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Topical Review

4D printing: interdisciplinary integration of smart materials, structural design, and new functionality

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Abstract

Four-dimensional printing allows for the transformation capabilities of 3D-printed architectures over time, altering their shape, properties, or function when exposed to external stimuli. This interdisciplinary technology endows the 3D architectures with unique functionalities, which has generated excitement in diverse research fields, such as soft robotics, biomimetics, biomedical devices, and sensors. Understanding the selection of the material, architectural designs, and employed stimuli is crucial to unlocking the potential of smart customization with 4D printing. This review summarizes recent significant developments in 4D printing and establishes links between smart materials, 3D printing techniques, programmable structures, diversiform stimulus, and new functionalities for multidisciplinary applications. We start by introducing the advanced features of 4D printing and the key technological roadmap for its implementation. We then place considerable emphasis on printable smart materials and structural designs, as well as general approaches to designing programmable structures. We also review stimulus designs in smart materials and their associated stimulus-responsive mechanisms. Finally, we discuss new functionalities of 4D printing for potential applications and further development directions.

Keywords: 4D printing, 3D printing, smart materials, programmable structure, stimulus

1. Introduction

Smart materials that can perform multifunctional shape manipulations, such as programmability and fast reversible shape transformation, have been widely employed in a wide range of applications [1, 2]. Integrating these materials into 3D architectures that enable programmable geometry changes could lead to novel functionalities, making it highly attractive for engineering applications such as soft robotics, sensors, and biomedical devices [3]. As a revolutionary technology, 3D printing has changed the nature of industrial manufacturing [4–7]. By creating high-resolution and geometrically complex structures from computer-aided design files with precisely-controlled deposition/curing/fusion of material, 3D printing can facilitate rapid design-to-fabrication processes and reduce material waste in the production of detailed components [8–10]. When combined with stimulus-responsive smart

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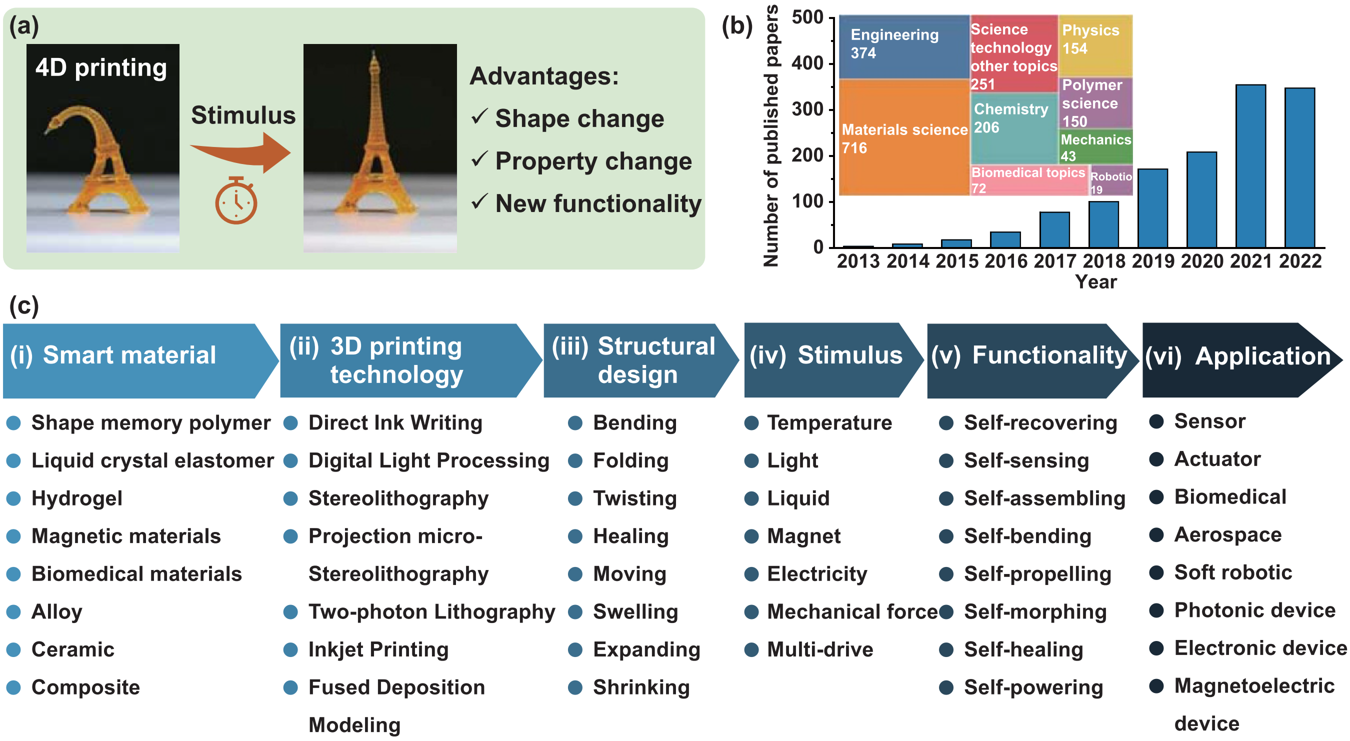

Figure 1. General introduction of 4D printing technology. (a) Concept of the 4D printing technology. Reproduced from [37]. CC BY 4.0. (b) The development trend and multidisciplinary characteristics (inset) of 4D printing. Statistical data of Publication Years and Research Areas were from the Web of Science (statistics time until 31 January 2023), by searching the topic '4D printing' and then using the Analyze Results option to collect. The data on biomedical topics are related to the sum of related biology topics, such as Biotechnology Applied Microbiology, Biochemistry Molecular Biology, Cell Biology, and so on. (c) General process and the key technical considerations in the implementation of 4D printing technology.

materials, 3D printing has given rise to 4D printing, where stimulus-triggered changes in shape, properties, or functionalities occur over time (figure 1(a)) [11–13].

The term '4D printing' was first introduced in 2013 when a controllable change in shape was achieved in 3D-printed objects [14–16]. Today, the scientific community defines 4D printing as a process that achieves targeted and programmable transformations of 3D-printed structures in response to predetermined stimuli that go beyond changes in shape and can include property and functionality evolution [17–19]. Given its ability to fabricate programmable systems, 4D printing has grown rapidly in the last few years (figure 1(b)), showing remarkable potential in soft robots [20–22], biomedical devices [23–26], fashion [27], sensors [28, 29], actuators [30], aerospace [31], among others. However, 4D printing involves multiple disciplines, including engineering, materials science, chemistry, physics, biomedical, robotics, optics, etc (inset in figure 1(b)). To realize its potential fully, an understanding of materials, architectures, and stimulus design is urgently needed.

While some previous reviews of 4D printing have covered specific aspects of materials and applications [2, 12, 24, 27, 32–36], interdisciplinary aspects of material-design-functionality relationship have not been fully explored. This lack hinders the rational design of the desired 4D-printed structures and their wider applications, from the appropriate selection of 3D printing techniques, choice of smart materials, architectural design and employed stimuli. Hence, in this review, we emphasize the prominent roles of interdisciplinary study in 4D printing, summarize recent significant developments in 4D printing, establish the inherent relationship between smart materials, 3D printing techniques, programmable architectural design, diverse forms of stimuli, and new functionalities, as shown in figure 1(c). We focus on printable smart materials and structural design, as well as the general approach (e.g. finite element analysis (FEA)) used to design programmable structures. Further, we review the prominent roles of stimulus design in smart materials and the corresponding response mechanism. Finally, we discuss the new functionalities of 4D printing for multidisciplinary applications and suggest further directions for 4D printing.

The framework of this review is presented in figure 2 from an interdisciplinary perspective. Specifically, the choice of smart materials, structural design, and stimuli selection in 4D printing will be successively discussed in sections 2–4. Then, new functionalities and diverse distinctive applications will be summarized in section 5. The summary and further development directions for 4D printing will be introduced in section 6.

2. Smart materials

Smart materials along with the appropriate 3D printing techniques are two important prerequisites for constructing 4D-printed structures. The amazing customizability of 3D

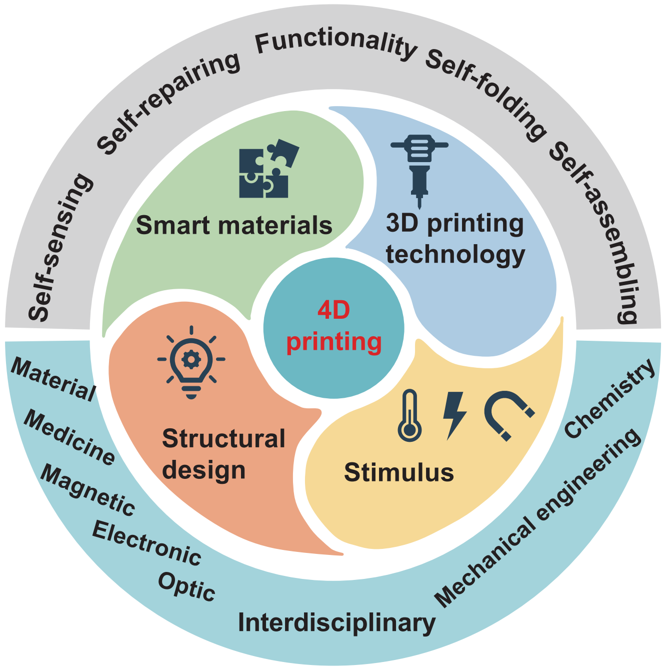

Figure 2. Overview of this review of 4D printing technology.

printing in fabricating complex geometries is the key to the realized successful 4D printing designs, especially for designs that require a unique layout of different materials with different size scales. Currently, the employed 3D printing techniques for smart architecture fabrication mainly include fused deposition modeling (FDM), direct ink writing (DIW), stereolithography (SLA), digital light processing (DLP), projection microstereolithography (PμSL), two-photon lithography (TPL), laser direct writing, and inkjet printing. Generally, the most commonly employed are DIW, DLP, and SLA. There have been many comprehensive reviews on 3D printing techniques to introduce their characteristic properties [6, 8, 9, 38]. Therefore, this review focuses on smart materials, unique designs and diverse applications in 4D printing.

