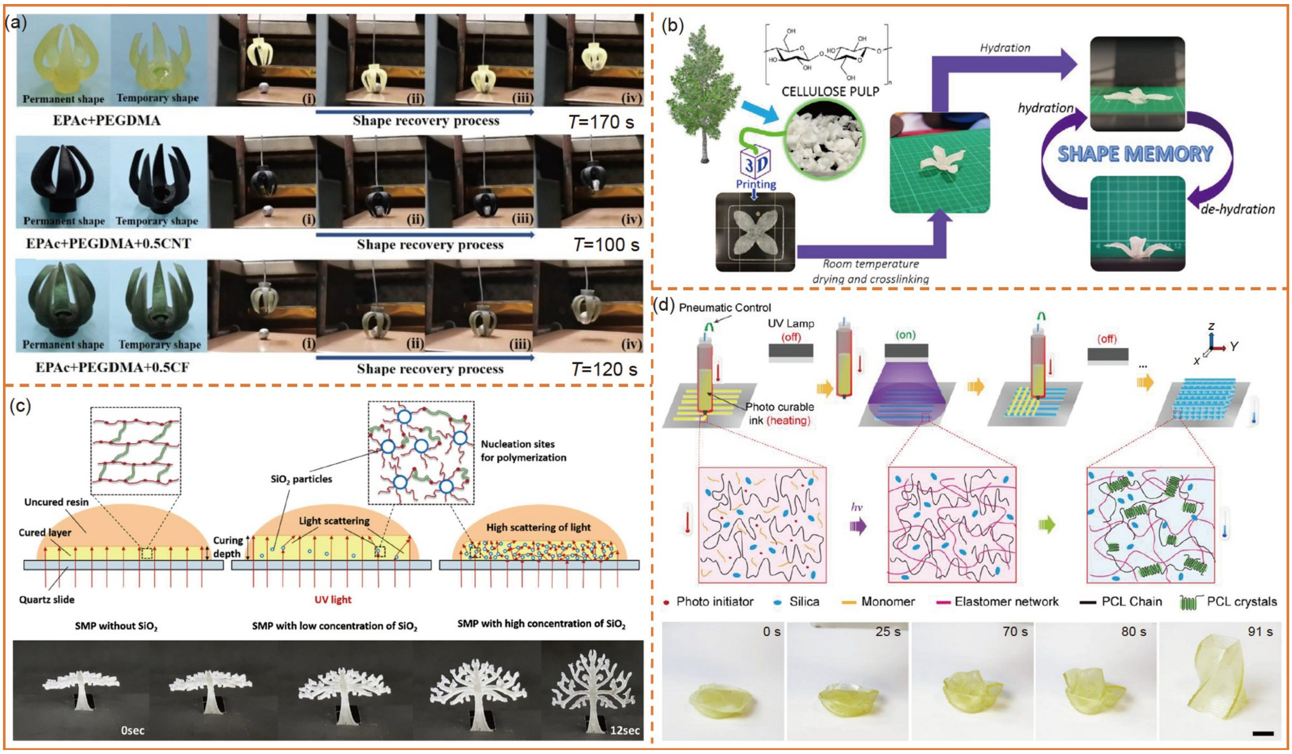

Figure 5 (Color online) (a) Shape recovery of DLP printed capture devices [52]. Reproduced with permission of ref. [52]. Copyright©2021, ACS. (b) Water absorption/dehydration effect of printed flower [53]. Reproduced with permission of ref. [53]. Copyright©2018, Elsevier. (c) Mechanism of SiO_2 nanoparticles in printable ink and shape recovery process of the printed tree [54]. Reproduced with permission of ref. [54]. Copyright©2020, Elsevier. (d) UV-assisted DIW printing and shape recovery of SiO_2 nanoparticles doped PCL-based composite [55]. Reproduced with permission of ref. [55]. Copyright©2018, ACS.

SMPCs were improved by an order of magnitude, and the elongation rate was increased by 85%. Kuang et al. [55] developed a new ink composed of polyurethane diacrylate and linear semi-crystalline PCL (Figure 5(d)), which can be used for printing elastomers with shape memory and self-healing properties. The addition of 200–300 nm SiO_2 particles to the ink gives the ink the rheological properties of shear thinning. A semi-interpenetrating polymer network elastomer was formed via UV-assisted DIW printing. The tensile strain of the elastomer reached 600%. Research has shown that printed shape memory elastomers have potential applications in vascular repair. The addition of SiO_2 nanoparticles can change the rheological properties and increase the curing speed of the photosensitive inks. This research provides a new understanding of the mechanism of the role and influence of SiO_2 nanoparticles in the development of rapid 3D printing, and it has opened up new high-performance materials.

3.2 4D printed electric drive SMPCs

Currently, thermal driving is the most common SMP drive mode. However, contact thermal driving is inconvenient for SMPs with remote-control requirements. Researchers have performed extensive work on the remote driving of SMPCs to eliminate external heaters and realize remote control. The usual method involves adding conductive fillers to the SMPs to realize the electric driving of SMPCs. There are two common types of conductive fillers. One is metal fillers [30,56,57]. Metal fillers are difficult to disperse uniformly and are easily oxidized in the polymer matrix; additionally, they are expensive compared with other fillers. Therefore, there is little research on metal-filled electro-driven SMPCs. The second type is carbon fillers. Currently, carbon fillers are most widely used in electro-active SMPCs because of their good electrical conductivity and thermodynamic properties, such as carbon black (CB) [58,59], CNTs [60–62], carbon nanofibers (CNFs) [63], short CFs, continuous CFs [64], graphene [65]. Carbon-filled SMPCs have excellent physical properties such as high strength, electrical conductivity, and thermal stability.

CNTs have extremely high inherent conductivity, high aspect ratio, and excellent self-entanglement performance, and they easily form conductive paths in polymer composites, making them the most widely used carbon material filler. So far, research on printing polymers and their composites has mostly focused on thermoplastic polymers, but the types of thermosetting resins that can be printed are very limited, and the printing research on thermosetting resins is progressing slowly. Wan et al. [66] prepared CNTs-doped

PLA-based composite ink and printed a U-shaped scaffold using DIW printing. The original and temporary shapes of the printed scaffold are shown in Figure 6(a). The folded scaffold recovered under a voltage of 25 V and the shape recovery process took 16 s. Liu et al. [67] studied the volume resistivity, temperature distribution, and shape memory behavior of CNT-enhanced shape memory polylactic acid (CNT-SMPLA) filament under DC voltage. Their shape memory behaviors were significantly affected by the printing speed, layer thickness, and printing filament angle. With slower printing speed, larger layer thickness, and printing filament angle of 0°, the shape of the printed structure recovers faster. Compared with the 0° sample, the temperature distribution of the 0°/90° sample was more uniform. A three-channel device was printed using an FDM printer, as shown in Figure 6(b), and it could be selectively remotely controlled by applying a voltage to different nodes. The three nodes of the device can achieve sequential and simultaneous shape recoveries, which has significant potential in the development of remote sequential control smart devices. Dong et al. [68] proposed a simple method for fabricating electroactive shape memory structures using FDM printing. Various 2D (strip and U-shaped) and 3D (pyramid, diamond, and crown) structures based on the PLA/CNTs composites were fabricated through FDM printing. The shape-recovery behaviors of the diamond and crown structures were realized under AC voltage, and their heat-distribution maps are shown in Figure 6(c).

