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4D Printing: History and Recent Progress

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Abstract 4D printing has attracted great interest since the concept was introduced in 2012. The past 5 years have witnessed rapid advances in both 4D printing processes and materials. Unlike 3D printing, 4D printing allows the printed part to change its shape and function with time in response to change in external conditions such as temperature, light, electricity, and water. In this review, we first overview the history of 4D printing and discuss its definition. We then summarize recent technological advances in 4D printing with focuses on methods, materials, and their intrinsic links. Finally, we discuss potential applications and offer perspectives for this exciting new field.

Keywords 4D printing; Shape memory polymer; Hydrogel; Multi-material structure; Single-material structure

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3D PRINTING STATUS IN QUO

In 1984, Chuck Hull of 3D Systems Corporation filed a patent for a stereolithographic process[1], capturing the world's interest and opening a booming time of 3D printing. However, the official term of 3D printing appeared later, which originally referred to a powder bed adhesive jetting technology developed at MIT[2]. At present, 3D printing is used generally by consumer communities and the media to represent a wide variety of printing technologies including fused deposition modeling (FDM), stereolithography (SLA), selective laser sintering (SLS), selective laser melting (SLM), electron beam melting (EBM), inkjet 3D printing (3DP), direct ink writing (DIW), *etc*[3, 4]. Another term additive manufacturing is used more formally by industrial end-use part producers, machine manufacturers, and global technical standards organizations. Both 3D printing and additive manufacturing reveal that all the printing techniques share the common characteristic of sequential layer-by-layer material addition under computer control. Attracting intense interests from both academia and industry, 3D printing has been developed toward high accuracy, high speed, diverse and robust material properties, and low cost. It has become increasingly clear that meeting these demanding goals requires interdisciplinary collaborations involving mechanical engineering, material science, data processing, and even art designing.

By far, parts produced by 3D printing have been applied mainly in new product development as visual prototypes before mass production, especially for relatively small quantities of parts with complex geometries. Compared to traditional manufacturing processes such as injection molding, several drawbacks should be overcome before 3D printing can become mainstream in producing end-use parts. (1) Speed. The printing speed is relatively low due to the distinctive layer-by-layer process. Although the continuous liquid interface production (CLIP)[5] technology from carbon pushes the vertical printing speed to nearly 10 mm/min, it is still not fast enough for most cases of industrial production. (2) Finishing. Most objects printed by the state-of-art printing techniques require a finishing step, either to mechanically remove or dissolve the internal supports for overhanging features during construction, or to improve the surface smoothness by for instance chemical vapor process, sanding, or polishing. (3) Function. The biggest concern so far is the uncertain quality of the final products (strength, durability, *etc.*), especially along different axes. Fewer than 30% of the printed parts are used for functional industrial end products, mainly printed by the SLS (polycarbonate, nylon 12, polyetherether ketone, *etc.*) and SLM (titanium, stainless steel, various alloys, *etc.*) technologies. Although 3D printing is not fully ready for true mass production of end-use parts, recent attempts have shown promises. In 2014, Local Motors debuted a functioning vehicle that was entirely 3D printed using ABS and carbon fiber except the powertrain[6]. Airbus claimed that its new A350 XWB aircraft included over 1000 components manufactured by 3D printing[7].

While facing challenges and opportunities in many aspects, the lack of high-performance printable materials is a common and perhaps the biggest barrier confronting various 3D printing technologies. Several leading 3D printing corporations such as 3D systems and Stratasys have already established their dedicated materials R&D teams. In the meantime, traditional material suppliers including DSM and Corning have also started launching printable materials (mainly polymers) adaptable to various printing processes.

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There is no question that material development is and will be a primary focus for the foreseeable future.

THE RISE OF 4D PRINTING

The state-of-art commercial printable materials are mainly formulated to be tough, elastic, transparent, colorful, or recyclable, *etc.*, to satisfy various end applications. But there are definitely more that can be done to make the printed parts more useful, especially with the fast development of the active or smart materials. At the 2012 TED conference[8], Tibbits demonstrated how a static printed object transformed over time (Fig. 1). This marked the start of the 4D printing concept, where the fourth dimension is time. Since then, 4D printing has become a new and exciting branch of 3D printing, increasingly gaining substantial attention from scientists and engineers of different disciplines. The essential characteristic of 4D printing is that the printed objects are no longer static. Instead, they can reshape in a pre-programmed and active manner over time, and may be accompanied with function evolvement in the process. Beyond such a somewhat vague description, there is currently no standard definition of 4D printing. Even if there is a strict definition, it is our belief that it will be challenged by future ground-breaking developments. One popular opinion is that the use of active materials compatible with the printers is crucial in 4D printing. Polymers, in particular, are much more diverse in terms of both active shape-changing behaviors and material designability over metals and ceramics. In fact, with the exception of some small efforts in printing shape memory alloys, 4D printing today is almost exclusively related to polymers. For this reason, we focus on active or smart polymers for 4D printing hereafter.

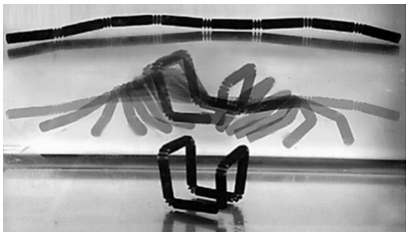


Fig. 1 4D printing example that shows a single strand self-folding into a wireframe (Reproduced with permission from Ref. [9]; Copyright (2014) The Atlantic Council of the United States)

Integration of 3D printing and active polymers, together with the necessary mathematical modeling and sequential stimulation, allows the printed objects to transform between multiple configurations. This sort of geometrically changeable polymers are not new. In fact, active polymers have been extensively investigated before 4D printing came into sight. One of the most popular classes of active polymers is known as shape memory polymers (SMPs)[10–13], for which external stimulation (*e.g.* temperature change) triggers a pre-programmed shape change. Another category is stimuli-responsive hydrogels[14–17], which can undergo a dramatic volume change in response to the external signals such as temperature, pH, or ionic strength. Additionally, dielectric elastomers (DEs)[18] and liquid crystal elastomers (LCEs)[19] are also active materials that have the shape morphing capability upon triggering. To date, SMPs and hydrogels are two main active polymers used in 4D printing. The most important feature that distinguishes SMPs from hydrogels is that the shape shifting pathway for SMPs can be programmed after they are printed, although some hydrogels can also be formulated to possess shape memory functions[11]. Both SMPs and hydrogels can be printed to form a single-material structure and undergo morphing afterwards. However, most of the early studies on 4D printing focused on multi-material structures which can either be a mixture of different active materials or a combination of active materials and non-active materials[9, 20–22]. The multi-material structures printed can achieve more versatile shape changes.

Although 3D printing of active materials seems to be a direct and effective method of 4D printing, Qi's recent research[23] revealed that by introducing a composition distribution through precisely control of the printing parameters, a printed single- and nonactive-material structure can also deform itself over time. Thus, it seems not precise enough to simply define 4D printing as "3D printing + active materials". In fact, any printing techniques that can fabricate dynamic structures with adjustable shapes or functionality can be categorized as 4D printing. Here we will further present a brief review of 4D printing from the materials standpoint. In consistent with the development course of 4D printing, the following article is organized in the order of multi-material structure, single-material structure, and non-active material structure.

MULTI-MATERIAL 4D PRINTING

The term "multi-material structure" here refers to the multiple polymer combination with precise geometric distributions and configurations enabled by 3D printing. Of importance here is that, multi-material printing is by no means an easy job. Currently, the only commercial printers marketed as "multi-material" are ProJet MJP series by 3D systems and PolyJet Connex series by Stratasy[24, 25]. These printers are all ink-jet-type, and would only work with the company's exclusive printing inks, all of which are based on acrylic-based photopolymer resins. Direct ink writing (DIW) is an alternative technique for multi-material printing. DIW was first developed as a method to produce geometrically complex ceramics by extruding a "ceramic ink" from a nozzle[26]. The so-called bioprinting is also based on the DIW technique, using "cell ink". The key of DIW lies in the regulation of the ink's rheological property to guarantee its shape retaining immediately after being extruded out of the nozzle. By applying a multi-nozzle array and different ink materials such as colloidal, polyelectrolytes, hydrogels, and sol-gel oxides, multi-material structures can be printed.