The choice and design of the smart material is the most fundamental requirement for 4D printing. Such materials have the ability to be fixed into an arbitrary temporary shape and then recover the original shape under external stimuli. In this section, we introduce the current 4D-printable materials separately in detail, which include shape memory polymers (SMPs), liquid crystal elastomers (LCEs), hydrogels, magnetic materials, alloys, ceramics, and composite, as shown in figure 3. The characteristics of the smart materials will be described in this section, along with their preparation methods.

2.1. SMPs

The most widely utilized materials in 4D printing are SMPs. Interest in SMPs predates that of 4D printing due to their ability in changing from their original (permanent) shape to a deformed state (temporary shape) and reversibly returning to their original shape upon triggering by an external stimulus, including water, light or heat [34, 39–41]. Such shape changes were generated either through eigenstrains or simply direct shape programming. In particular, arbitrary and highly complex shape changes for SMPs can be realized with the aid of 3D printing. Most SMPs for 4D printing are currently fabricated by the DLP or SLA technique (table 1). However, the preparation of 3D printable SMPs resins is a prerequisite, which involves complex chemical synthesis.

Typically, the process for the preparation of 3D printable SMPs resins adopts a systematic trial-and-error process approach instead of a fully deliberate design, leading to variations in formulation varies in different studies. For example, a series of photo-curable SMPs resins with different formulations were reported by Ge and co-authors, such as a methacrylate-based copolymer resin [37], Vero Clear based photoresist [42], and a mechanically robust and highly deformable SMPs system consisted of tert-Butyl Acrylate (tBA) and aliphatic urethane diacrylate (AUD) [43]. Meanwhile, a series of printable inks of SMPs with different formulations were prepared by Qi group, such as a resin containing isobornyl acrylate (IBOA) as the monomer and AUD as the cross-linker [44], a resin based on acrylates [45], and a semi-interpenetrating elastomer with an embedded semicrystalline thermoplastic polymer [46]. Peng *et al* reported the poly(l-lactide) (PLLA) based resins [47], and another resin based on the methyl acrylate and IBOA as comonomers and 1,6-hexanediol diacrylate (HDDA) as the cross-linker [48]. Many other types of SMPs resins have also been reported, such as bisphenol A glycerolate dimethacrylate (BPAGMA) based resins with recyclable, high strength and high recovery stress properties [49], polycaprolactone (PCL) based resins with various degrees of methacrylation [50], as well as DLP and DIW bifunctional resins consisted of monofunctional IBOA and diacrylate crosslinkers [33]. In general, selecting

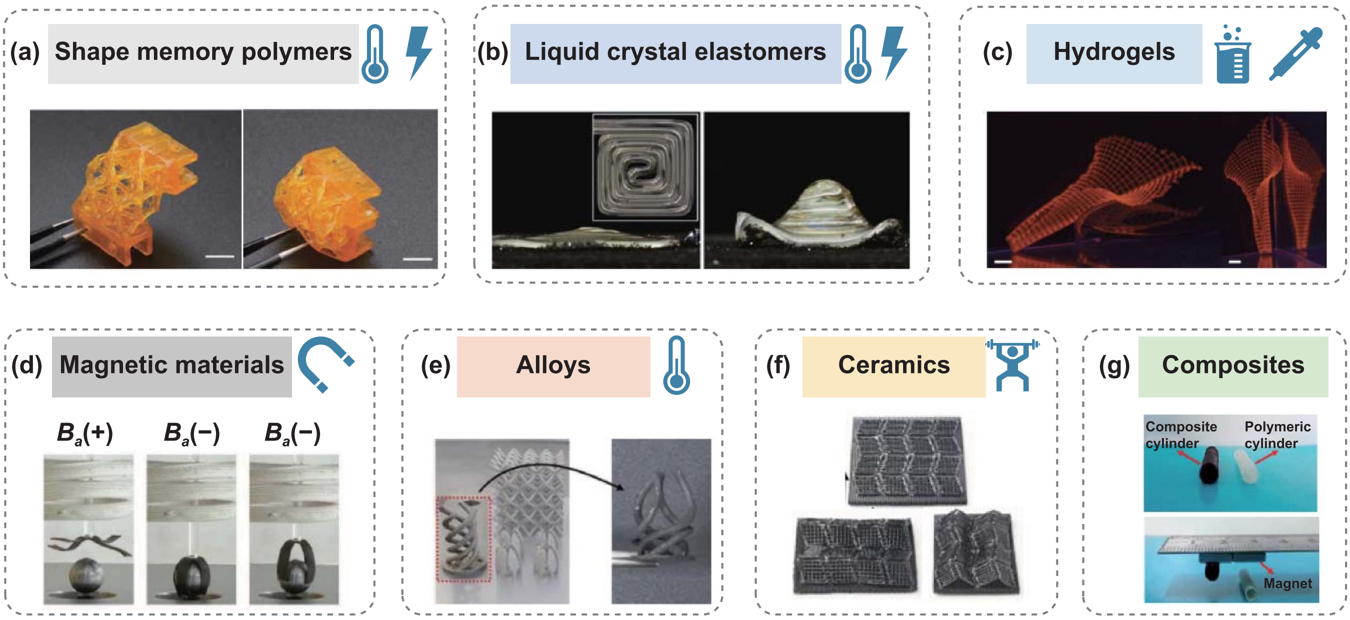

Figure 3. Smart materials in 4D printing. (a) Shape memory polymers. [43] John Wiley & Sons. [© 2021 Wiley-VCH GmbH]. (b) Liquid crystal elastomers. [51] John Wiley & Sons. [© 2021 Wiley-VCH GmbH]. (c) Hydrogels. Reprinted by permission from Springer Nature Customer Service Centre GmbH: [Nature] [Nature Materials] [52], Copyright (2016). (d) Magnetic materials. [53] John Wiley & Sons. [© 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim]. (e) Alloys. [54] John Wiley & Sons. [© 2022 Wiley-VCH GmbH]. (f) Ceramics. Reproduced from [55]. CC BY 4.0. (g) Composites. Reprinted with permission from [56]. Copyright (2017) American Chemical Society.

the type, as well as the formulation of monomers and crosslinkers is crucial in controlling the behaviour of the SMP resins (e.g. curing behaviour) and the properties of the printed SMPs (e.g. glass transition temperature (T_g) and mechanical performance).

2.2. LCEs

Another class of shape-changing materials is LCEs. Typically, LCEs are composed of slightly crosslinked liquid crystalline polymeric networks that contain mesogens capable of exhibiting liquid crystalline behaviour. LCEs can transit between their liquid crystalline state (e.g. nematic) and their isotropic state upon exposure to various stimuli such as temperature, electric field, light, and magnetic field [57–59]. Together with the entropy elasticity of the polymeric network, actuation can occur in transit between the different states, making them attractive candidates for actuators [57, 60]. Different from the case for SMPs, most LCEs' structures for 4D printing are fabricated by the DIW technique (table 1).

By way of illustration, Ware and co-authors reported a new type of ultraviolet (UV)-responsive shape-switching LCEs via the integration of 2-ureido-4[1H]-pyrimidinone (UPy) hydrogen bonding, dynamic Diels–Alder covalent bonds, and azobenzene [30]. Electrothermally (Joule) heat-responsive innervated LCEs actuators were also reported where the monodomain LCEs inks were prepared using a two-stage thiol–acrylate Michael addition and photopolymerization reaction [60, 61], or an aza-Michael addition method [51]. Using a similar aza-Michael addition method, another novel class of highly deformable hygroscopic LCEs with humidity-responsive properties were prepared with a reactive LC monomer and a chain extender [62]. Different from the typical cases of the 4D-printed LCEs where monomeric precursors were printed at temperatures below the nematic-to-isotropic transition temperature (T_{NI}), Zhang *et al* prepared a single-component ink that consisted only of a biphenyl-based liquid crystal main chain polymer, which can be printed at its T_{NI} (200 °C) [61].

2.3. Hydrogels

Besides SMPs and LCEs, hydrogel is another choice of material for 4D printing. Hydrogels are mainly crosslinked hydrophilic polymer that is capable of absorbing a large amount of water yet does not dissolve in water typically due to the existing crosslinks between the polymeric chains [32, 63]. With a well-defined structure in both dried and swelled states, printable hydrogels can be fabricated into smart or stimuli-responsive materials where their physicochemical properties change in a controlled manner under a specific external stimulus. Smart hydrogels with reversible properties are highly attractive for biomedical applications especially. Most hydrogels responsive to swelling/deswelling changes are printed by the DIW, DLP, or PμSL technique (table 1).

Many smart hydrogels can be responsive to various stimuli, including water, pH, solvent, ion concentration, temperature, and electric field. For example, inspired by the botanical systems, Lewis and co-authors developed water-responsive hydrogels that exhibited localized, anisotropic swelling through the alignment of cellulose fibrils embedded in a soft acrylamide matrix [52]. Hu *et al*

Table 1. Overview of typical 4D printable materials.