In addition to CNTs, CNFs also exhibit good electrical conductivity, which can form conductive networks in matrix materials. The electrical resistance at the junctions of CNFs-networks is larger. Wei et al. [69] prepared silver-coated CNFs (Ag@CNFs) to improve the electrical conductivity of the networks. Ag@CNFs were added to printable PLA-based ink as a conductive filler. The gripper was obtained by DIW printing and triggered by a low voltage (1 V), as shown in Figure 6(d). The recovery process was within 20 s, indicating a fast electroactive behavior.

4D printed electro-induced SMPCs are mostly formed by FDM or DIW printing technology. 4D printed conductive composite materials can be used for the customizable preparation of electronic information devices, and their potential applications in flexible electronics, sensors, nerve catheters, wearable devices, and other fields. The common disadvantage of the above studies is that the printing structure is simple and the conductive path is single. Few studies have been conducted on the electric drive in complex structures. Continuous exploration and research are still needed to realize the electric drive of complex structures and device functionalization.

3.3 4D printed magnetic drive SMPCs

The deformation of 4D printed structures depends on the

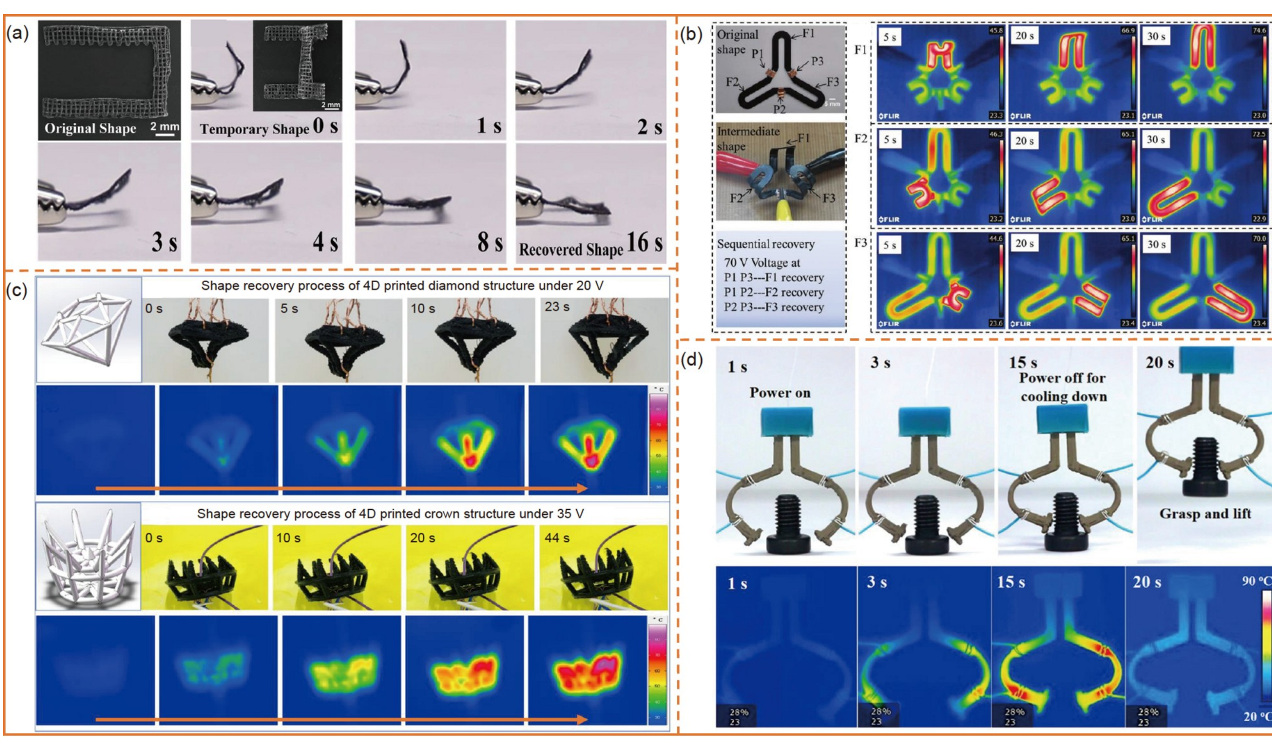

Figure 6 (Color online) (a) Shape recovery of 4D printed U-shaped scaffold [66]. Reproduced with permission of ref. [66]. Copyright©2019, Elsevier. (b)–(d) Heat distribution maps of 4D printed three-channel device, diamond, crown, and gripper in their shape recovery process [67–69]. Reproduced with permission of refs. [67–69]. Copyright©2019, Wiley; Copyright©2022, Elsevier; Copyright©2019, ACS.

stimuli of the surrounding environment, such as temperature and humidity. The deformation process of complex structures usually requires a long response time. The electric drive is a contact driving and remote control mode, whereas the magnetic drive can simultaneously achieve a non-contact drive and rapid response. The most common magnetic driving strategy is the addition of magnetic fillers to the SMPs, generally magnetic particles and short magnetic fibers. The hysteresis loss produced by the magnetic fillers is released as heat, causing the shape recovery of the SMPCs under an alternating magnetic field [70–74].

Smart structures based on soft materials can be reshaped and reorganized under a magnetic field and are widely used in soft robotics. Roh et al. [75] reported a novel type of smart structure that can perform complex reconstructions and shape changes in a magnetic field. Polydimethylsiloxane (PDMS) and magnetic particles were mixed to form a composite ink, which was shaped into a grid structure that floated on water by 4D printing, as shown in Figure 7(a). The printed soft actuator was easily deformed under the action of the magnetic force of the carbonyl iron particles and capillary force. A mesh structure that is reconstructed in a magnetic field and responds to external stimuli can be used as a bionic soft robot. Zhu et al. [76] blended iron nanoparticles with PDMS to prepare a printable PDMS/Fe composite ink. The soft magnetic particles in the composite ink have a lower magnetic force and higher magnetic permittivity, and the printed butterfly structure can immediately gain or lose high magnetization ability when the external magnetic field is turned on or off. The butterfly quickly flaps its wings, which takes 0.7 s for the apex of the butterfly wing to move from the lowest position to the highest position under the varying external magnetic field.