The basic principle of 4D printing with multi-material structures is to create precisely controlled localized internal stress within a printed construct, which upon subsequent stress release can undergo further 3D shape shifting in a predictable manner. The internal stress can be generated through swelling of hydrogels or programming of SMPs with

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precise geometric distribution of different materials realized by 3D printing.

Hydrogel-based Shape Changing

As a pioneering work of 4D printing, Tibbits' group[9, 21, 22] constructed a series of dynamic primitives (linear stretching, ring stretching, and folding) with a rigid plastic base and a soft material that expanded upon exposure to water, using Stratasy Connex 500 printer. The expandable material was cross-linked hydrophilic polymer that formed a hydrogel when exposed to water and in the process experienced a large volume expansion up to 200%. This expansion triggered different deformation modes for the primitives according to the geometry and mechanical design, as shown in Figs. 2(a)–2(c). The stretching length or the folding angle of the primitives could be precisely tuned by varying the distribution of the two materials. In order to achieve complex morphing, the authors further utilized these dynamic primitives as joints and arranged them in different orientations in a main grid. Depending on the design, a planar grid could convert into a sinusoidal wave (Fig. 2d) or a hyperbolic surface (Fig. 2e) and the set of letters premade "MIT" can transform into another predesigned "SAL" (Fig. 2f). One limitation of this material system was that there was only 30% expansion of the linear stretching primitive, putting a limit on the complexity of the shape morphing. In addition, the structures experienced mechanical degradation upon multi-cycling of folding/unfolding (swelling/drying). The fragility of the hydrophilic material after expanding may account for the degradation. These limitations can be overcome by exploring new and more robust materials.

In a similar spirit, Naficy *et al.*[20] printed a hydrogel 3D architecture capable of reversible shape deformation in response to both hydration and temperature change. Two different hydrogel inks were prepared, based on the thermoresponsive poly(*N*-propylacrylamide) (NIPAM) and non-responsive poly(2-hydroxyethyl methacrylate) (HEMA). Polyether-based polyurethane was used as both a rheology modifier and a swelling modifier. UV exposure was combined with the DIW printing to ensure the construction of mechanically robust 3D structures. Bilayer hinges constructed from poly(NIPAM) and poly(HEMA) can morph from a dry flat state to a controllably bended state when fully swollen below 32 °C due to the disproportional swelling of the two hydrogel layers during the hydration process. By raising the temperature up to 60 °C, the swelling ratio of the poly(NIPAM) hydrogel decreased, and a new equilibrium shape was reached (Fig. 3a). These two processes of shape shifting were both reversible. Based on this principle, a more complex cubic box was obtained, exhibiting a reversible folding-unfolding behavior triggered by both hydration and temperature change (Fig. 3b). We note that the underlying principle for the bilayer shape morphing is well known[27, 28], but the adoption of 3D printing here allows more flexibility and freedom in the shapes involved.

SMPs-based Shape Changing

The above-mentioned shape changing behavior was based on the swelling properties of hydrogels. There are a few notable drawbacks that may need to be overcome for practical applications: the response speed was low especially for large objects because the swelling mechanism was intrinsically limited by mass diffusion; the actuated shape was not stable due to the volatility of water; most hydrogels are relatively brittle and may undergo mass loss during the hydration/dehydration cycles. In principle, these limitations can be overcome by incorporating recent advances in hydrogels with 3D printing. For instance, introducing porosity into hydrogels can significantly improve the response speed[29] and innovative molecular designs (*e.g.* double network[30]) can lead to robust mechanical properties. Integration of these approaches with various printing processes, however, is not straightforward.

An alternative active material to fabricate morphing structures is SMP, which is more robust and provides a wider range of mechanical properties. The essential programmability of the shape shifting pathways distinguishes SMPs from hydrogels[11]. During the programming process, a temporary shape as defined by an external deformation force can be fixed and the shape shifting (*i.e.* recovery) pathway goes from this temporary shape to the synthesized or fabricated original shape. Since the same original shape can be fixed into unlimited

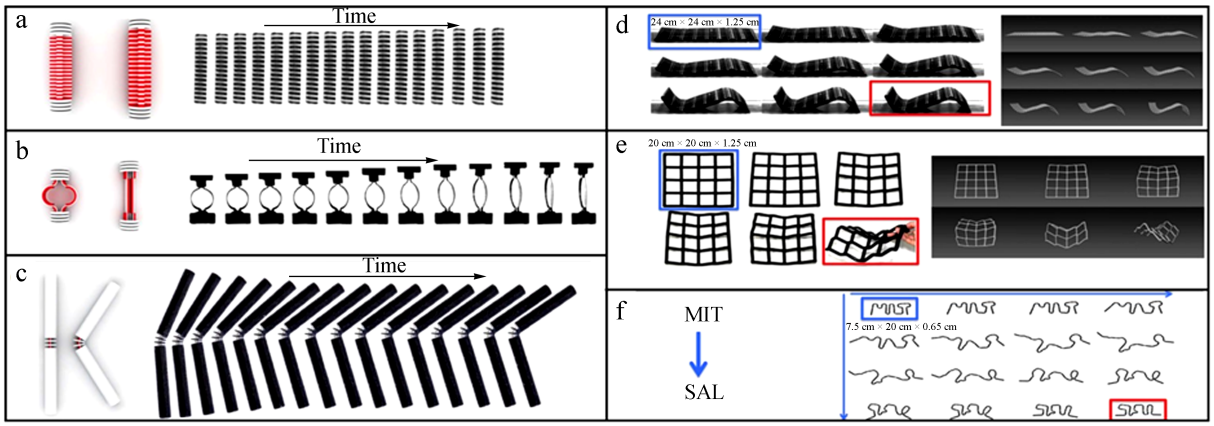


Fig. 2 (a–c) Left: rendered illustration of the linear stretching, ring stretching and folding primitive; Right: video frames of the fabricated primitive evolving in water over time; (d) Morphing of a grid into a sinusoidal wave; (e) Morphing of a grid into a hyperbolic surface; (f) Shape evolution with time from the letters "MIT" into "SAL" (Reproduced with permission from Ref. [21]; Copyright (2014) Nature Publishing Group)

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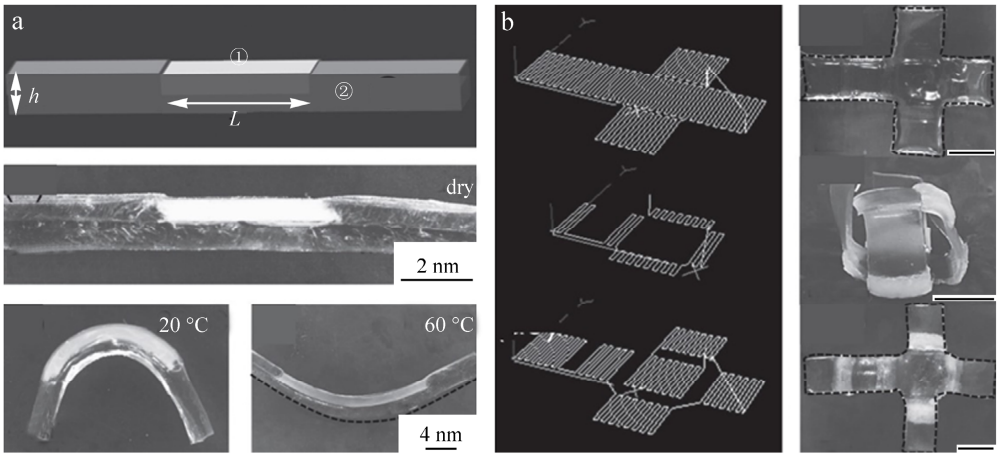


Fig. 3 (a) Schematic representation of a hydrogel hinge, made of the poly(NIPAM)-based top layer (1) and the poly(HEMA)-based PEO_{10}-PU bottom layer (2); (b) Demonstration of the printing path on the left and the shape changing behavior of a cubic box on the right (The scale bars are 1 cm.) (Reproduced with permission from Ref. [20]; Copyright (2016) John Wiley and Sons)

number of temporary shapes by variation of the external deformation force, the corresponding shape shifting pathway is also unlimited. As for hydrogels, their shape shifting is typically non-programmable, that is, they can only morph between two geometric shapes defined in the fabrication step, no matter how sophisticated they might be. The distinction between SMP and responsive hydrogels is reflected in the examples provided below.