Materials	3D printing technique	Stimulus	Functionality	Structure	References
Shape memory polymers *Advantages:* • Relatively stiff structure • Relatively high actuation speed *Drawbacks:* • Complex chemical synthesis • Requiring external loads	PμSL	Temperature	Recovery	Eiffel tower, grippers, flower	[37]
	TPL	Temperature	Recovery	Hinge	[42]
	DLP	Temperature	Recovery	Kelvin foam	[43]
	DLP	Temperature	Mechanically robust	Balloon, mesh, tent, dog	[44]
	SLA	Volatilization, heat	Self-folding	Buckyball, flower, Miura-ori	[45]
	DIW	Temperature	Self-healing	Archimedean spiral, honeycomb, vase, Gumby	[46]
	IJP	Temperature	Transformation	Leaf and snail shell	[47]
	DLP	Temperature	Strain isolation, active deployment	Microlattice	[48]
	DLP	Temperature	Recovery	Microlattice	[49]
	SLA	Temperature	Recovery	Cardiovascular stent, Eiffel tower, bird	[50]
	DLP, DIW	Temperature	Self-folding	Infinity rings, cubic grids	[33]
	—	Temperature, magnetic	Recovery	Cantilever, gripper	[53]
	PμSL	Temperature	Mechanically tunable	Microlattices with octet-truss and Kelvin foam	[72]
	FDM	Temperature	Recovery	Sanxingdui bronze mask	[73]
	DLP	Temperature	Recovery	Gothic architecture, fox, gripper	[74]
Liquid crystal elastomers *Advantages:* • No need for aqueous environments or external loads *Drawbacks:* • Complex chemical synthesis	DIW	UV-light	Actuator	Flower, braille-like	[30]
	IJP	Temperature (Joule heating)	Recovery	Laminated hinge	[60]
	DIW	Temperature	Self-sensing	Spiral architectures	[51]
	DIW	Humidity	Self-folding	Bilayers, flower, concentric square array, soft gripper,	[62]
	DIW	Temperature	Recovery	Mesh	[61]
	DIW	Temperature	Recovery	Texture, honeycomb	[75]
	DIW	Temperature, UV	Lock-in	Square cone, Möbius strip	[76]
	DIW	Water	Color change	Beetle	[77]
Hydrogel *Advantages:* • Multiple stimuli-response • Aqueous environments for biomimetic and biomedical applications *Drawbacks:* • Soft structures • Slow responsive speed • Unstable actuated shapes • Requiring aqueous environments	DIW	Solvent (water)	Biomimetic	Flowers, orchid	[52]
	DIW	Ca^{2+} ions	Self-folding	Tubes	[65]
	LDW	pH	Biomimetic, particle capture	Flower, microcage	[64]
	PμSL	Temperature	Biomimetic	Gripper, dumbbell	[66]
	PμSL	Osmotic pressure	Soft robotic actuation	Gripper	[69]
	IJP	Temperature	Biomimetic	Fish, octopus	[68]
	DLP	Solvent (acetone)	Actuators, electronic devices	Origami	[70]
	DLP	Solvent (water)	Changing	Theatre, helix, tulip flower	[78]
	DIW	pH	Living cell	Pillar gripper, flowers	[79]
	DIW	Temperature, pH, enzyme	Cargo transport and delivery	Hexagon, cube lattice, cylinder	[80]
	DLP	Solvent (water)	Biomimetic	Tetragonal lattice, sea stars	[81]
	DIW	Temperature	Biomimetic	Flower, palm	[82]
	LDW	pH	Biomimetic	Flytrap	[83]
	SLA	Solvent (water)	Biomimetic	Benchy, stent-like mesh	[84]
	DIW	pH	Biomedical, cell culture	Scaffolds	[85]
	DIW	Fe^{3+} ions, sodium lactate/UV	Biomedical	Bilayer strips	[86]

(Continued.)

Table 1. (Continued.)

Materials	3D printing technique	Stimulus	Functionality	Structure	References
Magnetic materials *Advantages:* • Fast response speed • Simply making composites	DIW	Magnetic field	Soft robotic actuation	Auxetic structure, annular ring,	[87]
	DIW	Magnetic field	Biomimetic	3D butterfly	[88]
	—	Magnetic field	Soft robotic, sequential logic circuits	Grippers, antennas	[53]
	DIW	Magnetic field	Biomedical	Scaffold, microspiral, waviness	[56]
	DLP	Magnetic field	Biocompatible	Needles	[89]
Alloy *Advantages:* • Stiff structures *Drawbacks:* • High responsive temperature	SLM	Temperature, loading	Recovery	—	[90]
	SLM	Temperature	Recovery	Curved sheet, spring coil	[91]
	SLM	Temperature	Recovery	Rings	[92]
	L-PBF	Temperature	Self-healing	Spider-like, lattice, metamaterial structure	[54]
	TPL	Electrochemically driven reaction	Recovery	Tetragonal microlattices	[93]
Composite *Advantages:* • Multiple stimuli-response • Multiple materials	DIW	Temperature, water	Recovery	Ladder, bench, ring	[94]
	—	Temperature	Recovery, healing	Micropillar array	[95]
	DLP	Heat	Recovery	Flower	[96]
	IJP	Temperature	Biomimetic	Wavy, 3D dome, flower	[97]
	FDM	Magnetic	Biomedical	Occluders	[98]
	FDM	Temperature, press	Self-sensing	Scaffold	[99]
	—	Solvent	Lighting, microscopy	Lenses	[100]
	DIW	Temperature, water	Recovery	Raster, ring, butterfly	[101]
	DIW	Near-infrared light (NIR)	Brain model	Hand gesture, exerciser, folded brain, dilated heart	[102]
	—	Temperature	Self-assembly in a modular fashion	Miura-, kresling-patterned, interlock-loop, origami	[103]
	FDM	Microwave, water, Temperature	Biomimetic	Flower	[104]
	DLP	Joule heat	Flexible actuators	Bat wing	[105]
Ceramic	DIW	Stress	Mechanical robustness	Origami	[55]

reported a pH-responsive hydrogel where the polymer side chains consisted of a large number of carboxyl groups and achieved a fast response speed (<500 ms) [64]. Calcium ions-responsive hydrogel developed for hollow self-folding tubes exhibited unprecedented control by employing methacrylated hyaluronic acid (HA-MA) and methacrylated alginate (AA-MA) biopolymers [65]. Many temperature-responsive hydrogels have also been reported, such as those based on poly(*N*-isopropylacrylamide) [66, 67], as well as the agarose nanofibers and polyacrylamide [68]. The osmotic pressure-responsive electroactive hydrogel was also reported, which consisted of acrylic acid (AA), poly(ethylene glycol) diacrylate (PEGDA) and phenylbis(2,4,6-trimethylbenzoyl) phosphine oxide as the monomer, cross-linker, and photoinitiator, respectively [69]. Fan and Qi co-authors developed a desolvation-induced hydrogel based on a photo-cross-linkable resin containing PEGDA oligomers, Irgacure 819 photoinitiators, and Sudan I photoabsorbers [70]. However, despite the above, hydrogels are soft materials with a low elastic modulus of a few tens to hundreds of kPa. The low stiffness of printed structures limits their applicability [71].

2.4. Magnetic materials

Different from complex chemical synthesis for the aforementioned SMPs, LCEs and hydrogels, magnetic materials for 4D printing can be easily fabricated by simply incorporating magnetic particles into the soft polymer to achieve untethered control in shape change and motion. For example, the common silicone polymer (polydimethylsiloxane, PDMS) can be endowed with magnetic properties to achieve complex programmable shape changes through the incorporation of magnetic particles, such as iron (Fe) [88, 106] and neodymium–iron–boron (NdFeB) [87]. The employed printing technique for these magnetic soft materials usually is DIW (table 1), where the embedded magnetic particles not only play the stimulus functionality but also serve as a rheological modifier to induce a jamming effect to the printing ink, so as to achieve rheological behaviour favourable for extrusion-based 3D printing, such as shear thinning and shear yielding.

Apart from the silicone rubber matrix, Zhao and co-authors used SMPs as the matrix to develop a novel smart composite material containing two types of magnetic particles (Fe_3O_4 and NdFeB) embedded within. As the Fe_3O_4 particles would heat up under a high-frequency alternating current magnetic field, the such function would then enable the mechanism for shape locking and unlocking. On the other hand, the NdFeB particles can be magnetized with predetermined magnetization profiles, which would allow the material to perform controllable actuation under an applied external magnetic field [53]. Such design integrated various functionalities into one smart material, including untethered, fast and reversible actuation, as well as programmability and shape locking. In general, 4D-printed magnetic materials exhibit fast responsiveness to a non-intrusive external magnetic field, therefore, they have drawn great interest recently, especially in soft robotics and biomedical devices.

2.5. Alloys

Shape memory alloys (SMAs) are a category of metallic alloys capable of recovering back to their original shape upon exposure to certain external stimuli, such as temperature and tensile loading [39]. One of the most common 4D-printed SMAs is temperature-responsive NiTi alloys fabricated through the selective laser melting (SLM) technique (table 1) [90–92]. Very recently, Kim *et al* fabricated complex 3D structures with temperature-responsiveness, using Fe–Mn–Si-based SMAs fabricated through the laser powder bed fusion (L-PBF) technique, which exhibited high strength and stiffness [54]. Besides SMAs, Greer and co-authors ingeniously developed smart silicon-lithium (LiSi) alloy microlattices that were capable of transforming into sinusoidal patterns in response to electrochemically-driven lithiation, via a cooperative beam buckling mechanism [93]. The authors first printed polymer lattices using the TPL technique, then sputtered the Ni layer and an amorphous Si layer using plasma-enhanced chemical vapour deposition on the polymer lattices. The Si microlattices were then conducted galvanostatically for lithiation and delithiation to achieve a reversible structural transformation by controlling cutoff voltage.

2.6. Composite

As shown in table 1, each type of smart material for 4D printing has its advantages and drawbacks. For example, SMPs can offer a large amount of actuation but generally only in one-way actuation. SMAs offer reversible actuation and stiffness but shape changes are typically small. Hydrogels do not require programming after printing but printed structures are soft [94]. Hence, the composites based on multiple active materials are complementary that can integrate the advantages of two or more active materials, as well as realize sophisticated multiphysics constitutive behaviour through more than one stimulus. Moreover, the functional filler can also modify the rheological properties of resins or inks to make them printable, especially for extrusion-based printing. Various types of smart composites have been developed for 4D printing, such as SMPs and hydrogel [94, 95], SMPs and nanosilica [96], SMPs and elastomer [97, 101], poly(lactic acid) (PLA)-based SMPs and magnetic Fe_3O_4 [56, 98, 107], SMP and graphene [102], PLA and carbon black [99], silicon/PDMS/Ag [100], and PLA/polycaprolactone (PCL) [108].