Zhang et al. [77] mixed magnetized microparticles (NdFeB) with PDMS to create a composite ink and coupled 3D injection printing with the origami-based magnetization technique for the easy fabrication of magnetoactive soft material objects, such as a bionic hand, butterfly, and turtle. The rock-paper-scissors game was played using a printed bionic hand, which could easily achieve on-demand shape-shifting from paper to scissors to rock. The printed butterfly can flap its wings every 1.5 s under magnetic actuation. In addition, the bionic turtle crawls on land under magnetic actuation, as shown in Figure 7(b), and it can also crawl underwater and swim in the water. These behaviors verify the good controllability and reprogramming ability of the 4D-printed magnetoactive soft material objects. Wu et al. [78] printed a gripper using an SLS printer based on a composite material consisting of magnetic $Nd_2Fe_{14}B$ powder and thermoplastic PU powders. The experimental results are consistent with the numerical simulation results for the magnetic induction distribution. The deformation of the printed gripper can be regulated by tuning the magnetic particle content and the distance from the external magnet, as

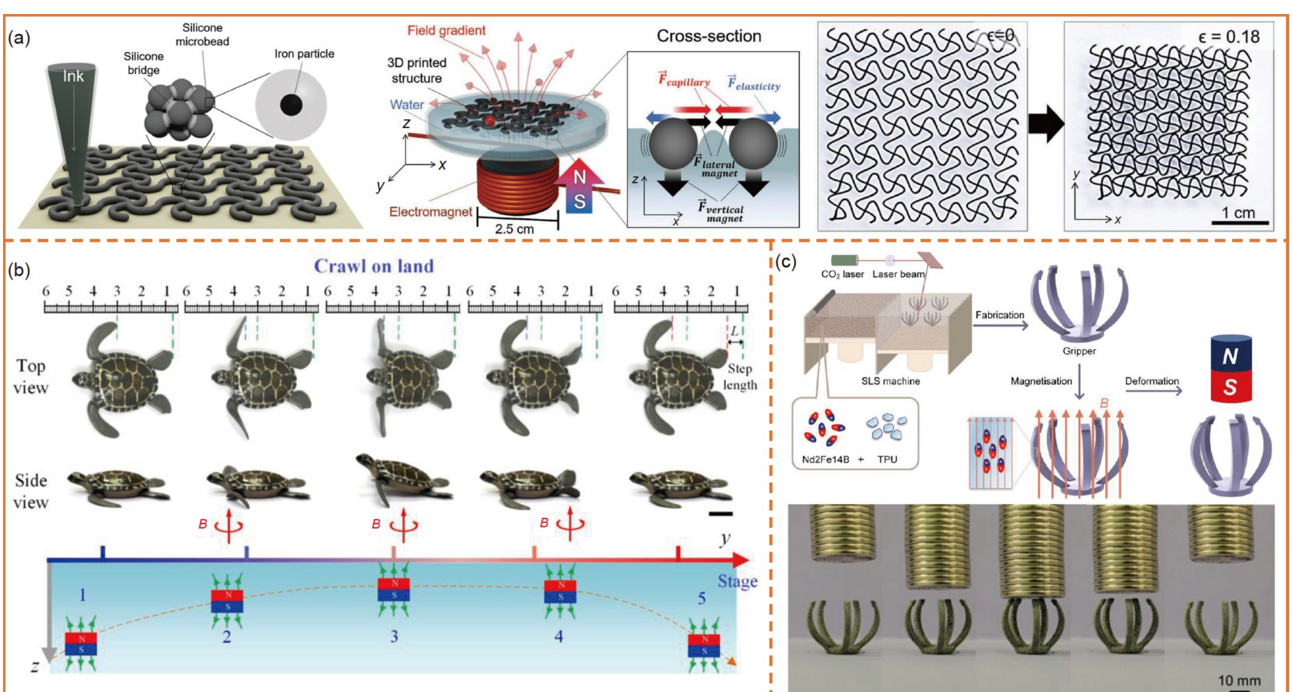

Figure 7 (Color online) 4D printing of SMPCs filled with magnetic particles. (a) The structural change of the printed grid structure under the action of an external magnetic field [75]. Reproduced with permission of ref. [75]. Copyright©2019, Wiley. (b) Crawling behavior of a bionic turtle on land [77]. Reproduced with permission of ref. [77]. Copyright©2021, ACS. (c) The SLS fabrication, magnetization, and deformation processes of the magnetism-responsive gripper [78]. Reproduced with permission of ref. [78]. Copyright©2021, ACS.

shown in Figure 7(c). The striking contributions are the calculation of the magnetic driving force and establishment of a quantitative relationship between the driving stimulus and the deformation response of the grippers. What is most worthy of our reference is the idea of combining experiments with simulations.

3.4 4D printed light-driven SMPCs

SMPCs convert the absorbed light wave energy into heat, which can cause the SMPCs to reach their transition temperature, thereby triggering the shape memory effect [79–82]. Compared with electric drives and magnetic drives, the clear advantage of light-driven is that it can perform area selective drive. This is because of the flexibility of the light source, and the size, direction, and position can be adjusted arbitrarily. Infrared light has an evident thermal effect and is easily absorbed by objects, which can be used as a stimulus factor to drive SMPCs. Zhang et al. [83] synthesized PU with PCL, then introduced a high-efficiency photothermal agent, aniline trimer, into the reaction system, and finally synthesized a PU-based SMP (PDAPU). A fist structure was printed using DIW printing, and then the index finger was irradiated with far-infrared light. The index finger gradually extended, as shown in Figure 8(a). The temporary shape returns to its original shape because of the activity of the molecular chain after being irradiated with infrared light. Moreover, fingers can be selectively irradiated locally or as a whole. The shape-recovery behavior can be conducted in a targeted manner, and accurate deformation can be achieved simultaneously. It has potential application prospects and it will promote the further development of functional 3D printed parts in smart devices, such as robots. Chen et al. [84] prepared Fe^{2+} ion-complexed polymers and achieved stress-free reversible actuation behavior with a semi-crystalline supramolecular metallo-network using crystalline transition as the actuation phase. Reversible bending allows the sample to crawl forward continuously on a designed track by turning the light on and off, as shown in Figure 8(b).

Another common drive type is the light-driven. Light-driven SMPs have specific light-responsive functional groups on the molecular chain, and photoisomerization reaction occurs under light irradiation at a specific wavelength such that the material exhibits macroscopic photo-induced deformation behavior. When the light irradiation is stopped or light with a different wavelength is used, the corresponding molecular chain segment undergoes a reversible photoisomerization reaction; thus, the material exhibits a macroscopic shape memory recovery behavior. Azobenzene derivatives are commonly used photosensitive molecules. The *trans*-isomer of azobenzene is a rod-shaped molecule, whereas the *cis*-isomer has a curved structure, as shown in Figure 8(c). Hagaman et al. [85] synthesized a type of SMP, which was polymerized by polymethylhydrosiloxane and 4-hexyloxyazobenzene and dissolved in toluene to make printable ink. A double-layer polymer actuator was fabricated through 4D printing, and light irradiation of the appropriate wavelength could cause the *trans*-*cis* isomerization