An early example of SMP based 4D printing is the concept of printed active composites (PACs) introduced by Ge *et al.*[31], involving fabrication using a multi-material 3D printer (Object Connex 260, Stratasy). The PACs consisted of glassy polymer fibers embedded in an elastomeric matrix. The glassy polymer fibers exhibited a shape memory effect with a shape fixity ratio (R_f) around 80% whereas the elastomeric matrix was not capable of shape fixing ($R_f = 0$). Typically, a bilayer laminate comprising a pure elastomer lamina and a PAC lamina with a prescribed fiber architecture (shape, size, and orientation) was printed, heated, stretched, cooled, and released. Upon release of the deformation stress, the laminate turned into a complex temporary shape due to the R_f mismatch between the elastomer lamina and the shape memorizing PAC lamina (Fig. 4a). Depending on the fiber architecture, various complex 3D configurations can be

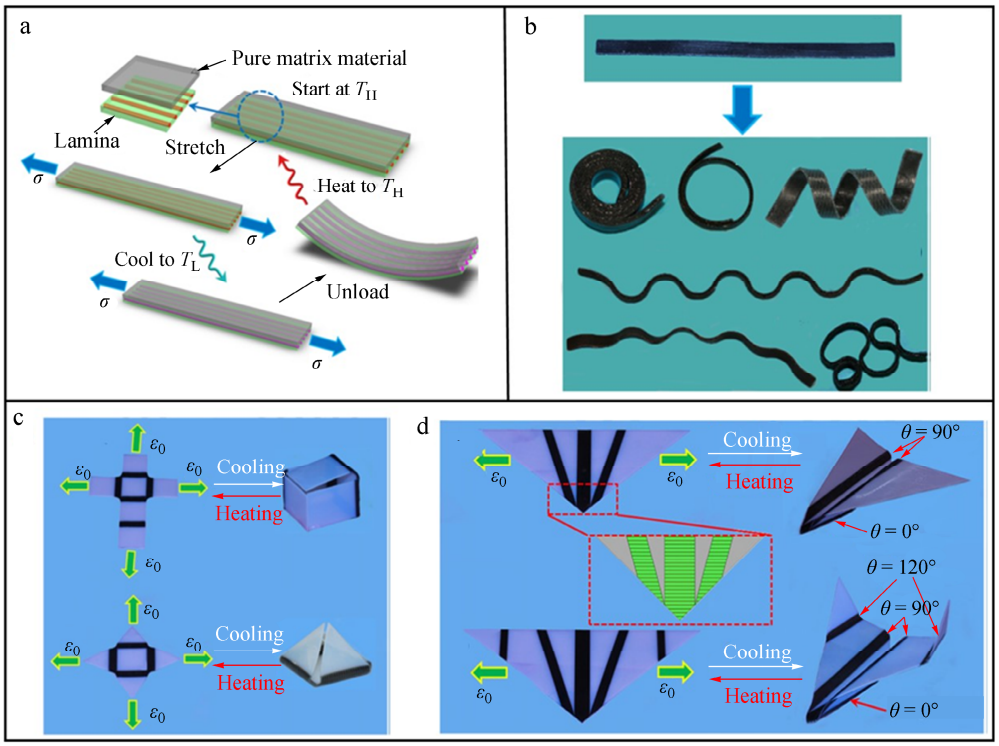


Fig. 4 (a) Schematic demonstration of the laminate architecture and the programming process and (b) representative images for folding with different fiber architectures (Reproduced with permission from Ref. [31]; Copyright (2013) AIP Publishing LLC); (c, d) Active origami structures of a box, a pyramid and an airplane (Reproduced with permission from Ref. [32]; Copyright (2014) IOP Publishing)

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assumed including bent, coiled, twisted, and folded shapes (Fig. 4b). Furthermore, the PAC laminate can be integrated with other structures or functional components to create active devices. For instance, the PAC laminate could be used as hinges to enable active origami as a means to creating 3D structures. Alongside the experimental effort, a theoretical model was also developed to describe the behavior of the printed active hinges and to provide guidance in selecting design parameters such as fiber dimensions, hinge length, and programming strains and temperature[32]. Using the model, several active origami structures were fabricated that assembled and folded from flat polymer sheets, including a box, a pyramid, and origami airplanes (Figs. 4c and 4d).

In the case of origami with complex self-folding patterns, the folding sequence of the individual parts can play an important role in the final configuration. One potential solution to the sequence controlled folding was the use of complicated localized heating systems to provide a spatially nonuniform temperature profile to actuate the active hinges[33, 34]. In contrast, Mao *et al.*[35] demonstrated an alternative and much simpler method by printing active hinges with differing shape memory behaviors. The different time-dependent behavior of the individual hinges allowed sequential activation when the structure was exposed to a uniform temperature. The materials exploited to form the hinges were the so-called digital SMPs, referring to mixing of two base materials (a rigid plastic VeroWhite and a rubbery TangoBlack, compatible with the multi-material 3D printer Objet Connex 260) at specific ratios on a digital voxelized domain to achieve prescribed shape memory behaviors (*e.g.* glass transition temperature T_g). At the same recovery temperature, programmed hinges fabricated with higher T_g materials needed longer time to recover to their folding states, leading to sequential folding (Fig. 5).

Typical 4D printing with SMPs involves a series of thermomechanical programming steps including heating, mechanical loading, cooling, removal of load, and reheating. Specific jigs and fixtures are often needed to apply mechanical loads in such a process. Ding *et al.*[36] recently reported a direct SMP-based 4D printing process, where the programming steps were integrated into the printing step. The printed component could directly changed its shape upon heating, forgoing an extra postprocess of thermomechanical programming. Specifically, a laminated strip was printed with two materials—an SMP and an elastomer. The as-printed elastomer layer contained a compressive biaxial strain, which can be controlled by the material composition and printing parameters including curing light intensity and photocuring time. Because of the strong bonding of the elastomer to the SMP, the compressive strain was built into the flat laminate and locked by the SMP. After the printing, the temperature was raised above the T_g of the SMP, and the built-in compressive strain was released, which triggered the laminate to deploy into a permanent bending shape (Fig. 6a). Based on

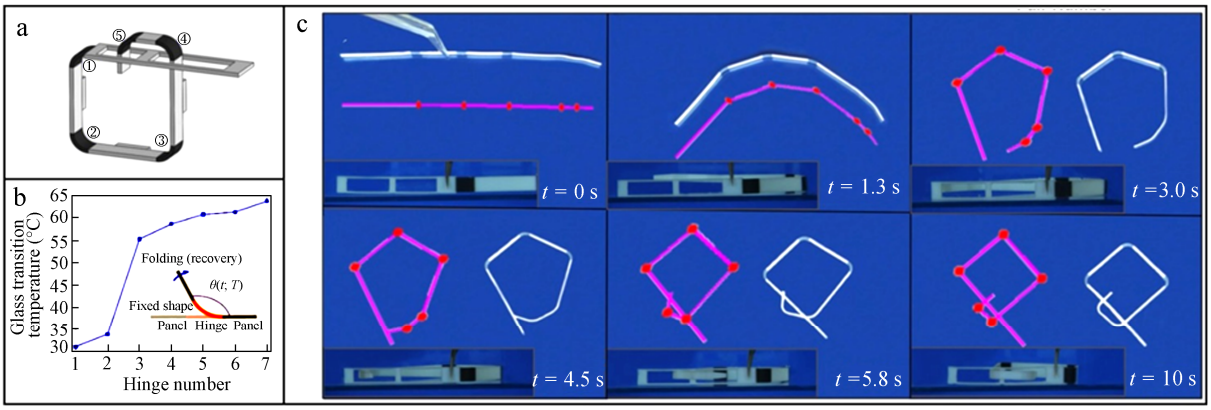


Fig. 5 Sequential self-folding structures: (a) the schematic diagram of an interlocking SMP component; (b) T_gs of the digital SMPs used for hinge materials (the inset shows a schematic view of the folding of an SMP hinge.); (c) the comparison of experiments (plane and side views) and the simulations (red lines) for the time-dependent folding (Reproduced with permission from Ref. [35]; Copyright (2015) Nature Publishing Group)