In terms of new functionalities, Qi and co-authors utilized two stimuli-responsive materials, hydrogel and SMP to print a smart composite, where the swelling of the hydrogel component would be the main driving force of the change of shape, while the temperature-dependent SMP's role is to regulate the time of shape change [94]. In addition, the authors also reported a new direct 4D printing approach by using a combination of SMPs and elastomers, where the programming of the SMP/elastomer composites was integrated into the 3D printing process [97]. Their method allows shape-changing to take place right after printing without the need for composition changes (e.g. swelling) like typical 4D-printed hydrogel or the need for thermomechanical training like many 4D-printed SMPs. Upon heating, the printed SMPs would soften and thereby releasing the constraint on the elastomer, allowing the material to be programmed into a new shape, which becomes fixed upon cooling. The material can be reprogrammed multiple times by repeating the above process. In addition, Choong *et al* prepared the SMPs/ nanosilica composite, where the added nanosilica fillers acted as a catalyst to alter the light scattering characteristics of the SMPs resin, and thus accelerated the printing speed by improving resin curability [96]. It should be noted that the aforementioned magnetic materials in section 2.4 are also mainly composite materials with magnetic particles embedded within polymeric matrixes. In this review, we classify magnetic materials and composites into two kinds of active materials based on the different responsive properties, i.e. one-way magnetic actuation for magnetic materials while more than one responsive stimulus for smart composites with new functionalities.

2.7. Ceramic

As compared to the aforementioned 4D printable materials, studies on 4D-printed ceramics are lesser. Nevertheless, there are a few interesting reports on 4D-printed ceramics. For instance, Lu and co-authors printed ceramic elastomeric precursors, in particular PDMS via the DIW technique. Such precursors are soft and can be easily deformed and stretched, so that they can be programmed into complex architectures, such as origami folding [55]. Following proper heat treatment, complex-shaped and elastomer-derived ceramics (silicon oxycarbide) were fabricated, making 4D-printed ceramic structures possible.

3. Structural design

After determining the appropriate smart materials and 3D printing techniques, the next critical step in 4D printing is to design printed and programmed structures. This section will discuss the progress of reported 4D-printed structures, with a focus on specific applications and designing programmable structures using techniques such as thermomechanical programming, multi-material distributions, and FEA simulations.

3.1. Structure

With the technical advantages of 3D printing techniques, arbitrary structures can be designed and printed as desired and required. Hence, a rich set of structures for 4D printing have been designed (table 1). As shown in figure 4(a), current 4D-printed structures can be roughly classified as object-shaped (e.g. Eiffel tower, balloon, vase, 3D dome, rings, ladder, square cone, Möbius strip), biomimetic (e.g. flower, gripper, fish, octopus, leaf, snail shell, cardiovascular stent), and configurable architectures (e.g. microcage, grid, scaffold, microlattice, microspiral, hinge, Archimedean spiral, honeycomb, micropillar array). In general, printed structures have gradually developed from model demonstrations (e.g. Eiffel tower, vase, 3D cube) to new functional structures (e.g. biomimetic) that can be practically applied in specific applications.

For example, the gripper is one of the most common designs among these 4D-printed structures (figure 4(a-ii)). The gripper can be achieved different functionalities simply by designing different sizes and numbers of digits, different layouts of the printed multi-materials, and different stimulus-responsive mechanisms of the grippers. The as-printed closed (opened) gripper can be controlled to open (close) via programming while the functionality of grabbing (releasing) objects can be triggered by various stimuli, e.g. temperature [37], humidity [62], osmotic pressure [69]. On the other hand, complex microcages can also be designed to capture microparticles through solution-responsive swelling and deswelling (figure 4(a-iii)). The capture functionality can be realized by making use of the different pore sizes in the expanded and contracted states [64]. These microgrippers or microcages are highly attractive for soft robotics, biomedicine, drug delivery devices, as well as other applications.

Yang and co-authors also fabricated a 4D-printed transformable tube array (TTA) that enabled high-throughput histological analysis of 3D cell cultures (figure 4(a-iii)) [109]. The histological analysis of 3D cell cultures has always been a manual and laborious task mainly due to the transferring process between the large multi-well plates and the small histology cassettes. To resolve this issue, the 4D-printed TTA is capable of switching between its expanded (3.6x) and original printed dimension to match the size of the multi-well plate and the histology cassette so as to transfer the 3D cell culture models in the exact order. Such an innovation possesses a strong potential to increase the efficiency of 3D cell culture, benefitting areas such as disease modelling, drug discovery and personalized medicine.

Xin *et al* fabricated chiral metamaterials with negative Poisson's ratio behaviour (figure 4(a-iii)) [110]. Through the introduction of crescent-shaped and arc-shaped ligaments microstructure, the 4D-printed metamaterial is capable of performing large deformation (90% strain), overcoming a limitation faced by typical chiral metamaterials. Such designed metamaterials with customization mechanical properties have potential applications in flexible electronics and tissue engineering.

3.2. Programming and simulations

A unique feature of 4D printing is the shape-changing ability of 3D-printed structures, while there have been a lot of simple and non-programmable shape changes. Achieving programming is a crucial step for real intelligent 3D configurations, which is an attractive feature for a wide range of novel applications. As a typical homogeneous 4D printing, programming of a thermal-responsive material (e.g. SMPs) generally requires a series of procedures: (1) 3D printing, (2) heating, (3) mechanical loading, (4) cooling, (5) removal of mechanical load; and (6) deployment/actuation, as shown in figures 4(b-i). The thermomechanical programming process would usually require special fixtures to apply mechanical loads in a well-regulated thermal environment [113]. On the other hand, *in-situ* programming of printed structures during the 3D printing process is also possible in the case of single-component LCEs in their isotropy state (at 200 °C), by designing the extruded printing pathway and printing speed [61]. During the printing process, the mesogen units of LCEs can be aligned along the printing path due to the shearing force between the LCEs ink and the nozzle interior. Thereby obtaining an orientation gradient perpendicular to the printing direction. Meanwhile, the printing speed associated with the shear force affects the orientation mesogens. The orientation gradient can be programmed into designed structures through the integration of bending and contraction actuation modes.

Heterogeneous 4D printing is another pathway to construct programmable structures by printing spatially scattered/distributed multi-materials with different responsiveness, as illustrated in figure 4(b-ii). Currently, multi-layer structures (bilayer or trilayer) by deposition of different materials at different layers can be easily fabricated [114]. For example, shape-shifting multiplex bilayer lattice structures were built