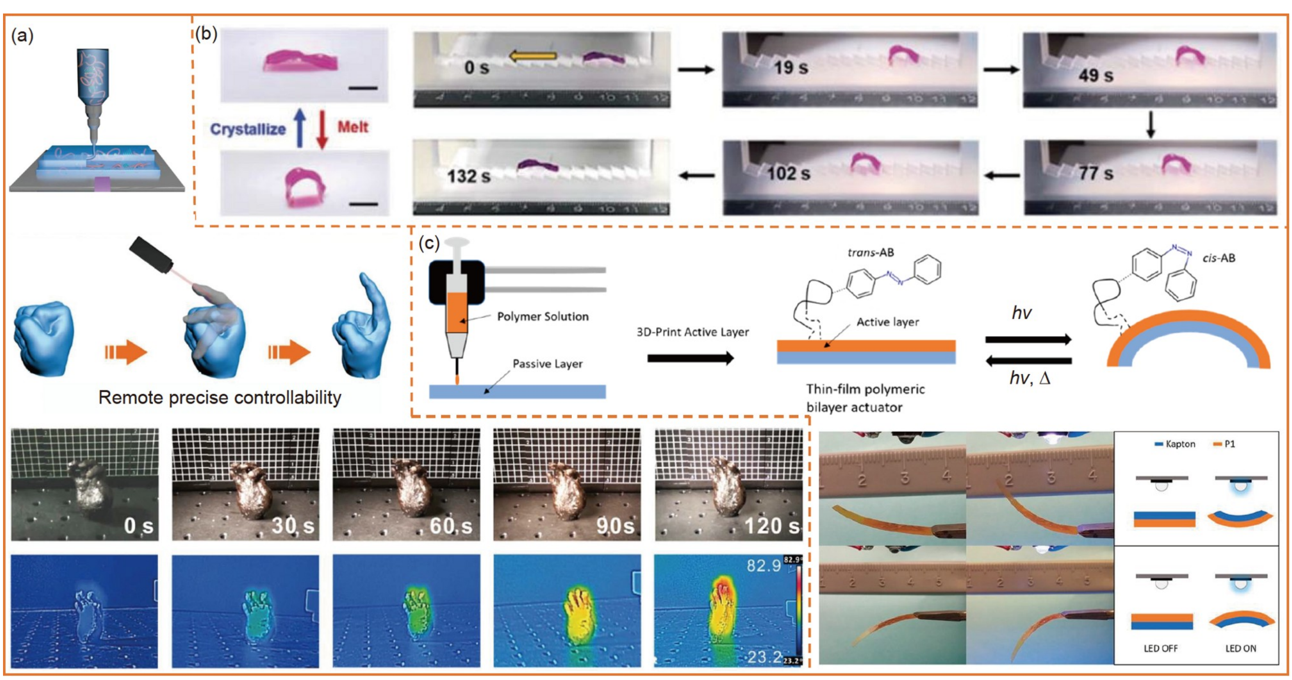

Figure 8 (Color online) 4D printing of light-driven SMPCs. (a) Infrared light repair and drive mechanism [83]. Reproduced with permission of ref. [83]. Copyright©2019, RSC. (b) The light-driven crawling of the soft machine [84]. Reproduced with permission of ref. [84]. Copyright©2021, RSC. (c) *cis-trans* isomer deformation mechanism of azobenzene derivatives [85]. Reproduced with permission of ref. [85]. Copyright©2018, ACS.

of azobenzene. The isomerization induces the original ordered liquid crystal phase to become an ordered isotropic phase considerably, which causes the liquid crystal to shrink in the same direction and realizes the bending of the specimen. Reversible changes between *trans-cis* isomers can be achieved through light irradiation of different wavelengths, and this process can be completed in a few seconds.

4 Application progress of 4D printing SMPs and SMPCs

4.1 Biomedical field

With the development of minimally invasive technologies, the demand for miniaturized medical devices is increasing. These devices can be implanted into tissues through small incisions. The invention of smart microdevices has opened new capabilities for clinical applications. In the field of biomedicine, specifically in minimally invasive areas, reducing the size of implanted devices and minimizing the wound area of patients have been a topic of concern in the medical field [86–88]. The 4D printed SMPs were processed to reduce the volume and transform them into a shape that is convenient for storage. After implantation in the affected area, certain stimulation is applied to the device to restore its shape and exert its therapeutic function. Currently, there are many studies on stents, including vascular, tracheal, bone, and heart stents. With the development of 4D printing technology, stents with complex structures can be quickly printed and tailored to ensure that the structure and size of the stent are fully suitable for the needs of patients. In addition, the materials used to manufacture shape-memory stents must have the characteristics of biocompatibility, appropriate mechanical properties, and appropriate transition temperatures.

Ischemic cerebrovascular disease is generally caused by cerebrovascular stenosis. Cerebral vascular stenosis reduces the amount of blood flowing through the cerebrovascular, resulting in hypoxia of the brain tissue, and finally leading to softening and necrosis. Wei et al. [89] developed and designed an SMP vascular stent. Magnetic Fe_3O_4 nanoparticles were added as functional particles to the PLA solution to prepare a composite ink suitable for DIW printing, and Fe_3O_4/PLA shape-memory nanocomposite vascular stents were successfully printed. The Fe_3O_4/PLA vascular stent can be implanted with minimally invasive surgery, thereby reducing pain in patients. The stent can be deployed in a magnetic field to complete non-contact driving and can also be degraded to avoid various complications. Based on the above characteristics, Fe_3O_4/PLA vascular stents have great application prospects in the field of minimally invasive vascular stents. Chang et al. [90] combined polylactic acid and rotational 3D printing to produce stents. The printed stents were fabricated at different extrusion flow rates, which were compressible and expandable to treat peripheral arterial diseases, as shown in Figure 9.

Tracheobronchial softening is a type of excessive collapse of the airway during breathing that can lead to life-threatening diseases. Morrison et al. [91] used 3D printing technology to create an external airway splint for the treatment of tracheobronchial softening. Medical devices can adapt to the growth of the airway while preventing external pressure within a predetermined time and can be degraded and absorbed by the human body. This treatment provides personalized treatment for patients, and the PCL tracheal stent can be degraded in the human body, avoiding the occurrence of postoperative complications. Zarek et al. [92] established a tracheobronchial model based on the patient's MRI and printed a shape-memory PCL tracheal stent. The permanent shape of the printed tracheal stent is an open structure. Before implantation, the printing stent is set into a temporary shape with a closed structure, and it is stimulated and driven to expand into a permanent shape after implantation in the body. The shape recovery time for the stent to be fully deployed is 14 s. Zhang et al. [93] designed various shape memory polylactic acid tracheal stents with S-shaped hinges of different angles as the basic units. 4D printed shape memory tracheal stent with Fe_3O_4 particles had a magnetic driving effect, which exhibited excellent shape memory performance, reduced volume, and suitable medical temperature, providing a good prospect for tracheal stents.