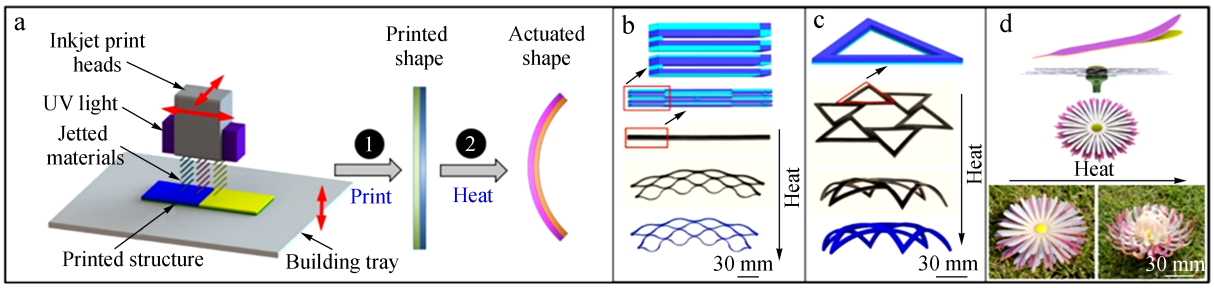


Fig. 6 Direct 4D printing with build-in internal stress: (a) printing process; (b–d) diverse structures that were printed in a collapsed configuration and deployed upon heating (Reproduced with permission from Ref. [36]; Copyright (2017) American Association for the Advancement of Science)

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this principle, a variety of complex 3D shapes could be obtained including a helix, 3D dome, and flower consisting of multiple petals with different curvatures (Figs. 6b–6d).

The printable SMPs and the corresponding components shown above all demonstrated a one-way (or irreversible) actuation. It is highly desirable to achieve reversible actuation, that is, reversible switching between two 3D complexed shapes. Hydrogels exhibited a reversible volume change in response to the environment. However, they are typically very soft. Mao *et al.*[37] integrated SMPs and hydrogels into a 3D architecture to create components that can reversibly switch between two stiff configurations. The swelling of the hydrogels provided the driving force of the shape changing, whereas the temperature-triggered modulus change of the SMPs regulated the time of such shape changing, that is, the shape changing induced by hydrogels was locked by the stiff SMP below its the transition temperature. The concept was demonstrated in a trilayer strip with a reversible bending actuation behavior (Fig. 7a). More complex architectures including a periodic macro-structure and a lotus flower are also demonstrated in Figs. 7(b) and 7(c). The limitation of this material design was the slow actuation speed, requiring ~10–20 h for a full actuation cycle. The speed can in principle be improved by adjusting the hydrogel formulation, which is difficult in reality because customized hydrogel inks may not be compatible with the multi-material printer.

As discussed above, most 4D printed multi-material structures were produced by an inkjet-type printer. The drawback of the inkjet based 4D printing lies in the fact that the users do not have the flexibility to freely tune the thermomechanical properties beyond what is possible with the available commercial resins. This severely constrains its potential for a wide range of applications. For instance, the actuation strain capability of the printed parts is limited by the printable materials with maximum strain around 10%–25%; the printed structures cannot be used in high temperature applications as the highest glass transition temperature of the available resin is about ~70 °C.

SINGLE-MATERIAL 4D PRINTING

An alternative approach for 4D printing is to directly print active materials such as SMPs and stimuli-responsive hydrogels. However, almost all of the early work was based on the multi-material structures and the focus was mainly on designing various mechanical structures. This is in a large part because early work was mostly conducted by scientists and engineers with background in architecture, design computation or mechanics and they naturally have more expertise on structural design and mechanical simulation using existing materials from 3D printing suppliers. More recently, 4D printing started to attract significant attention from material scientists. In particular, from the perspective of those in the field of active materials, 3D printing is an exciting technique to endow the smart materials with nearly unlimited geometries. This is in sharp contrast to the simple geometries of active devices (*e.g.* ribbons, filaments, and cylinders) accessible by traditional processing techniques such as casting or extrusion.

Photopolymerization-based Printing

We note that parts printed by SLA and DLP (digital light processing) using commercial photocurable resins are typically thermoset in nature and therefore intrinsically possess a shape memory effect. For commercial applications, however, their shape memory transition temperatures are usually irrelevant and their maximum recoverable strains are typically too low. Therefore, photocurable resins should be specifically formulated as a candidate SMP precursor. The first attempt to purposely print a photocured SMP structure was made by Cohn and co-workers in late 2015[38]. The researchers fabricated complex shape memory structures with a viscous polycaprolactone dimethacrylates (PCLDA) melt using a commercial SLA printer (Picoplus39, Asiga) and a customized heated resin bath (Fig. 8a). Various complex geometries, *i.e.*, a cardiovascular stent, an Eiffel Tower and a bird with a considerable resolution were printed, which are otherwise difficult to obtain by traditional methods. PCLDA,

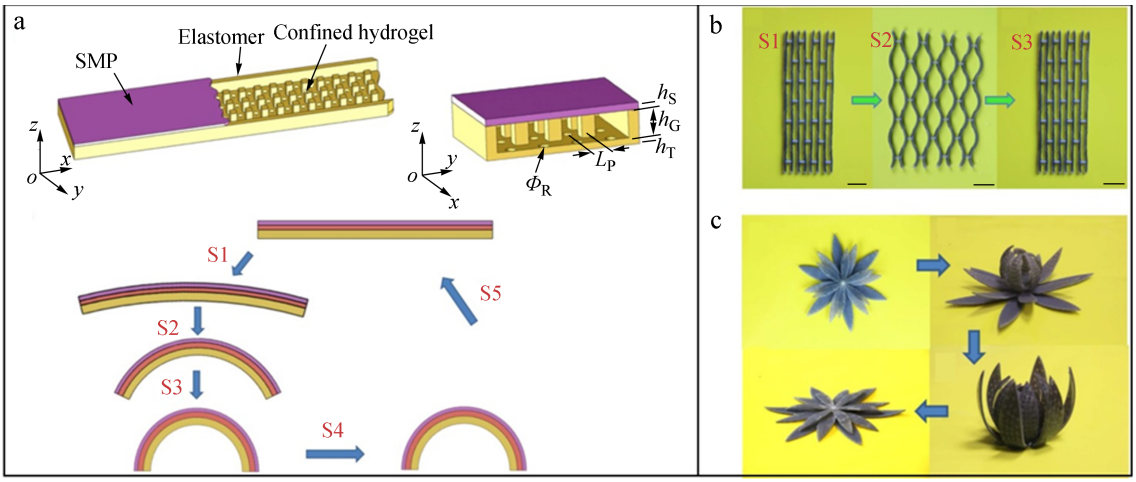


Fig. 7 (a) Schematic demonstration of a reversible actuation device in which a hydrogel is confined by an SMP and elastomer layers; (b, c) The self-folding/unfolding periodic macro-structure and lotus flower (The scale bars are 15 mm.) (Reproduced with permission from Ref. [37]; Copyright (2016) Nature Publishing Group)