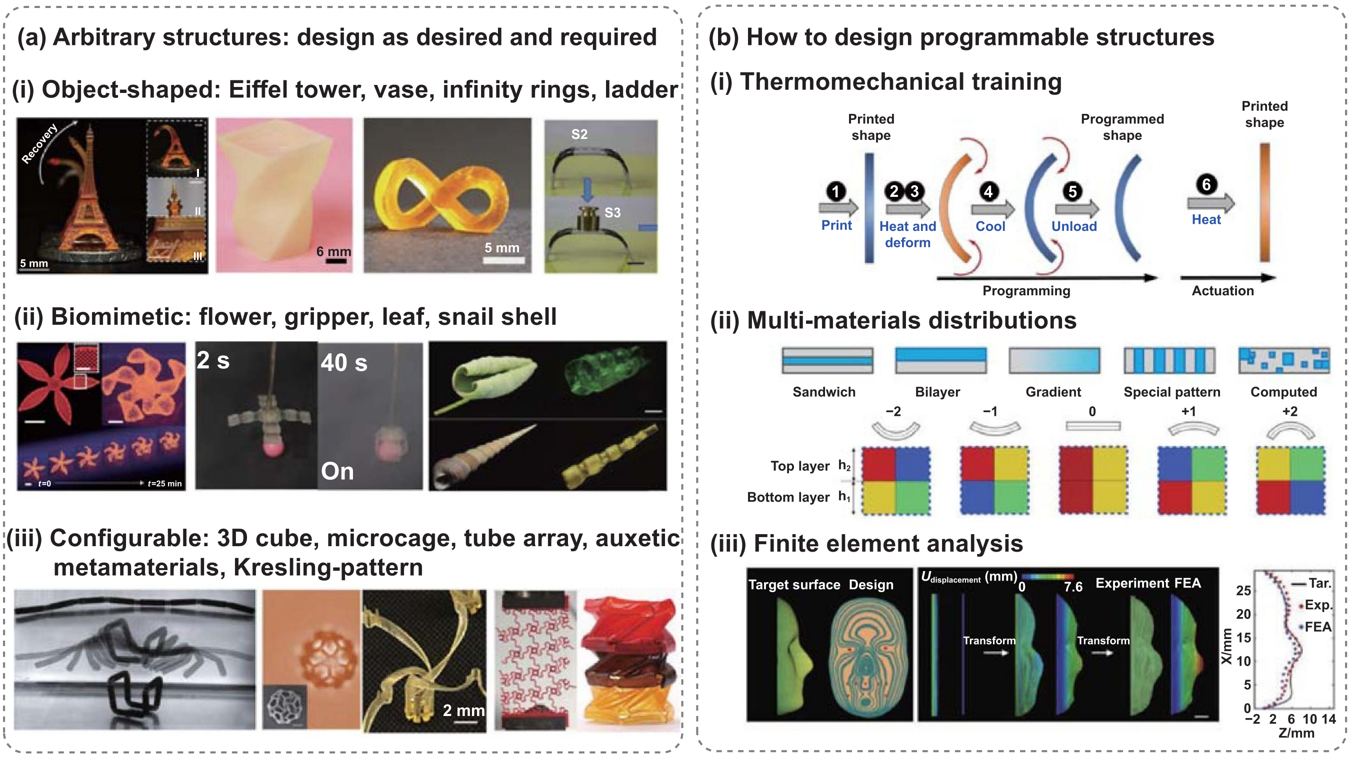

Figure 4. Structural designs behind mechanical engineering. (a) Designs of some typical structures. (a-i) Object-shaped structures. Reproduced from [37]. CC BY 4.0. Reprinted with permission from [46]. Copyright (2018) American Chemical Society. Reproduced from [33]. CC BY 4.0. Reproduced from [94]. CC BY 4.0. (a-ii) Biomimetic. Reprinted by permission from Springer Nature Customer Service Centre GmbH: [Nature] [Nature Materials] [52], Copyright (2016). [62] John Wiley & Sons. [© 2021 Wiley-VCH GmbH]. [47] John Wiley & Sons. [© 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim]. (a-iii) Configurable architectures. [111] John Wiley & Sons. [Copyright © 2014 John Wiley & Sons, Ltd]. [64] John Wiley [© 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim]. [109] John Wiley [© 2020 Wiley-VCH GmbH]. [110] John Wiley [© 2020 Wiley-VCH GmbH]. Reprinted from [103], Copyright (2020), with permission from Elsevier. (b) Programming and simulation. (b-i) Thermomechanical programming requires five steps. From [97]. © The Authors, some rights reserved; exclusive licensee AAAS. Distributed under a CC BYNC 4.0 license http://creativecommons.org/licenses/by-nc/4.0/. Reprinted with permission from AAAS. (b-ii) Multi-materials distributions. Reprinted from [35], Copyright (2021), with permission from Elsevier. Reproduced with permission from [112]. Copyright © 2023 National Academy of Science. All rights reserved. (b-iii) FEA simulations for a balloon structure transforming into a human face. [44] John Wiley & Sons. [© 2021 Wiley-VCH GmbH].

[112], where four different combinations of out-of-plane curvature ranging from maximum concave to maximum convex were incorporated, while no curvature when the lattice had asymmetric cross-section. Moreover, the complex scattered distributions (e.g. gradient and computed) can also be designed because of the technical advantages and capabilities of 3D printing.

In order to achieve more sophisticated and complex shape transformation, a better understanding of the mechanism behind the shape transformation behaviour is necessary. In view of this, FEA simulations can aid in describing the shape transformation behaviour of the printed structures thereby elucidating their mechanism [115]. For FEA, a theoretical model is first created, which contains the key elements, such as the 3D printing parameter, and material behaviours during its processing, programming and deployment phases. This theoretical model is then used to simulate 4D printing using a finite-element code [44, 45]. With guidance from the FEA tool, the structural topologies necessary to achieve specific transformation behaviours can be predicted. According to the matching degree between FEA simulations and experiments, the design parameters can be further optimized (figure 4 (b-iii)). Such understandings of the relationship between the phenomena and the geometry, the materials and the process behaviours, are valuable for designing components with arbitrary shapes and complexities. Beyond FEA, new simulation methods involving machine learning [116–118], topology optimization [119], and inverse-design algorithm [120] can also be developed to predict and construct a targeted 3D morphed geometry. For example, topology optimization was used as a powerful digital tool to optimize architectures with more functionalities [119].

4. Stimuli selection

Stimulus is the key influencing factor to achieving the transformation in shape, property and functionality of the 3D-printed architectures. The type of stimulus necessary depends on the responsiveness of smart materials and largely determines the nature of the applications [121, 122]. This section summarizes the types of stimuli for 4D printing, provides a comparison of the benefits and drawbacks of different stimuli, and establishes the relationship between stimulus responses

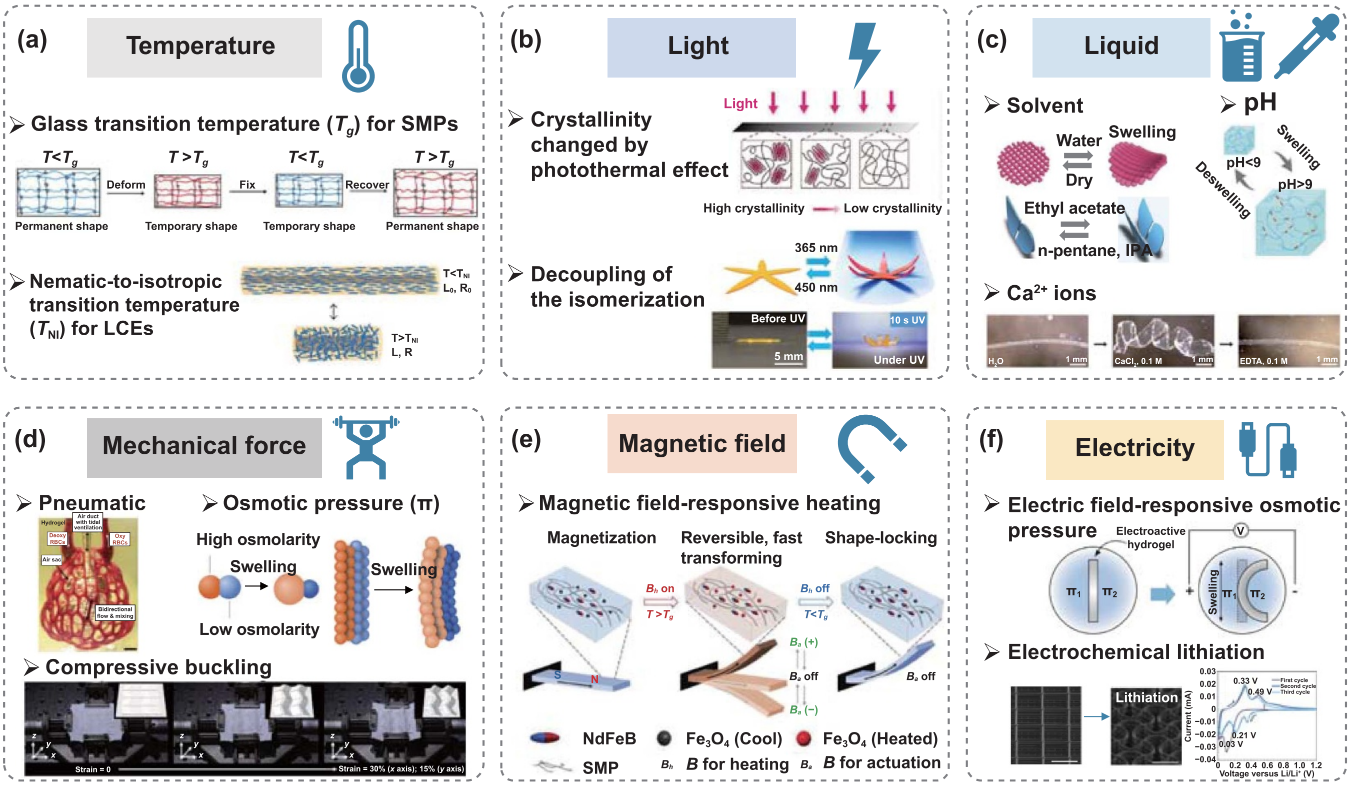

Figure 5. Stimuli behind chemistry and physics. (a) Temperature. Reprinted by permission from Springer Nature Customer Service Centre GmbH: [Springer] [Bio-Design and Manufacturing] [108], Copyright (2021). [51] John Wiley & Sons. [© 2021 Wiley-VCH GmbH]. (b) Light. [47] John Wiley & Sons. [© 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim]. [30] John Wiley & Sons. [© 2020 Wiley-VCH GmbH]. (c) Liquid environment. Reprinted by permission from Springer Nature Customer Service Centre GmbH: [Nature] [Nature Materials] [52], Copyright (2016). [127] John Wiley & Sons. [© 2021 Wiley-VCH GmbH]. [64] John Wiley [© 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim]. [65] John Wiley & Sons. [© 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim]. (d) Mechanical force. From [128]. Reprinted with permission from AAAS. From [129]. Reprinted with permission from AAAS. Reproduced from [55]. CC BY 4.0. (e) Magnet. (f) Electricity. [53] John Wiley & Sons. [© 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim]. Reprinted with permission from [69]. Copyright (2018) American Chemical Society. Reprinted by permission from Springer Nature Customer Service Centre GmbH: [Nature] [Nature] [93], Copyright (2019).

and the physiochemical properties of materials (figure 5 and table 2).

4.1. Stimulus types

As summarized in table 1, the types of stimuli can be classified into temperature (usually heating), light (e.g. UV, NIR), liquid environment (e.g. water, solvent, pH, ions), mechanical force (e.g. pneumatic pressure, compressive strain), magnetic field, and electric field. Generally, one type of smart material is usually responsive to a single stimulus according to its physiochemical properties. For example, the printed structures of SMPs, LCEs or SMAs are only responsive under thermal stimulus. Stimulus-responsive mechanisms and their relationships with the physiochemical properties of the triggered smart materials will be introduced in detail in section 4.2.

On the other hand, multi-stimuli-responsiveness is an attractive feature that can significantly broaden the practical applicability of the printed structure [25, 80, 101, 123, 124]. A common and simple way to achieve multi-stimuli-responsive 4D printing is to incorporate functional fillers into a smart matrix, which has more responsiveness than the original one. For example, 3D-printed protein-based hydrogels were developed by adding methacrylated bovine serum albumin into the inks with *N*-isopropylacrylamide and 2-dimethylaminoethyl methacrylate (pH-ink), which can change shape in response to the temperature, pH and enzyme stimuli [80]. However, in this pathway, most of the composites usually are enabled with the stimuli-responsive capability to convert light to heat [102], magnetism to heat [98], and electricity to osmotic pressure [69], therefore, these multiple stimuli-responses are essentially only responsive to one type of stimulation. Another pathway is to construct multi-material structures through the combination of two (or more) smart materials that respond to different stimuli. For example, temperature-responsive SMPs can be combined with water-responsive hydrogels [94, 101], and thermally responsive swelling gel with a passive thermally non-responsive gel [125].