Atrial septal defect (ASD) is a common congenital heart disease that causes abnormal blood flow from the left atrium to the right atrium, eventually leading to pulmonary hypertension and heart failure. Lin et al. [94] combined SMPLA and 3D printing technology to prepare a

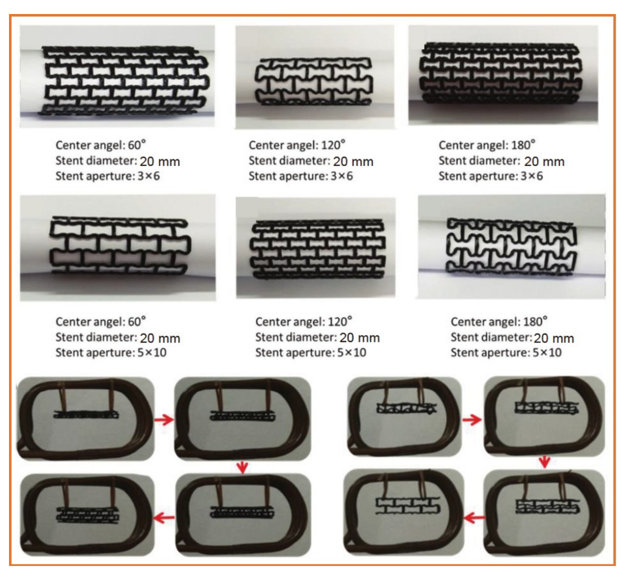

Figure 9 4D printing of SMPs-based vascular stents [90]. Reproduced with permission of ref. [90]. Copyright©2021, Springer.

programmable ASD occluder (Figure 10(a)) that includes a frame-type support structure and choke film. The introduction of magnetic Fe_3O_4 nanoparticles into SMPLA can realize the remote controllable deployment of the structure. The feasibility of stent implantation was analyzed based on three aspects: Tissue inflammation, tissue growth, and scaffold degradation. The feasibility verification shows that the occluder can quickly and completely realize the programming recovery and occlusion process, and it can become a potential replacement device for the metal occluders. Lin et al. [95] also printed left atrial appendage occluder with wavy ligaments to enable the mechanical properties to reduce tissue wear. The scaffold enabled remote-controlled magnetism-induced 4D transformation, as shown in Figure 10(b). This design concept is also applicable to other implants that are conducive to reducing complications, whose application prospects are fantastic.

Human tissue damage and defects can cause dysfunction. Autologous tissue transplantation is the traditional repair method. Although satisfactory results can be achieved, it is performed at the expense of autologous healthy tissue, which can cause many complications and additional damage. Implant repair has attracted considerable attention. Selecting suitable materials and printing biomimetic bone tissue structures have become a hot research topic in bone repair. Zhao et al. [96] and Zhang et al. [97] used FDM printers and shape-memory PLA/Fe_3O_4 composites to successfully print porous scaffolds (Figure 11(a)) and verified their expandability in a magnetic field, which can realize minimally invasive surgical implantation and non-contact deployment, providing a new method for the treatment of bone tissue damage. In addition to magnetic driving, bone tissue scaffolds can also be driven by near-infrared light. Zhang et al. [98] fabricated a compressible scaffold based on a shape memory PU matrix and Mg composite using low-temperature rapid prototyping 3D printing technology. The compressible scaffold was placed at a specific location and driven by near-infrared light, as shown in Figure 11(b), which was proven to support cell survival, proliferation, and osteogenic differentiation. You et al. [99] printed a bilayer membrane with microscale topography, and a light-programmable hydrogel layer achieved macroscopic fitting for geometrically complex bone defects, as shown in Figure 11(c). Topography can promote bone formation through fast cell proliferation and effective osteogenic differentiation to achieve the purpose of treating bone defects.

In tissue engineering, mechanical stimuli (such as strain patterns and perfusion) can be used to regulate cells, which can respond to biophysical cues, affect cell behavior, and regenerate tissue quality [100,101]. However, bioreactors are expensive and have a limited scope and monitoring capabilities. Therefore, SMPs with intrinsic mechanical stimulation are likely to be used as substitutes. Hendrikson et al. [102] constructed a scaffold (Figure 12(a)) based on shape memory PU composites using 4D printing, and stretched and unstretched scaffolds were stained to evaluate the effects of deformation stimulus on cell morphology. The cells were elongated along the fibers of both the stretched and unstretched scaffolds. The results indicated that a single mechanical stimulation was sufficient to cause changes in the morphology of the adherent cells. In addition to biomedical applications, it may also be used as a mechanical stimulation

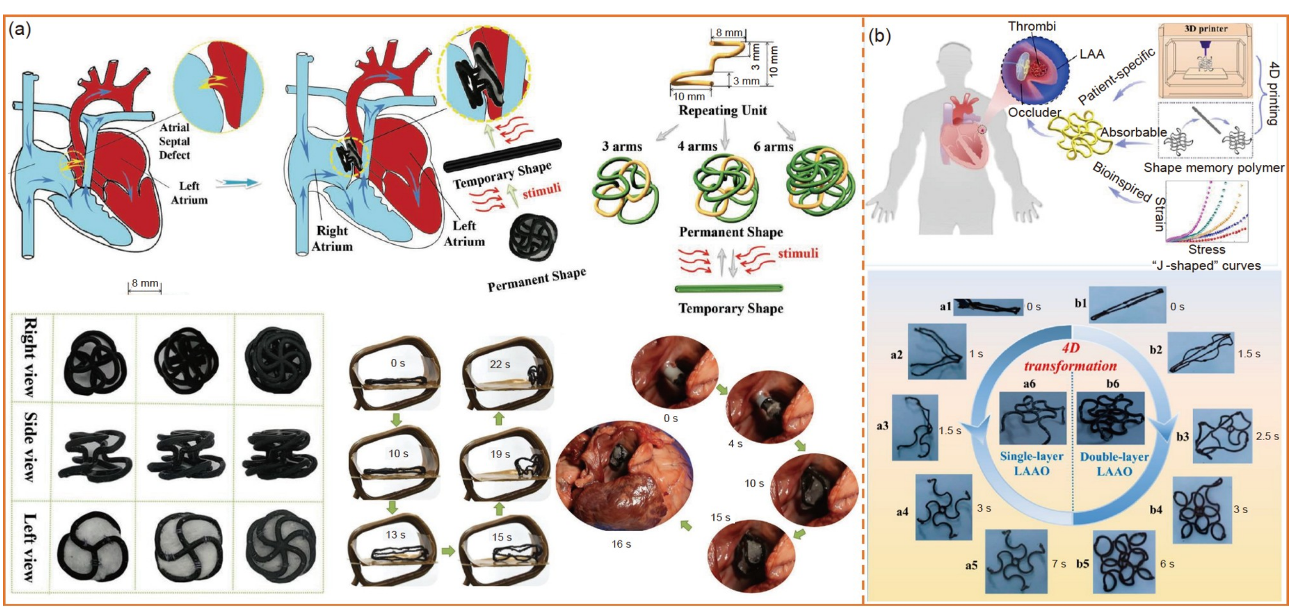

Figure 10 (Color online) (a) 4D-printed occluder frames with 3, 4, and 6 arms and shape recovery process of 4-arm occlude [94]. Reproduced with permission of ref. [94]. Copyright©2019, Wiley. (b) Heat-induced 4D transformation of left atrial appendage occlude [95]. Reproduced with permission of ref. [95]. Copyright©2021, ACS.