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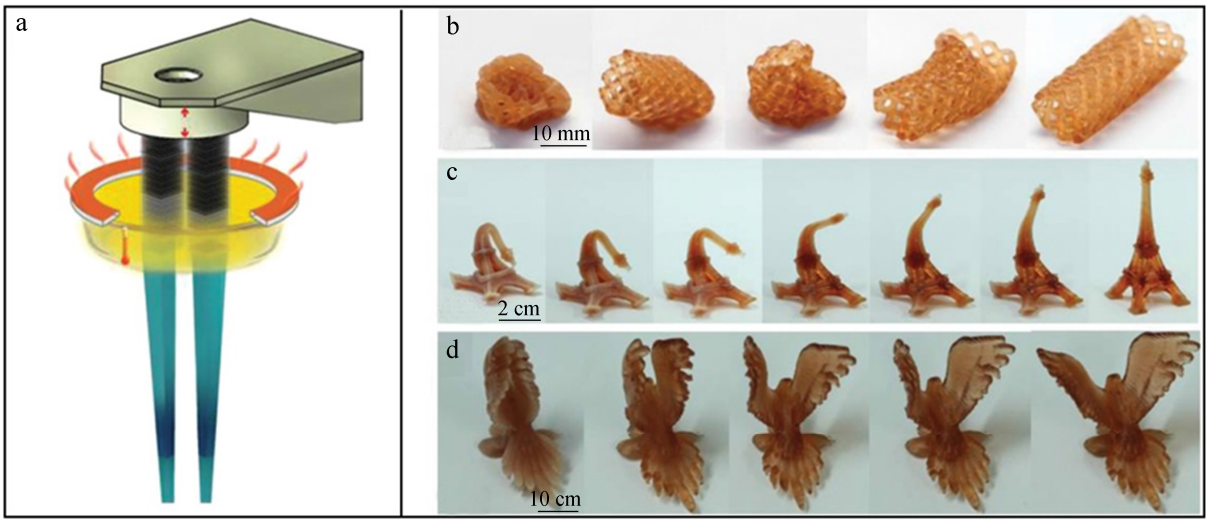


Fig. 8 3D printing of shape memory polymers: (a) an SLA 3D printer with a customized heated resin bath; (b–d) demonstration of the temporary shapes recovering to their permanent 3D shapes (from left to right) including a cardiovascular stent, an Eiffel Tower, and a bird (Reproduced with permission from Ref. [38]; Copyright (2015) John Wiley and Sons)

a well-studied SMP monomer, offered excellent shape memory behaviors (Figs. 8b–8d). A printed part was further integrated with electronics[38], medical devices[39], jewellery and fashionwear[40], revealing its potential applications for smart electronics, minimal invasive surgery, and personalized products. More recently, a variety of customerized photocurable resins including soybean oil epoxidized acrylate, *tert*-butyl acrylate-*co*-di(ethylene glycol) diacrylate, and epoxy-acrylate hybrid were also utilized to fabricate 3D shape memory structures using the SLA printing technique[41].

The aforementioned 3D printed shape memory components can only switch between a permeant shape and one temporary shape, which is a typical dual-shape memory effect. A research focus of SMPs is to design materials to enable additional temporary shape fixing in a so-called multi-shape memory cycle[11]. The multi-shape memory effect can be conveniently achieved by properly designing the programming process for polymers with a broad range of transition temperature (T_g, or T_m[10]). Utilizing this principle, Yu *et al.*[42] selected the Gray 60 resin from the material library of the Objet Connex 260 printer to fabricate SMP components. The Gray 60 resin has a glass transition from ~40 °C to ~80 °C, providing a sufficiently broad temperature range to set multiple temporary shapes. The triple-shape memory performance was first quantified with a printed SMP strip under both uniaxial stretching and bending conditions (Fig. 9). More complex architectures such as a truss structure were then printed, in which SMP hinges were introduced to enable local rotation. The shape changing sequence of the printed architecture followed a typical triple-shape memory

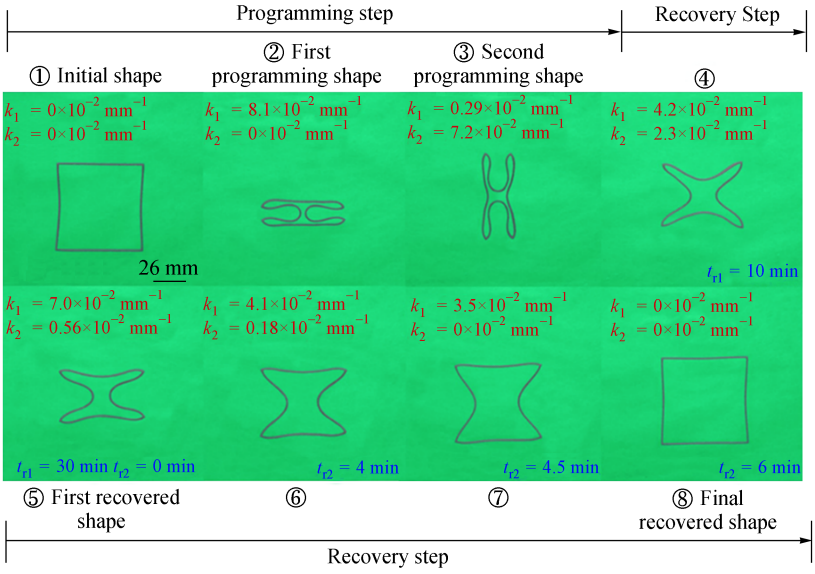


Fig. 9 Multi-shape memory effect of 3D printed shape changing architecture (Reproduced with permission from Ref. [42]; Copyrigtht (2015) Elsevier)

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cycle with two distinct recovered shapes. Compared with the authors' previous work[35] where multiple SMPs with different T_gs were utilized, the use of a printed triple-shape polymer offered an easier route to achieve a programmed sequential shape changing with only one SMP.

The above examples employed well-known 3D printing techniques based on photocuring such as SLA and DLP to print active morphing polymers. From the standpoint of the printing process, they are all based on the classical layer-by-layer process. While providing versatility in printed part geometries, such a process is intrinsically time-consuming, which is one of the major drawbacks of 3D printing. A new approach that can overcome such a limitation is our group's recent effort in ultrafast digital 4D printing. Omitting the time-consuming layer-by-layer buildup in the z dimension, we printed a 2D flat sheet of a crosslinked hydrophilic poly(HEMA) by brief light exposure using only a commercial projector and a glass mold[43] (Fig. 10a), that is, without any other accessories typically associated with 3D printing. Digital control of the light exposure time at each pixel level within the 2D film enabled the fabrication of a pixelated polymer network with spatially variable degrees of monomer conversion and cross-linking density (Fig. 10b). Upon subsequent immersion in water, an internal stress was created due to the swelling contrast between the pixels, turning the flat sheet into a prescribed 3D architecture (Fig. 10c). The geometry parameters of the 3D structures can be precisely tuned by the exposure layout (Fig. 10d). Depending on the light pattern, a variety of 3D shapes can be obtained (Fig. 10e). By proper choice of the UV monomer system, various stimuli-responsiveness can be conveniently designed into the printed 3D hydrogel structure. Figure 10(f) shows that a printed 3D shape can further morph into a drastically different 3D shape when the ionic strength is changed. In principle, the hydrogel can be designed to possess multi-stimuli-responsiveness, leading to multiple shapes (> 3) with one single printing. Another advantage of this printing approach lies in its simplicity. Since there is no mechanical moving involved, the typical viscosity requirement for photocurable resins could be disregarded. This allowed the concept to be readily expanded to a variety of active material systems such as SMPs. Overall, this ultrafast printing process utilizes digitally controlled photocuring to encode heterogeneity into a 2D sheet, which is then developed into a 3D object outside the printing process. The printing process itself is typically accomplished within one minute.

Extrusion-based Printing

Compared with typical photopolymerization-based SLA printing, extrusion-based FDM shows many advantages including cost-effectiveness, simple setup, and relatively high printing speed. The parts are produced by extruding small strings of a molten thermoplastic polymer to form layers as the material hardens immediately after being extruded from the nozzle. Direct ink writing (DIW) is quite similar to FDM. However, DIW is compatible with a wider range of materials. Besides thermoplastics, colloidal, polyelectrolytes, hydrogels, and sol-gel oxides can also be formulated into inks for DIW. The key to DIW lies in the regulation of the ink's rheological property to guarantee its shape retention within a short timeframe after the ink left the nozzle. Despite the difference, both FDM and DIW have been utilized to print active morphing materials in a very much similar fashion in terms of the printing process.

Yang *et al.*[44] exploited thermoplastic shape memory polyurethane and a FDM printer to fabricate 3D structures (Fig. 11a). Carbon black was introduced into the resin as a filler, yielding 3D morphing structures that can be triggered by the photo-thermal mechanism (Figs. 11b and 11c).