4.2. Stimulus-responsive mechanism

4.2.1. Temperature. Temperature is one of the most common stimuli for many smart materials, including SMPs, LCEs, SMAs, and hydrogels. Typically, heating methods

Table 2. Overview of typical stimuli for 4D printing.

Stimulus	Responsive materials	Responsive mechanisms	Responsive speed	Limitations
Temperature	SMPs, LCEs, SMAs, Hydrogels	Glass transition temperature (T_g), nematic-to-isotropic transition temperature (T_{NI})	Middle	Need to heat up to a high temperature
Light	LCEs	Photothermal effect	Low	Need a UV light
Liquid	Hydrogels	Swelling ratio	Middle	Need to be in a liquid environment
Mechanical force	SMPs, Hydrogels, Ceramics	Pneumatic pressure, osmotic pressure, compressive buckling	Fast	Need gas, water, or external force
Magnetic field	Magnetic materials	Magnetization	Fast	Need a magnetic field but is safe and effective
Electricity	LCEs, Hydrogels, Silicon	Joule heating, Electric field-responsive osmotic pressure, Electrochemical lithiation	Low	Need an external electric circuit

can be used to trigger such stimulation, including hot water, Joule heating by electrical current, and electromagnetic field. Different thermal-responsive materials have different stimulus-responsive mechanisms, for instance, thermal-responsive SMPs and LCEs, which as discussed below.

4.2.1.1. Thermal-responsive SMPs. Polymers with thermal-responsive shape memory effect typically fulfil two molecular requirements: (1) soft segments or domains with a low transition temperature (T_{tran}), which can be T_g or T_m, to facilitate the shaping/programming process. (2) Crosslinks, either chemical or physical, to maintain the solid integrity of the material in the softened state (figure 5(a)). In one programming cycle, SMP has to be heated above its T_{tran} first before it can be shaped by an external force into the desired shape. This is followed by cooling where the shape would be fixed below T_{tran}, where the soft segments harden, and the external load can be released. To recover the SMP back to its original shape, heating it above T_{tran} would provide the soft segment sufficient mobility to return to its original and most relaxed conformation [37, 53].

4.2.1.2. Thermal-responsive LCEs. Thermally-driven LCEs with reversible shape changes are basically crosslinked polymer networks that contain rigid mesogens of high aspect ratio (usually 2–3 linked benzene rings). These mesogens will lose their liquid crystalline alignment upon heating above their nematic-to-isotropic transition temperature (T_{NI}). As such, the heating and cooling cycles would induce a significant change in the microstructure, which would then lead to a macroscopic deformation of the LCEs (figure 5(a)) [51, 60]. Unlike SMPs, LCEs do not require external loads to undergo a programmed shape change. However, the alignment of should take place before the crosslinking of the polymer network, which can be achieved either through stretching mechanically, interactions with specific surfaces or external magnetic fields, aligning the monomer solution via interactions with surfaces, or applying magnetic fields [76].

4.2.2. Light. Light is another common stimulus for SMPs and LCEs materials but eventually leads to a heating effect through a photothermal conversion process [126]. This section would introduce some of the light-responsive SMPs and UV-responsive LCEs reported in the literature.

4.2.2.1. Light-responsive SMPs. PLLA-based SMPs were developed, and their 4D transformation was achieved by spatial-selective programming of crystallinity via cold crystallization through the photothermal effect (figure 5(b)) [47]. PLLA typically remains highly amorphous after thermal processing due to their low chain mobility. At room temperature, crystallization the chain of PLLA remains frozen below its T_g ($\sim$60 °C). When a localized region is exposed to fluorescent light, the local temperature increases above the T_g due to the photothermal effect, and consequently, cold crystallization occurs. This local crystallization pattern is therefore used to control the shape-changing behaviour.

4.2.2.2. UV-responsive LCEs. A 4D printable azobenzene-functionalized LCEs was developed, which induced deformation upon UV irradiation and then can be recovered through heating (figure 5(b)) [30]. The high extinction coefficient of the azobenzene moieties helps to facilitate the absorption of UV photons at the surface region upon UV irradiation. Therefore, *cis-trans* photoisomerization of azobenzene along with the associated alignment reduction of mesogens occurred mainly on the surface of the actuator. As such, the bending of the material took place due to an uneven distribution of the anisotropic deformation. In brief, the UV isomerized azobenzene from *trans* to *cis*, and temporarily broke the supramolecular crosslinks, resulting in a programmed deformation.

4.2.3. Liquid environment. A liquid environment is a common stimulus mainly for hydrogel materials. A change in the liquid environment could be the solvent (e.g. water, acetone, ethyl acetate, *n*-pentane, isopropyl alcohol), pH or the presence of certain ions (figure 5(c)). The induced reversible actuation is usually based on swelling and deswelling ratios. With advantages in biocompatibility, water content and tuneable mechanical properties, liquid-responsive hydrogels are highly suitable for biomedical applications.

4.2.3.1. Solvent-responsive hydrogel. An example of solvent-induced responsiveness is a hydrogel comprising cellulose fibrils [52]. Due to the orientation and alignment of the cellulose fibrils, shape transformation upon immersion in water takes place anisotropically. In such a system, controlling the orientation and alignment of the cellulose fibrils is the key to manipulating the anisotropic swelling, which would allow control over the shape transformation of the printed structures. Moreover, the shear-responsive alignment of fibrils can be easily achieved using extrusion-based DIW printing with proper adjustment to the printing parameters. In another example, a hydrogel that can transform between folded and wide-open structures was achieved through the evaporation of solvents with different surface tensions (including ethyl acetate, *n*-pentane, and isopropyl alcohol), based on the different capillary forces between the structure and the substrate [127]. In another case, a PEGDA-based hydrogel was prepared and achieved desolvation-induced self-folding origami structures, where acetone was used as the solvent to form swelling and volatilization transition [70].

4.2.3.2. pH-responsive hydrogel. An example of pH-induced responsiveness is a hydrogel that possesses a large number of acidic carboxylic groups in its side polymer chain [64]. The pendant carboxylic groups can be deprotonated when immersed in a solution with a pH value greater than 9. Due to the negative charge on the carboxylate ions, electrostatic repulsion will take place between the polymer chains leading to an expansion. On the other hand, the carboxylate ions can be protonated and deionized when pH goes below 9.

4.2.3.3. Ion-responsive hydrogel. An example of ion-induced responsiveness is a methacrylate alginate acid (AA-MA) based hydrogel [65]. As the carboxyl groups of alginates are known for ionic interaction and hence, complex with multivalent cations, the hydrogel experiences a process of deswelling in response to the presence of Ca^{2+} ions in the aqueous environment. Likewise, the re-swelling can take place in a Ca^{2+}-free solution, and importantly, the shape transformation takes place very quickly, in the order of seconds.

4.2.4. Mechanical force. Mechanical force is a common stimulus for many of the smart materials, and they can come in the form of pneumatic and osmotic pressure, as well as compressive buckling (figure 5(d)).

4.2.4.1. Pneumatic pressure-responsive hydrogel and SMPs. An example of pneumatic pressure-induced responsiveness is a hydrogel with intravascular 3D fluid mixers and bicuspid valves printed within [128]. The designed distal lung subunit was ventilated with humidified oxygen gas through an air sac, leading to the enlargement and an alteration in the curvature of concave airway regions. In another example, a pneumatic pressure-responsive SMP is capable of transforming into a complex 3D shape that exhibits robust mechanical properties, through manipulating pneumatic pressure and the spatial distributions of the SMPs [44].

4.2.4.2. Osmotic pressure-responsive hydrogel droplets. An example of osmotic pressure-induced responsiveness is a tissue-like material that was printed using aqueous droplets, which were designed with different osmolarities and joined by a lipid bilayer [129]. Water flowing through the bilayer leads to the swelling or shrinkage of the droplets due to the different osmolarities, thereby inducing an overall deformation of the network. Osmolarity gradients of the aqueous droplet networks can also be programmed to shape and transform into many complex structures, however, the stimulus time could take over 3 h.

4.2.4.3. Compressive buckling-responsive ceramic. The 4D-printed ceramic was achieved by 3D printing Miura-ori patterns on the substrate using ceramic precursors [55]. Due to the periodicity and symmetry of Miura-ori patterns, they can serve as the elementary geometric construction for a compressive buckling-responsive self-morphing process, resulting in a maximum compressive strain of 30% on the *x*-axis and 15% on the *y*-axis.

4.2.5. Magnetic field. The magnetic field offers a non-intrusive stimulation alternative, which is especially attractive for biomedical applications. Magnetically responsive materials are usually developed by incorporating magnetic-responsive particles into a soft matrix [87]. The corresponding response mechanism via an applied magnetic field.

A very good example is an ingenious magnetic composite (named M-SMP) that has two types of magnetic particles (Fe_3O_4 and NdFeB) incorporated into an amorphous SMPs matrix (figure 5(e)) [53]. The Fe_3O_4 particles endowed the composite with inductive heating ability under a high-frequency alternating current (AC) magnetic field, whereas the NdFeB particles can be magnetized with predetermined magnetic profiles, so that programmable shape transformation can take place with an applied actuation magnetic field. Therefore, a magnetization profile can be programmed and subsequently reprogrammed on a cantilever fabricated using an impulse magnetic field. The magnetized cantilever is stiff and unable to any deformation under an applied actuation magnetic field (B_a) at room temperature. However, with an applied high-frequency AC magnetic field (B_h), the inductive heating effect of the Fe_3O_4 particles would heat the composite to a temperature above the T_g of the SMP, leading to a significant reduction in the elastic modulus of M-SMP. With that, an applied B_a can then result in a fast shape transformation of the composite. In addition, the removal of B_h would lock the shape of the composite in once the temperature of the M-SMP drops below its T_g and the composite regains its stiffness.