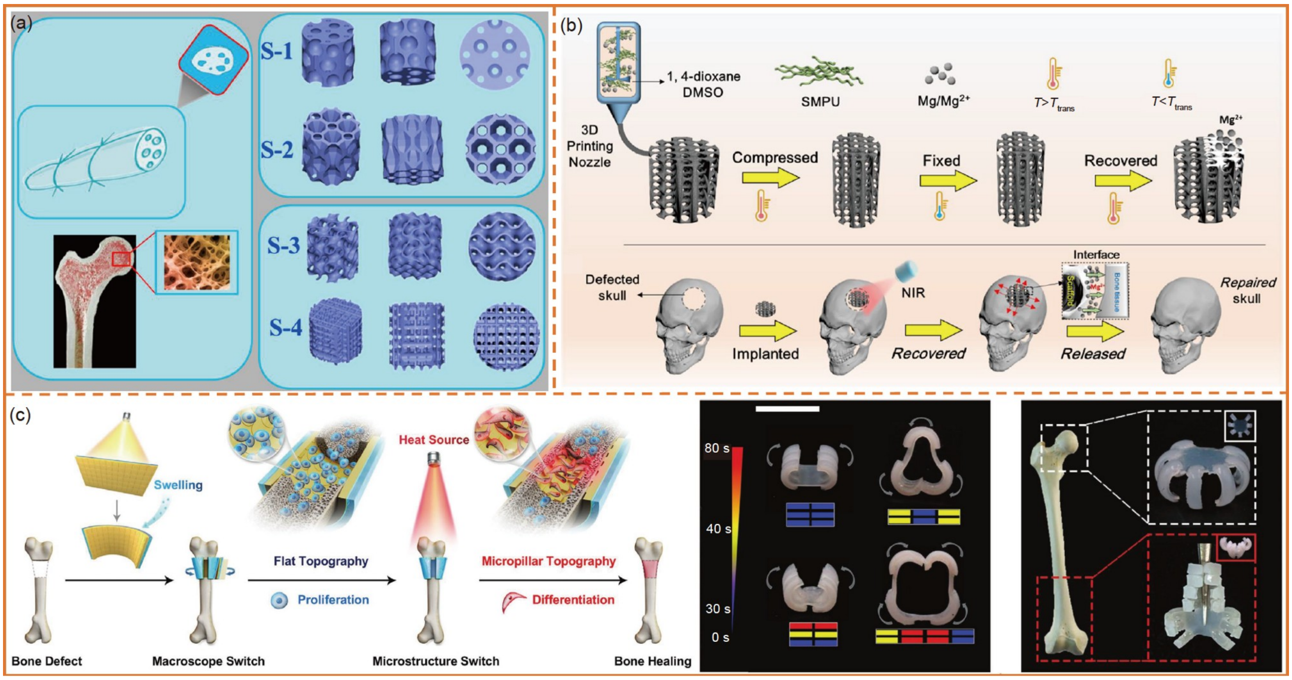

Figure 11 (Color online) 4D printing of imitated bone tissue structure. (a) Design schemes of the porous scaffolds [96]. Reproduced with permission of ref. [96]. Copyright©2021, Elsevier. (b) Schematic illustration of the printed SMPU/Mg scaffold [98]. Reproduced with permission of ref. [98]. Copyright©2022, Elsevier. (c) Schematic demonstration of bone repair and the 4D printed bilayer membrane [99]. Reproduced with permission of ref. [99]. Copyright©2021, Wiley.

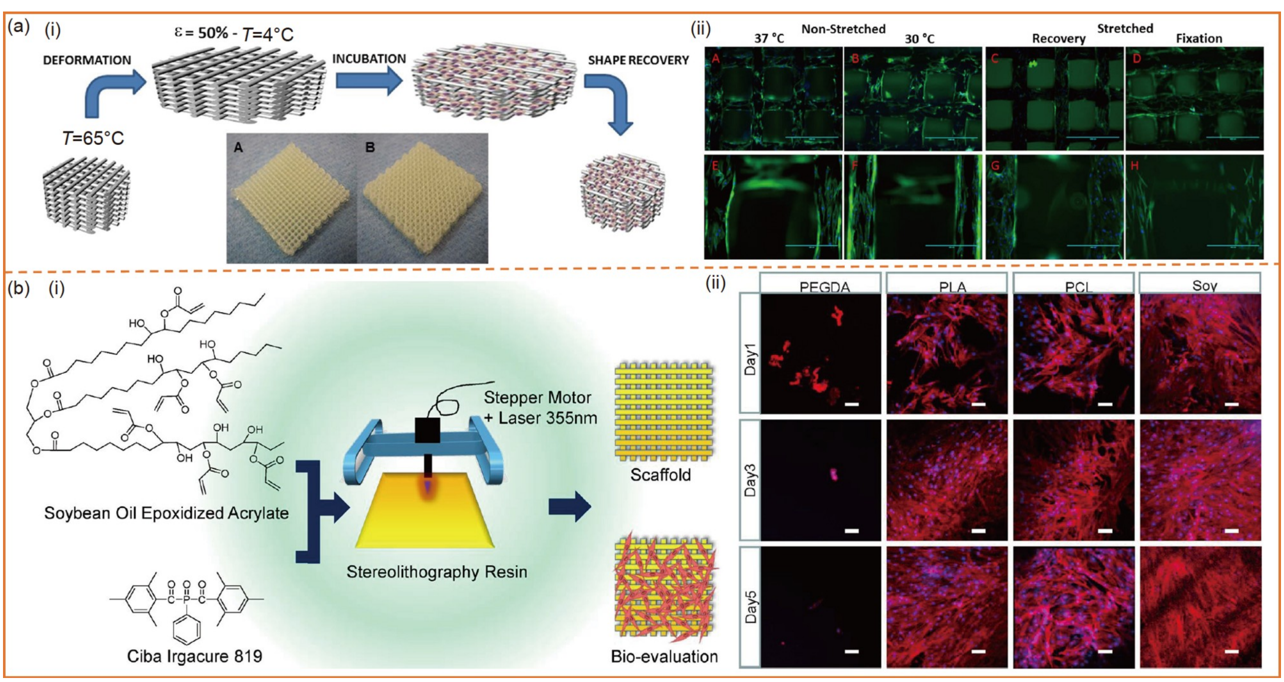

Figure 12 (Color online) 4D printing of cell culture scaffold. (a) Using scaffold deformation to give mechanical stimulation to cells [102]. Reproduced with permission of ref. [102]. Copyright©2017, IOP Publishing. (b) Renewable new biomaterial scaffold [103]. Reproduced with permission of ref. [103]. Copyright©2016, Springer.

bioreactor in tissue engineering applications. Miao et al. [103] constructed a smart, highly biocompatible scaffold based on renewable soybean oil epoxy acrylate using 3D laser printing technology that supports the growth of human bone marrow mesenchymal stem cells, as shown in Figure 12(b). This research will significantly promote the use of renewable resources and is of great significance to the development of renewable vegetable oils and advanced additive manufacturing technologies for biomedical scaffold materials.