With regard to shape fixity and shape recovery, most thermoplastic SMPs have relatively poor performance over their thermoset counterparts, which limit their application potential. On the flip side, traditional thermoset SMPs are chemically cross-linked and not melt-processable once the crosslinks are established in the polymer network. Thus, printing thermoset SMP using an extrusion process is not typically feasible. Facing this dilemma, Yang *et al.*[45] presented a series of Diels-Alder reversible thermoset resins, which possessed thermoset properties at use temperatures while capable of melting at the printing temperature (Fig. 12a). Specifically, the dynamic furan-maleimide Diels-Alder links in the network can be de-crosslinked during

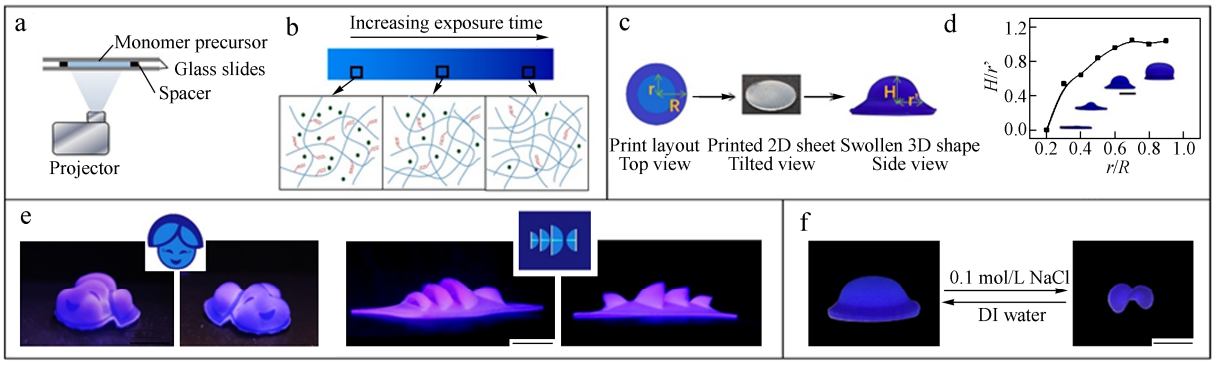


Fig. 10 Digitally defined transformation: (a) printing setup; (b) spatio-chemical heterogeneity resulted from digital controlled light exposure; (c) illustration of a planar sheet with patterned concentric circles swollen into a cap-shape 3D structure; (d) control of geometry by the printing 2D layout; (e) demonstration of printing versatility: a cartoon face, a multi-scale buckled structure, and a theater; (f) printed 3D object changing its shape under certain stimulation (The scale bars are 1 cm.) (Reproduced with permission from Ref. [43]; Copyright (2016) John Wiley and Sons)

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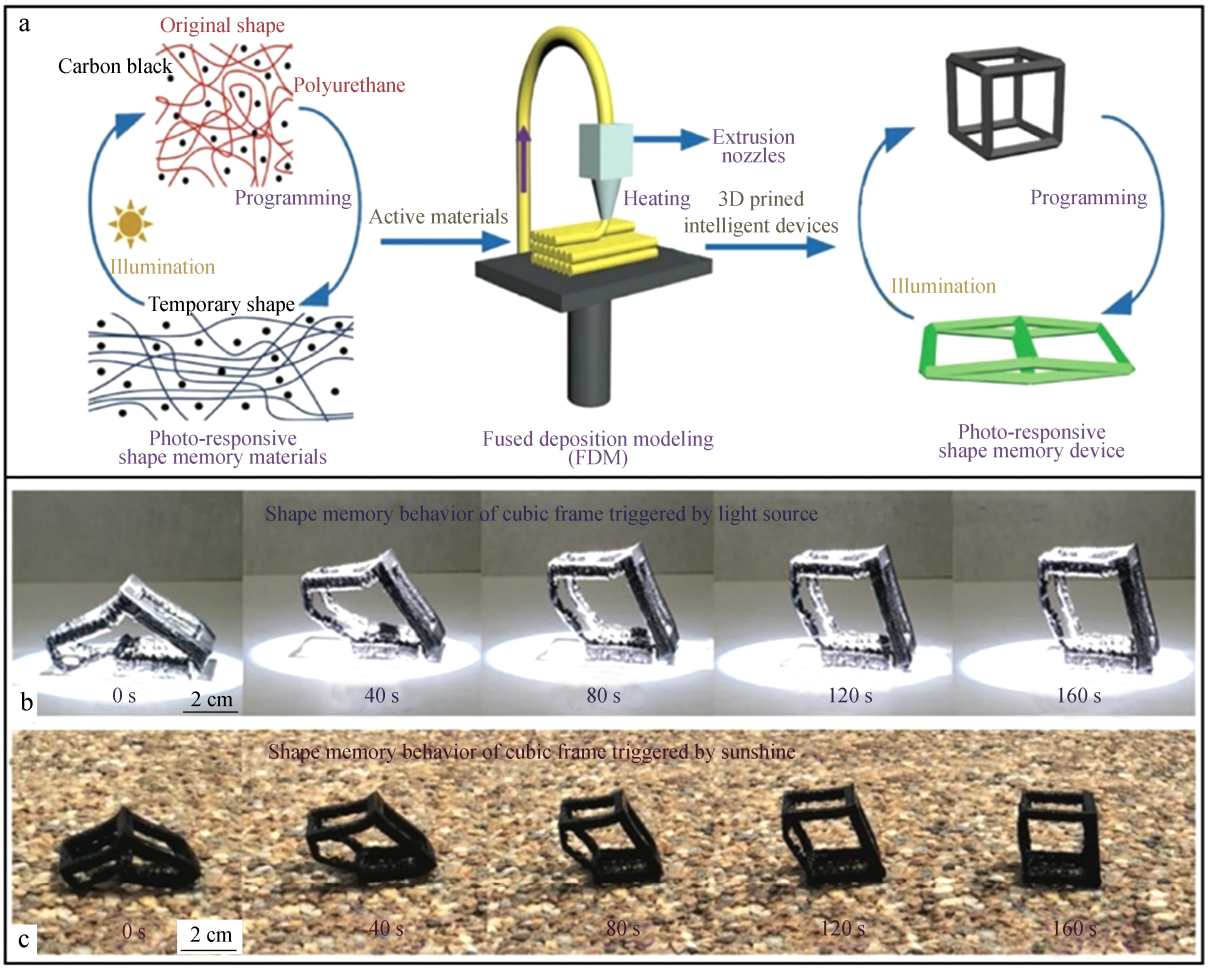


Fig. 11 (a) Photoresponsive materials based on carbon black and polyurethane extruded from a FDM printer to form a 3D object with photoresponsive shape memory effect; The shape recovery of cubic frame under (b) 87 mW/cm^2 of light source and (c) 76 mW/cm^2 of sunshine (Reproduced with permission from Ref. [44]; Copyright (2017) John Wiley and Sons)