4.2.6. Electricity. Electrical energy can also act as a trigger for stimulus-response. The most common mechanism would be Joule heating, which is essentially an electrothermal conversion, used to trigger actuation for SMPs, LCEs and hydrogels, similar to that discussed in the aforementioned temperature part. Besides, there are some other unique electricity-responsive stimuli, such as electric field-responsive osmotic pressure and electrochemical lithiation, which are discussed below (figure 5(f)).

4.2.6.1. Electric field-responsive osmotic pressure. An osmotic pressure (π) can form between the anode (π_1) and cathode (π_1) of a gel that contains mobile ions. As such, when an electric is applied across an electroactive hydrogel (EAH) that contains mobile cations, an imbalance of π would results ($\pi_1 > \pi_2$) due to the attraction of the cations to the cathode side [69]. This would lead to the concentration gradient of the cations and non-uniform swelling of the EAH, resulting in its bending.

4.2.6.2. Electrochemical lithiation. An interesting example shows an electrochemically-driven silicon-lithium alloying reaction employed to achieve architectural reconfiguration of silicon lattices [93]. This was achieved due to silicon's ability to exhibit approximately 300% of volumetric expansion after full lithiation, along the cooperative beam buckling of the 3D tetragonal microlattices.

5. New functionalities for multidisciplinary applications

Four-dimensional printing enables the creation of programmable smart 3D-printed objects equipped with novel functionalities such as self-recovering [130], self-sensing [51, 99], self-assembling [131, 132], self-bending [43], self-propelling [59, 87], self-morphing [42, 133], self-healing [46, 50, 123], self-powering [134], self-folding [135], and self-reconfiguring [136]. These functionalities have tremendous potential across various fields [137, 138], including but not limited to, sensors [29], actuators [139], biomedical [140–142], aerospace [43], soft robotics [143], photonic and electronic devices [42, 144–146]. However, most conventional 4D-printed objects only focus on physical geometry variations, with limited attention given to changes in their other properties and practical functionalities [134]. Recently, newer studies explore the potential of 4D printing to provide innovative functionalities for multidisciplinary applications. In this section, we will summarize some typical designs that demonstrate the new functionalities of 4D printing, exploring the interdisciplinary aspects of the technology. This knowledge will introduce readers to the diversity of 4D printing and help them solve specific problems by leveraging its potential.

5.1. Self-recovering for self-powered sensor

A self-recovered triboelectric nanogenerator (TENGs) was constructed by printing an SMPs-based film and adding sprayed silver nanowire electrodes to its surface. This printed TENG was incorporated into a self-powered angle-sensor, which can accurately detect the bending angles of human joints. The contact electrification and in-plane-sliding induced charge transfer simultaneously influence the output signal of the angle-sensor, producing a positive or negative pulse signal that corresponds to flexion or extension of joints. Due to the 6-blades design, different output signal phases correspond to various bending angles, with a phase of π for 30°, 2π for 60° and 3π for 90° (figure 6(a)) [130].

5.2. Self-sensing for actuators

An innervated and self-sensing actuator with closed-loop control was realized through 3D actuation of LCEs [51]. As shown in figure 6(b), the actuator was fabricated by printing in a squarish spiral manner. Repeated actuation can be achieved using Joule heating above its T_{NI}, which also led to a change in electrical resistance. The actuator can transform from a 2D sheet into a cone-like structure with a height of 8.7 mm at a low power input of just 5 mW mm^{-2}. In addition, an integrated sensor-actuator was also developed, which was capable of simultaneous actuation and sensation by incorporating bioinspired gradient gaps [99].

5.3. Self-assembling for biomedical applications

A 4D-printed membrane capable of temporal control in its multi-scale structural transformation was developed by Wang and co-authors, which can be applied for *in vivo* bone repair (figure 6(c), top) [95]. This programmable membrane can macroscopically fit geometrically complex bone defects and at the same time, provide microscale changes to its topography. In another example, Kuribayashi-Shigetomi *et al* designed a cell origami that can be folded through by applying cell traction force of biological origin. (figure 6(c), middle) [131]. Leng and co-authors developed a magnetic-responsive self-expandable intravascular stent (figure 6(c), down) [56, 98]. Such stimuli mechanisms allow a non-intrusive guiding and actuation of the smart material in the human body. As the stent reaches the area where the vessel is narrowed due to thrombus, the stent can re-expand to allow a normal blood flow.

5.4. Self-bending for aerospace

A smart hinge that allows solar panels to be folded while in storage, and expands quickly when deployed through triggering by Joule heating has been developed. Such designs are highly attractive for the deployment of solar panels in aerospace applications, as demonstrated by the

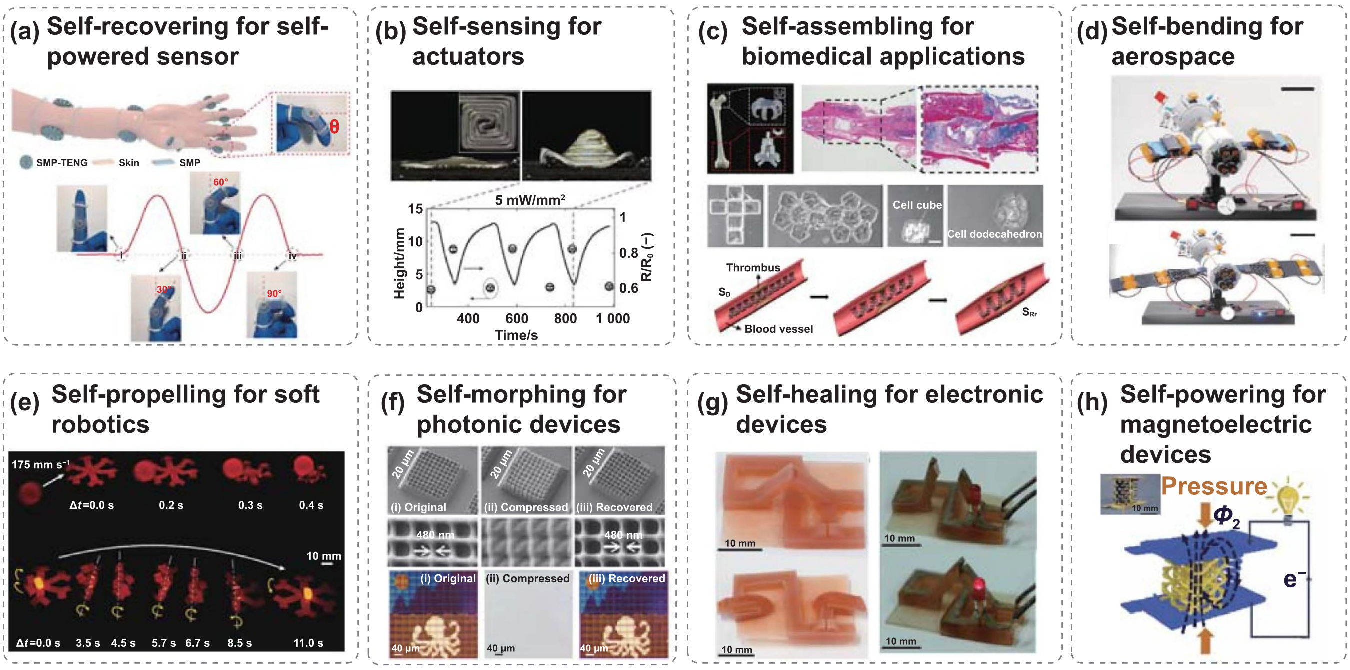

Figure 6. New functionalities of 4D printing for multidisciplinary applications. (a) Self-recovering for the self-powered sensor. Reprinted from [130], Copyright (2021), with permission from Elsevier. (b) Self-sensing for actuators. [51] John Wiley & Sons. [© 2021 Wiley-VCH GmbH]. (c) Self-assembling for biomedical applications. [95] John Wiley & Sons. [© 2021 Wiley-VCH GmbH]. Reproduced from [131]. CC BY 4.0. Reprinted with permission from [56]. Copyright (2017) American Chemical Society. (d) Self-bending for aerospace. [43] John Wiley & Sons. [© 2021 Wiley-VCH GmbH]. (e) Self-propelling for soft robotics. Reprinted by permission from Springer Nature Customer Service Centre GmbH: [Nature] [Nature] [87], Copyright (2018). (f) Self-morphing for photonic devices. Reproduced from [42]. CC BY 4.0. (g) Self-healing for electronic devices. [50] John Wiley & Sons. [© 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim]. (h) Self-powering for magnetoelectric devices. Reproduced from [134]. CC BY 4.0.

authors through powering a motor and lighting a LED (figure 6(d)) [43].

5.5. Self-propelling for soft robotics

A printed soft robot capable of crawling and rolling motion, catching fast-moving objects and even transporting drugs has been reported (figure 6(e)) [87]. In particular, the soft robot with hexagonal structures can stop a fast-moving object and wrap the object (e.g. pharmaceutical pill) through a rotating magnetic field generated by a permanent magnet. The employed magnetic-responsive composite fabricated with programmed ferromagnetic domains (NdFeB) embedded within a soft silicone matrix, has high actuation speed and power density.

5.6. Self-morphing for photonic devices

A photonic device with structural coloration was achieved through TPL printing sub-micron grids using SMP (figure 6(f)) [42]. By tuning the writing speed of TPL, the nominal height of the structure and the laser power, a wide range of colours can be achieved. Due to the nature of structural colours, the printed information would become invisible once the nano- or sub-micron structures are flattened. However, recovery of the printed information can be achieved within seconds by heating above the SMP's T_g. Such a designed structure could prove valuable in encryption and anti-counterfeiting applications.

5.7. Self-healing for electronic devices

An electrical temperature device was constructed by printing an SMPs-based object with electrical circuits using silver nanoparticle ink. At room temperature, the temporary shape creates an open electrical circuit. Upon heating above T_{tran} melting temperature of SMPs, the circuit is closed, self-repaired, and resulted in the lighting of an LED (figure 6(g)) [50]. Four-dimensional printing concept also included the design of a self-folding electronic device based on the locally engineered residual stress [146].