4.2 Smart bionic device

Many artificial shape-deformation systems have been inspired by the instinctive movement of plants and animals in response to environmental stimuli. Biomimetic materials are one of the new materials developed in this century and respond to external stimuli by changing their properties and structures in combination with advanced technologies such as information communication, artificial intelligence, and innovative manufacturing to realize the intelligentization, informatization, integration, and functionalization of structures and materials [104–106]. People are increasingly interested in functional materials and their 4D printing technology to meet growing complex functional requirements. Research on 4D printing technology for functional polymers and nanocomposite materials mainly involves sensors, actuators, robotics, electronics, and medical equipment [107–111].

Hairy caterpillar crawling, plant vine winding, butterfly or dragonfly wing waving, and claw grasping are hot topics in the research of bionic smart structures. Zhu et al. [112] blended silicon polymers with magnetic particles to make printable ink and used a printer to print the structure onto a pre-stretched substrate. As shown in Figure 13(a), deformation of the printed structure is achieved by releasing the substrate and applying a magnetic field. The advantage of this magnetically driven biomimetic structure is its rapid response to magnetic stimulation and continuous deformation, which is suitable for specific applications. Wang et al. [113] designed similar magnetically driven composites using Fe_3O_4 magnetic particles. The printing proceeded in a magnetic field so that the magnetic particles were arranged directionally. In Figure 13(b), the printed bug and dragonfly exhibit different deformation structures in the magnetic field in different directions and intensities to achieve controllable deformation. Li et al. [114] designed a sandwich structural soft actuator and fabricated it by combining a magnetic composite layer, MXene film, and polytetrafluoroethylene tape, which is an electrothermal/magnetic coupling actuation. They printed claws, dragonflies, insects, and other biomimetic structures and completed the action imitation using the electrothermal-magnetic coupling effect, as shown in Figure 13(c).

Compared with biomimetic research of single materials, the printing and biomimetics of multi-materials have more research value and practicability. Ge et al. [115] achieved multi-material printing through the automatic exchange of printing inks during printing. Printed multi-material bionic manipulators have different sizes and functions. Recently, the development of soft actuators has attracted considerable attention. Actuators can move, deform, and respond to environmental stimuli. Therefore, soft aquatic organisms are gradually entering the field of vision, specifically octopuses, starfish, and jellyfish. McCracken et al. [116] optimized 10 types of printable gel materials and combined gel materials with 3D printing technology, successfully printing a software driver. The jellyfish-like soft drive was printed using several gel materials, and different parts of the gel or gel composite

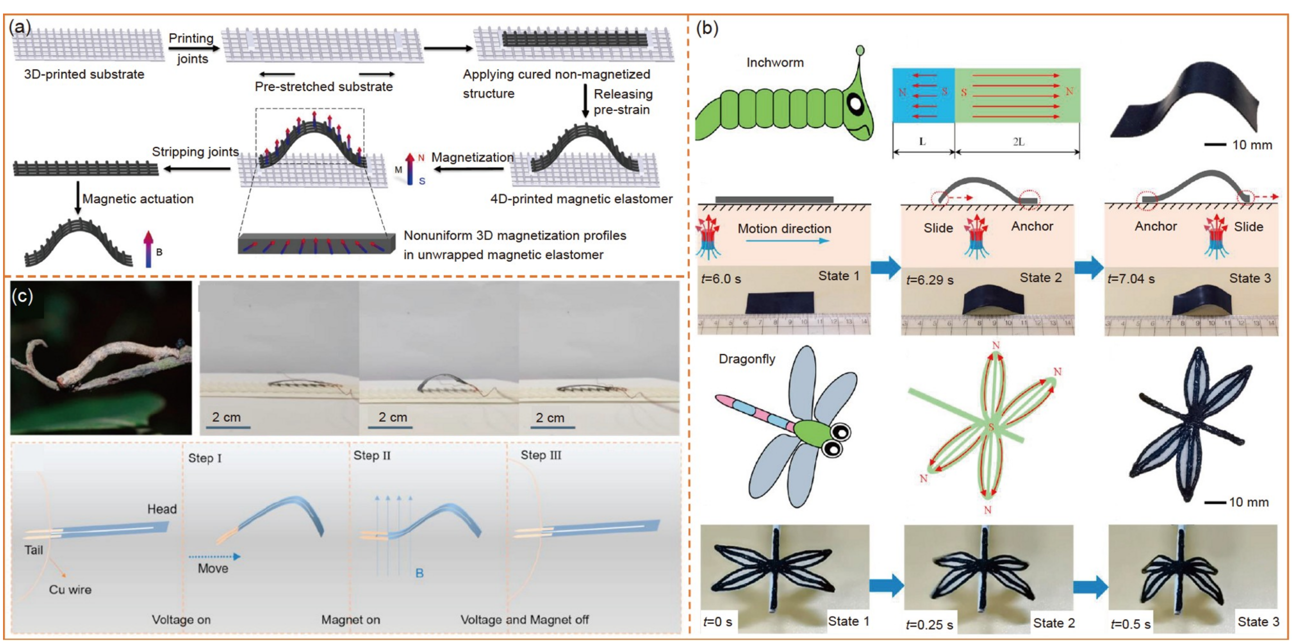

Figure 13 (Color online) 4D printing of smart bionic devices. (a) Magnetization and morphing mechanism of the printed profiles [112]. Reproduced with permission of ref. [112]. Copyright©2022, Springer. (b) Bionic soft robots fabricated by the 4D electrohydrodynamic printing process [113]. Reproduced with permission of ref. [113]. Copyright©2022, Elsevier. (c) U-shaped soft robot crawling [114]. Reproduced with permission of ref. [114]. Copyright©2022, Elsevier.

materials were used to achieve different functions. Currently, researchers have only imitated the appearances and some simple behaviors, and they still need to conduct in-depth and thorough research on complex behaviors, diverse components, and action mechanisms. Research cannot be achieved overnight and needs to rely on smart materials and structures, manufacturing technologies, information, and other fields of common progress and development.

4.3 Electronics

As an emerging advanced fabrication technology, 4D printing has attracted increasing interest in the field of electronics owing to its inherent advantages, including freeform construction and controllable 4D structural prototyping. When combined with conductive materials, printed SMPC-based devices can function as electronic devices, including sensors [117,118], batteries [119,120], and capacitors [121,122].