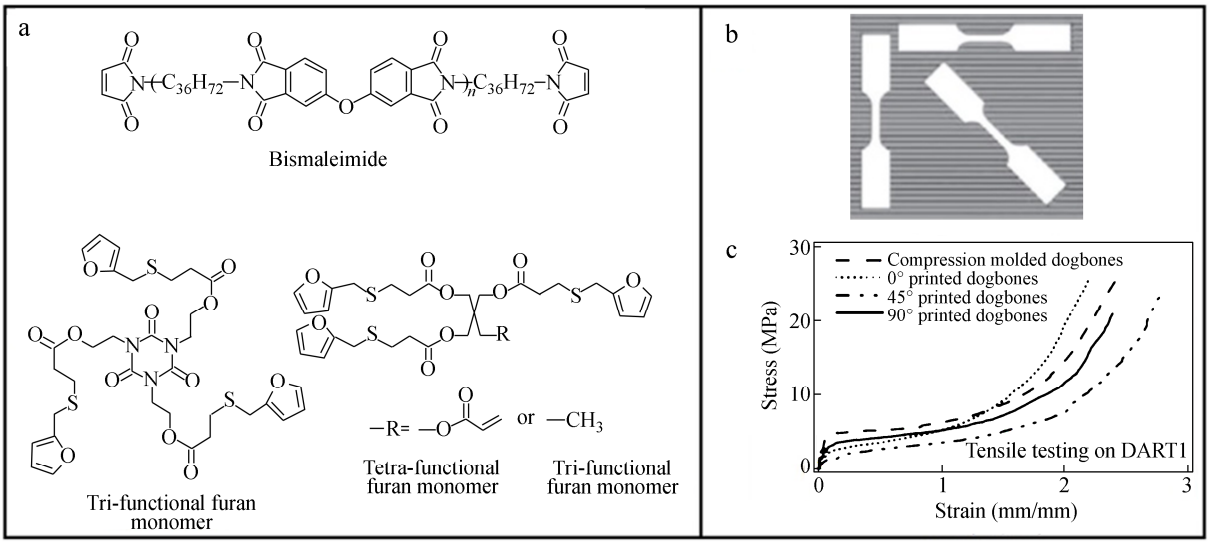


Fig. 12 Diels-Alder reversible thermoset 3D printing: (a) chemical structures of monomers; (b) dogbones punched out of the printed sheet in three directions: perpendicular to the print direction (0° or *X*-axis), askew (45°), or parallel to the build direction (90° or *Z*-axis); (c) stress-strain curves of molded and printed dogbones (Reproduced with permission from Ref. [45]; Copyright (2017) John Wiley and Sons)

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printing between 90 and 150 °C and re-crosslinked after being deposited onto the platform at lower temperatures. Particularly noteworthy for this material system was its excellent interlayer adhesion and very low anisotropy (Figs. 12b and 12c), two performance categories that typical FDM produced thermoplastic parts often fall short. These desirable features were possible since all the printed layers were fused into each other after deposition owing to the dynamic Diels-Alder chemistry. On the negative side, the glass transition temperatures of the printed samples were around 20 °C, which restricted their application as SMPs. However, by further tuning the chemical structures of the monomer system, T_g, Young's modulus, and other mechanical properties can in principle be easily tailored.

Alternatively, Wei *et al.*[46] exploited a UV cross-linkable ink containing poly(lactic acid), dichloromethane, and benzophenone, which was compatible with a typical DIW setup. Once the ink was extruded out of the nozzle, the evaporation of dichloromethane was fast so that the ink underwent a rapid liquid-solid transition to fix the printed structures. UV LEDs were utilized to further trigger the cross-linking reaction between the poly(lactic acid) chains to guarantee a good shape memory behavior (Fig. 13a). In addition, Fe_3O_4 particles were further introduced to achieve a remote actuation characteristic *via* an induction heating mechanism. Utilizing such a material system, a spiral scaffold was printed and programmed to show a self-expanding behavior, which might be useful for further development of user-defined intravascular stents (Figs. 13b and 13c).

Besides SMPs, various hydrogels can also be printed utilizing the DIW printing and subsequent UV curing. Gladman *et al.*[47] developed a viscoelastic hydrogel composite ink which was composed of stiff cellulose fibrils embedded in a soft acrylamide matrix. During the printing process, the fibrils underwent shear-induced alignment as the ink flowed through the nozzle, leading to an anisotropic swelling behavior along different directions of the printed architecture (Fig. 14a). The as-printed architectures were thus encoded with localized swelling anisotropy that can induce complex shape deformations upon immersion in water. A series of simple bilayer architectures were first printed to explore the relationships between the anisotropic swelling and the mean/Gaussian curvatures of the target surface (Fig. 14b). By further combining 2D patterns that generate simple curvatures, 3D flower architectures were obtained (Fig. 14c). Such a shape transformation was reversible when the poly(*N*,*N*-dimethylacrylamide) matrix was replaced by the stimuli-responsive poly(*N*-isopropylacrylamide) matrix.

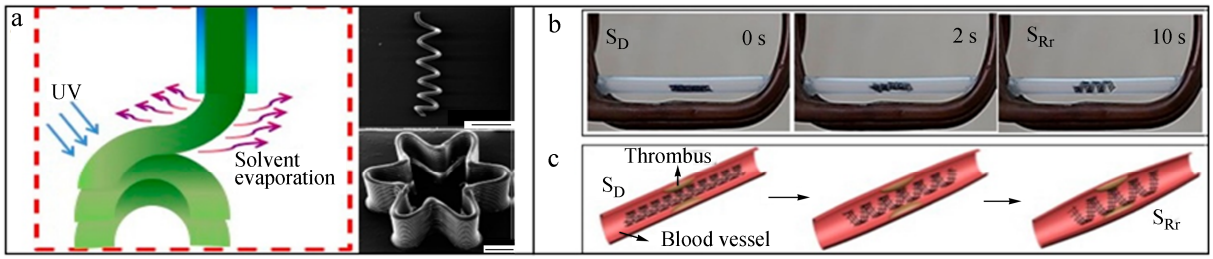


Fig. 13 DIW printing of shape memory polymer: (a) schematic illustration of the printing process (The scale bars are 1 mm.); (b) demonstration of the shape recovery process triggered by magnetic field; (c) potential application as an intravascular stent (Reproduced with permission from Ref. [46]; Copyright (2017) American Chemical Society)

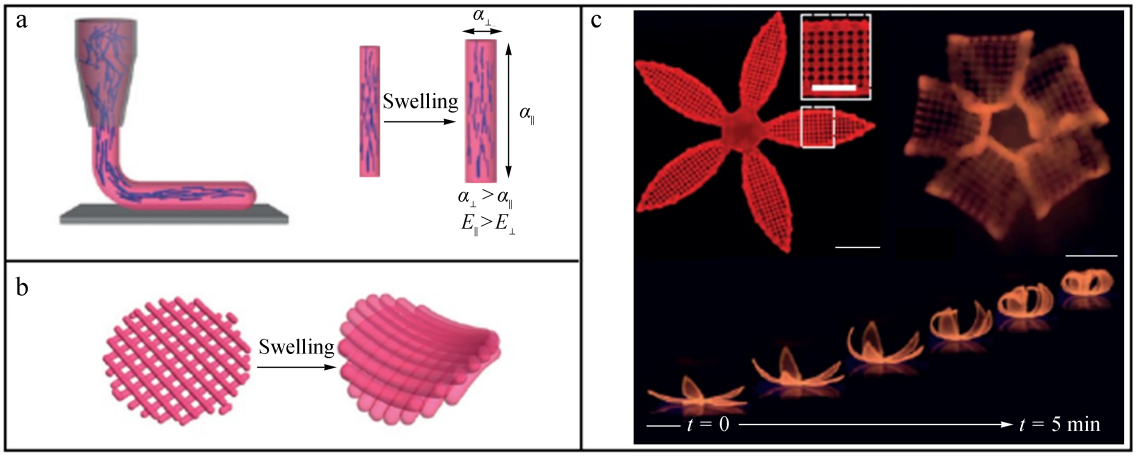


Fig. 14 DIW printing of hydrogel: (a) schematic illustration of the printing process; (b) anisotropic swelling induced deformation; (c) flower structures with time-lapse sequences during the swelling process (The scale bars are 5 mm.) (Reproduced with permission from Ref. [47]; Copyright (2016) Nature Publishing Group)

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4D PRINTING WITH NON-ACTIVE MATERIALS

In several examples above, the driving force for shape shifting from a 2D film to a 3D object originates from stress induced in hydrogels or SMPs, either being encoded within the structure during printing or imposed externally after printing. On a more general basis, internal stresses exist commonly in non-active materials, which often form during the manufacturing processes including for instance the volume shrinkage during polymerizations and the stretching stress during extrusion. Oftentimes, this type of internal stresses negatively affect the mechanical performance and dimension stability of the products, thus should be carefully treated and/or eliminated. However, if precisely controllable, internal stresses can also act in a positive way to achieve desired shape morphing even for non-active materials. Examples of this are presented in this section.