5.8. Self-powering for magnetoelectric devices

A flexible integrated magnetoelectric device was reported, which consisted of both conductive and magnetic components (figure 6(h)) [134]. The as-prepared devices are able to convert mechanical pressure into electrical signals and even own self-powered piezoelectric behaviour although neither both component do not possess piezoelectric individually. The device exhibits variations in the piezoelectric effect under the applied pressure, which has the potential to be employed as a pressure-sensitive monitor.

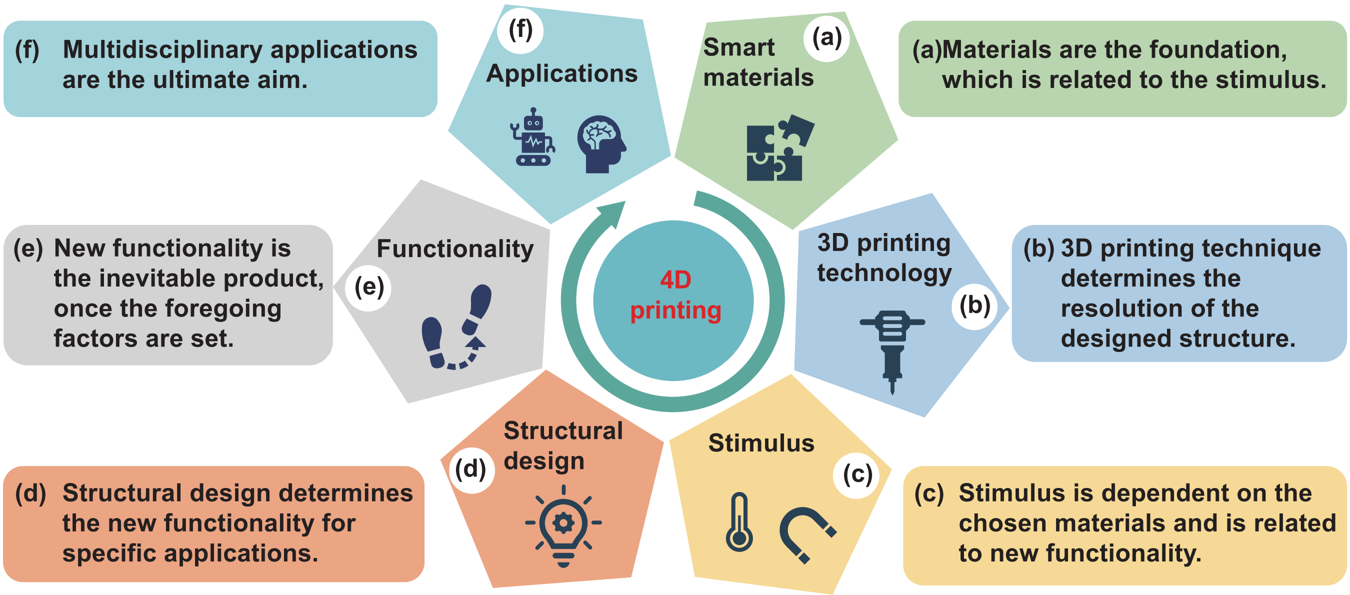

Figure 7. The relationship between smart materials, 3D printing technology, stimulus, structural design, new functionality, and applications in 4D printing.

6. Summary and perspective

The revolutionary 4D printing technology has captured the interest of researchers across various fields owing to its potential impact on design concepts for multifunctional applications of 3D architectures. In this review, we provide a comprehensive summary of recent advancements in 4D printing technology with an emphasis on smart materials, structural design, responsive mechanisms, and new functionalities that enable multidisciplinary applications. In essence, we observe an inherent relationship between these factors in 4D printing illustrated in figure 7, where materials form the foundation, closely linked to the stimulus, while the chosen materials determine the resolution of designed structures. Additionally, the stimulus is responsible for new functionality arising from the design structure of specific applications. Invariably, the end product of these prerequisites is new functionalities, aimed at solving technical and scientific challenges in multidisciplinary applications. Therefore, a targeted approach to 4D printing design requires holistic consideration of all aspects.

Despite significant progress in 4D printing, further concerted efforts are needed to fully unleash its potential in multidisciplinary fields such as materials, mechanical engineering, chemistry, medicine, optics, and magnetics. Figure 8 provides an overview of the barriers, challenges, and research directions regarding the combination of multiple factors.

Firstly, in terms of printable smart materials, research on 4D printing metamaterials, which have unique properties that make them highly attractive for various applications, should be prioritized [72, 110, 147]. Additionally, printing multi-materials, such as polymers, hydrogels, metals, ceramics, biomaterials, and 2D materials together to enhance programmability and enable more complex transformations is advisable [148–153]. These multi-material architectures can also respond to multiple stimuli, increasing their range of applications. Moreover, controlling intermediary states and persistent transformations with fast response speed is crucial for the adoption of 4D printing technology. It is also important to address the concern of volatile organic compounds that emit from shape transformation processes, especially in polymer materials containing small organic molecules that respond via high-temperature stimulus [154].

Secondly, in terms of printing techniques, the hurdle of multi-material 3D printing needs to be overcome. Although the DIW technique achieves multi-material printing [155], research on integrated multi-process techniques, such as DLP, FDM, SLA, is needed. Other printing advancements, such as low cost, fast printing time, and reliability, are also important. High-resolution 3D printing technology needs to be developed to create complex nanostructures, for example, PμSL [156], multiphoton lithography (MPL) [157], 3D nanoprinting [158]. These developments would increase the design freedom of 4D printing at nano-, micro-, meso-, and macro-scales [159–161].

Thirdly, in the design paradigm, the architectures shall be performed via multi-representation, from voxel, bullet, region, skeleton, to lattice, so that their actuation can be precisely controlled [35]. Multi-function can be achieved via artful designs that include multi-states, multi-configurations, and multi-transformations. For example, most current 4D printing involves two states, i.e. the as-printed state and the as-transformed state. The precise control of both states and the intermediate states is a challenge to realizing the on-demand re-programmability of structures. This requires the programmable shapes to be permanent, evolving with time under environmental stimuli [97]. Future designs should aim towards a multi-world, such as digital, cyber, physical, and social, to build an intelligent world.

Fourthly, 4D printing technology requires the culmination of knowledge from multidisciplinary fields. Incorporating design variables and constraints into a systematic design

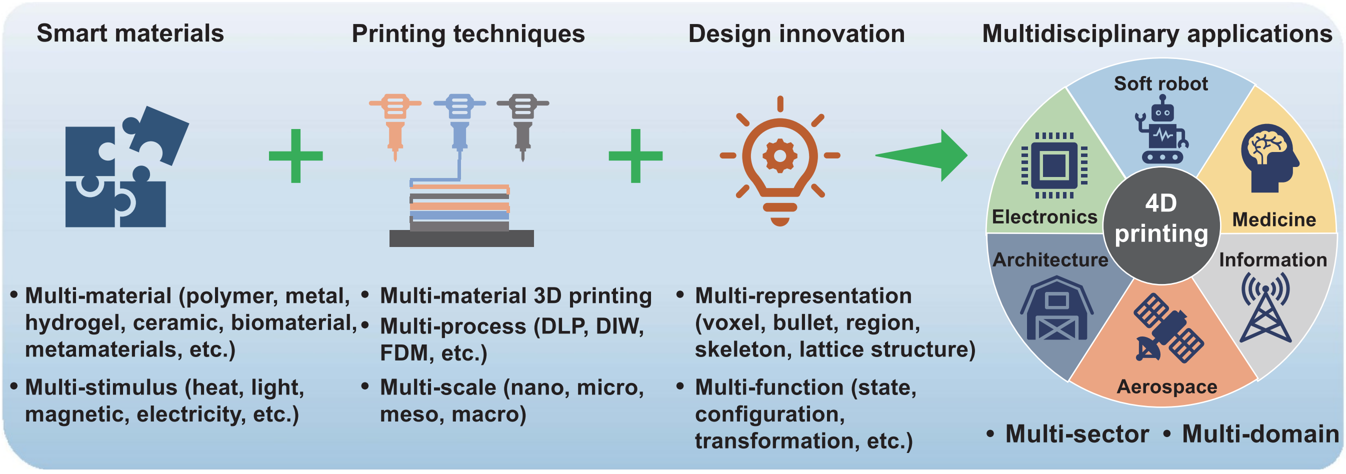

Figure 8. Remaining challenges and further development directions for 4D printing.

framework creates functional shape-changing materials and structures based on specific applications. Novel applications can be explored in sectors including the automotive, aerospace, photonics, electronics, orthopaedics, micromachines, and drug delivery, among many others [36, 162–167]. For example, biomimetic and biologically compliant architectures whose properties and functionalities can controllably vary based on their environment are interesting and very important in diverse applications [168, 169]. These concepts can be adopted by developed by 4D printing.

In conclusion, although 3D printing technology has proven to be widely known and successfully applied across various disciplines, 4D printing technology remains relatively unknown, particularly in civil engineering, transportation, architectural design, electronic information, and other areas. However, if researchers in these fields can design adaptable and responsive pipelines, walls, spaces, and circuits that exhibit dynamic responses for systems of all sizes, these novel functionalities could revolutionize our world and promote smart technology. We believe that more interdisciplinary approaches and collaboration are crucial to enhance the technical readiness of 4D printing for real-world applications. This article emphasizes the significant role of interdisciplinary designs in realizing the full potential of 4D printing for multidisciplinary applications in time. We anticipate that 4D printing technology will rapidly develop based on its unique advantages, broader popularity, and increasing cross-disciplinary collaborations. We encourage researchers experienced in interdisciplinary fields to read this article and consider integrating 4D printing technology into their work to achieve groundbreaking innovations.

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