4D printed devices not only meet the requirements of complex shapes at the macroscopic level, but also meet the various conformational changes caused by external stimuli at the microscopic level. Inspired by sunflowers, Yang et al. [123] prepared a CB-doped shape memory PU composite and printed a light-responsive sunflower through FDM printing, as shown in Figure 14(a). The sunflower gradually unfolded under light irradiation and the entire unfolding process took approximately 280 s. The temperature of the flower increased from 0.4°C to 34.4°C under light irradiation showing that the device has a high light-to-heat conversion efficiency. Zhou et al. [124] printed electrodes on stretchable substrates as shown in Figure 14(b). The stretchable electrodes demonstrated superior mechanical robustness and stretchability without sacrificing outstanding electrochemical performance. All-solid-state stretchable supercapacitors were fabricated by assembling two printed stretchable composite electrodes with gel electrolytes that could be connected to a circuit to illuminate light. Chan et al. [125] deposited a copper coating on a printed spring surface, which rendered the spring conductive. The spring was connected to a circuit to light the lamp. Based on the above principle, a multi-temperature sensing electrical safety device was fabricated, as shown in Figure 14(c). Three circuits connected in parallel turn on at different temperatures to light different-colored lights. These simple printing strategies provide significant opportunities for the design and manufacture of electronic devices.

4.4 Aerospace

The advantage of shape memory materials in the aerospace field is that shape memory devices can be compressed and packaged in the spacecraft, which can effectively reduce the volume, and then be unfolded after being transported to a designated location in space. Compared with shape memory alloys, SMPs have two absolute advantages: Less density and more deformation. Deployable structures based on SMPCs are self-expanding, lightweight, and have a high carrying capacity; therefore, they have great application

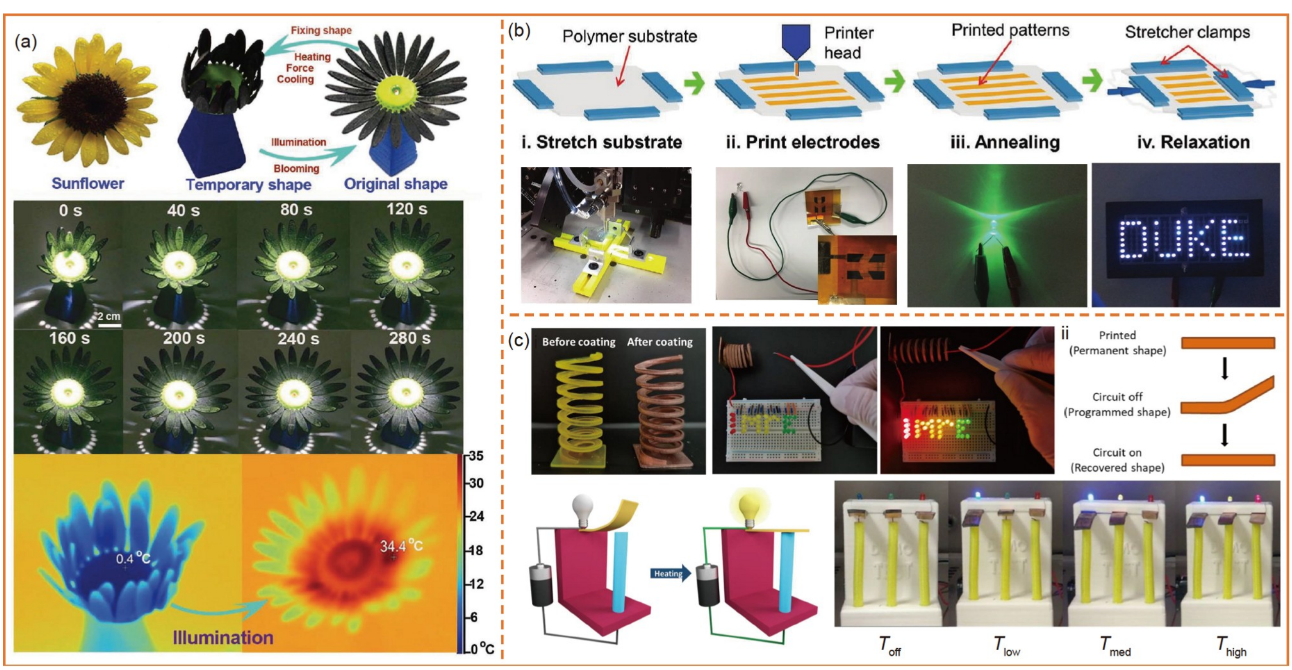

Figure 14 (Color online) 4D printed electron devices. (a) Shape recovery process of the printed sunflower [123]. Reproduced with permission of ref. [123]. Copyright©2017, Wiley. (b) Printed electrodes and assembled stretchable supercapacitors [124]. Reproduced with permission of ref. [124]. Copyright©2020, Wiley. (c) Coated and printed structures as a simple electrical switch and multiple-temperature sensing electrical safety device [125]. Reproduced with permission of ref. [125]. Copyright©2022, Elsevier.

value in the aerospace field. Currently, SMPCs are mainly used in deployable antennas, solar panels, hinges, and other mechanisms [126–132].

The application of 3D printing technology in the aerospace field has significant advantages: It shortens the research and development cycle, improves the utilization rate of materials, reduces costs, optimizes the structure of parts, increases the service life, repairs parts, and reduces losses. Chen et al. [133] were inspired by the opening and closing mechanism of scissors and made a ring-shaped self-folding outer frame by replacing the hub of the scissors with an SMP driver. 3D printing technology was used to transform the SMP material into the origami bottom layer to realize the autonomous deformation of the origami structure in the ring. The ring frame and the origami structure were assembled to form a self-expanding soft solar panel array. The shape memory effect of SMP is used to realize the process from the folded state to the unfolded state. Compared with the folded state, it shows a 10 times area change in the unfolded state, and the entire unfolding process takes approximately 40 s. In this study, although 4D printing technology was not used for the integrated manufacturing of the entire solar panel array structure, it demonstrated the unlimited potential of 4D printing technology in the aerospace field. With an increasing demand for spacecraft performance, 4D printing technology will play an important role in the aerospace field.

5 Conclusions and outlook

Since the concept of 4D printing was proposed, 4D printing has attracted significant interest and attention from researchers. Similar to many other emerging technologies, 4D printing currently has many drawbacks and faces many challenges in the fields of mechanics, materials, and computers. 4D printing technology is not mature; printers can only match a specific smart material and multi-material printing technology is still to be developed. Simultaneously, it also has the disadvantages of low printing precision, low printing efficiency, and low printing structure strength. Most SMPs and SMPCs are slow in response to external stimuli and lack a driving force; therefore, they can only simulate simple deformation movement, resulting in limited function. In addition, most SMPs drives are single-thermal drives. Electrical, magnetic, and light-driven SMPCs can be used to achieve contactless or remote-control drives, but they have high equipment requirements and are only suitable for specific applications.

The future development of 4D printing depends on interdisciplinary research and technological progress in various fields, including 3D printing technology, smart materials, novel designs, and modeling tools. We propose to make technological breakthroughs in three aspects: Developing high-resolution, high-speed, multi-material 3D printing technology to meet the rapid integration processing of multi-scale, high-precision complex structures; developing new multi-functional materials with fast response, stable performance, and printability; developing powerful software and establishing theoretical models and design methods to accurately predict and optimize shape changes. Only when these fields develop and progress simultaneously can 4D printing technology be further developed into a complete and efficient system that can meet various functional applications.

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