Zhang *et al.*[48, 49] reported that during the FDM printing of thermoplastic polymers (typically PLA, ABS), the heating and rapid cooling cycles would accumulate internal stresses in the printed material due to the constraint of the platform or the existing layers. The accumulated stress could be released when the polymer chains were activated above the T_g, triggering the shrinkage and spontaneous pattern transformation of the printed object. For instance, the printed thin-walled PLA rings, arranged initially in a hexagonal or square pattern, transformed into hexagons (Fig. 15a) or quadrangles (Fig. 15b) when heated up to 90 °C, respectively. The internal stress could be mediated by varying printing parameters including nozzle temperature, platform temperature, and building speed. In follow-up work, the same group printed PLA strips on a paper sheet[49]. For such a system, the release of the internal stress generated during printing counteracted the deformation caused by the mismatch of the coefficients of thermal expansion within the composite materials. As a result, the printed composite sheet assumed a flat state when being heated, but transformed into 3D configuration when being cooled down (Fig. 15c). The fabricated architectures were based on thin strips which to some extent limited its applications. Nevertheless, the work offered new insights into the design and manufacturing of the polymer with 2D or 3D architectures.

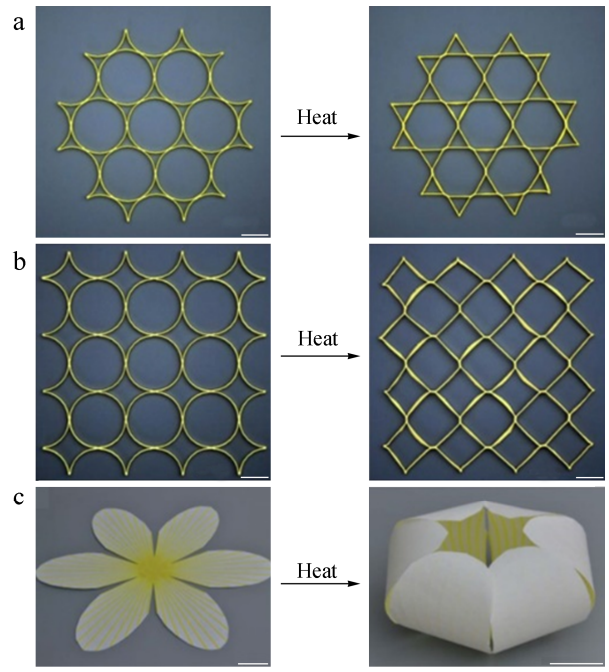


Fig. 15 Pattern transformations of heat-shrinkable polymer: (a, b) pattern transformation of 2D lattice materials under heating; (c) initial planar sheet transforming into flower structure under heating (The scale bars are 15 mm.) (Reproduced with permission from Ref. [48]; Copyright (2015) Nature Publishing Group; Reproduced with permission from Ref. [49]; Copyright (2016) Nature Publishing Group)

Zhao *et al.*[23] explored a desolvation-induced self-folding mechanism to achieve the transformation of a printed flat plane into a complex origami structure. Photo-curable poly(ethylene glycol) diacrylate oligomers were exposed to a light field with an intensity variation in all three dimensions including the thickness dimension *via* a DLP printing setup. Through digital control of the light field during the printing, a continuous distribution of cross-linking density was realized in the sample, importantly with unreacted oligomers dispersed in the partially cross-linked network. Removing the residual unreacted oligomers in water caused the sample to contract nonuniformly, leading to an internal driving force to turn the 2D sheet into a 3D structure (Fig. 16). Interestingly, the authors proposed a photopolymerization-induced volume shrinkage mechanism to explain a similar 4D printing process in another work[50]. Although these two mechanisms appear significantly different, they do share some intrinsic relation, *e.g.*, a 3D heterogeneous chemical composition.

APPLICATION OF 4D PRINTING

Although materials, designs, and printers have been developed rapidly, 4D printing is still in its infancy as a research area. However, the U.S. army has already shown strong interest in 4D printing, and granted researchers in three different universities with the goal of pushing 4D printing forward. This new technology is expected to be used for military advancements[51] such as “an automobile coating that changes its structure to adapt to humid environment or a salt-covered road, better protecting the car from corrosion. Or consider a soldier’s uniform that could alter its own camouflage or more effectively protect against poisonous gas or shrapnel upon contact”. Besides, the self-assembly nature of 4D printing will reduce the manufacturing time and labor, which is beneficial for the future war. Another potential opportunity is 4D printing of deployable solar cell array or antenna array used in aerospace. Omitting the numerous mechanical components utilized in existing approaches, the operating reliability can be significantly improved in the extreme environment if parts are directly printed in one single piece by 4D printing.

Combining the merits of additive manufacturing and morphing capability, 4D printing is promising for the next-generation personalized minimally invasive medical devices. For example, a printed stent can be deformed into a temporary shape, inserted into the body through a smaller

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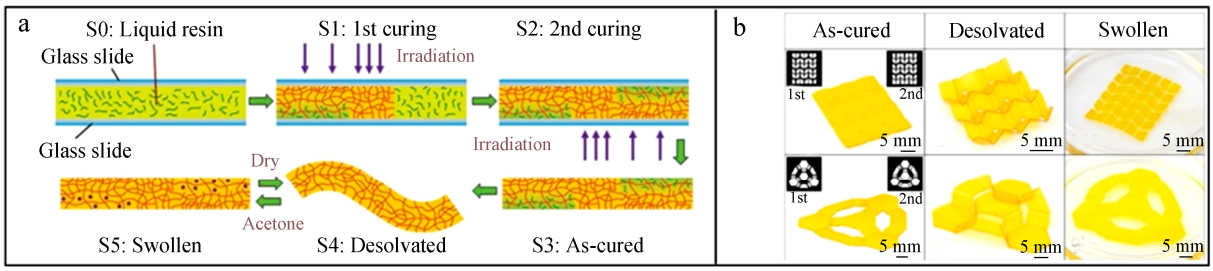


Fig. 16 (a) Schematic demonstration of the mechanism of the desolvation induced deformation and swelling induced recovery process; (b) Complex 3D origami structures obtained by different exposure layouts (Left: the as-cured flat pattern, middle: desolvated origami shape, and right: swollen flat shape) (Reproduced with permission from Ref. [23]; Copyright (2016) John Wiley and Sons)

surgical incision, and deploys into its original printed shape under a temperature variation[52, 53]. The basic technical requirement is that the printing materials should exhibit both biocompatibility and shape shifting capability in the physiological environment. Unfortunately, most of the reported materials are formulated for non-biocompatible use at this point.

In consumer product area, 4D printing can bring a significant change in people's daily life. The printed active products will adapt to users' demands and the environmental variations including temperature, pressure, humidity, or sound. The shipping volume will be dramatically reduced in a flat-pack manner which can be activated after delivery to resume its 3D dimension and function. Moreover, the products do not need to be thrown away when they fail, instead, they will self-correct and self-repair to meet new demands.

SUMMARY AND FUTURE OUTLOOK

The concept of 4D printing came into sight in 2012. In the first few years, only sporadic efforts were reported mostly by researchers with mechanics background, relying on commercial materials, printers, and printing processes. In the last two years, the pace greatly accelerated, particularly with the emergence of some advanced concepts that deviate significantly from the classical 3D printing processes. This was natural as the excitement around 4D printing started to attract increasing attention of researchers from almost every discipline (*e.g.* chemists, material scientists, and software engineers), who approach the same set of "problems" from very different angles. From the overall process standpoint, 4D printing can either be 3D printing of active structures that can evolve with time or 2D printing of films that can morph into 3D objects outside the printing process. With the greater flexibility of 4D printing, new technical challenges inevitably arise that demand closer multidisciplinary collaboration, for instance, how to predictably control the shape evolution. Interestingly, while the term of 3D printing is used almost exchangably with additive manufacturing, multiple examples of 4D printing do not involve the "additive" step. Admittedly, those non-additive 4D printing methods, despite having their own merits (*e.g.* printing speed), also have intrinsic limitations (*e.g.* complexity of the accessible shapes). Compromises like this will certainly be a subject of future studies. On a more general basis, it is impossible to foresee the whole picture of future innovations around 4D printing. However, one sure opportunity is to take further advantages of the latest advances in active and adaptive materials, which itself is a fast-growing exciting research area. Although still in its early days of development, we believe that 4D printing will have a profound impact on both industrial manufacturing and our daily lives in the near future. By then, imagination will be the only limit for 4D printing.

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