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Recent advances in additive manufacturing of active mechanical metamaterials

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ABSTRACT

Active mechanical metamaterials are emerging materials receiving tremendous attention in the past decades. Additive manufacturing (AM, or 3D printing) techniques empower the rational design and fabrication of complex, multiscale architectures that enable unprecedented mechanical properties and functionality of metamaterials. Moreover, the use of smart or stimuli-responsive materials for AM of active mechanical metamaterials offers new capabilities to program the mechanical, acoustic, or other functional properties. Herein, we present an overview of recent advances in AM of active mechanical metamaterials. The primary AM techniques used for mechanical metamaterial fabrication are discussed first. Several mechanical metamaterial structures and designs enabled by AM are summarized. Active mechanical metamaterial designs utilizing different stimuli, such as solvents, heat, and magnetic field, are introduced. Additionally, some functional applications of active material systems to create transforming mechanical metamaterials are included. Finally, the outlook and challenges for future research in this field are provided.

1. Introduction

The incessant quest to push the limits of material properties has led to the birth of a category of structures known as metamaterials. These carefully designed, manmade materials typically utilize periodic architectures to induce properties that are hardly found in nature and boast special characteristics such as auxeticity [1–7], negative stiffness [8–10], high specific stiffness [11–13], high thermal insulation [14,15], acoustic bandgaps [16–20], and wave guides [17,18,21]. The unique properties exhibited by metamaterials places them at the forefront of materials research.

With the recent development of simulation-based and machine learning-assisted design tools, the structures of metamaterials have become more complex [22–26]. This increase in geometric complexity presents a critical challenge of fabrication that traditional subtractive manufacturing approaches are no longer suited for, especially regarding features on the micro or nanoscale. Therefore, researchers have leveraged additive manufacturing (AM), or three-dimensional printing (3DP), to realize a breadth of otherwise unachievable geometries. Advances in AM now allow for the fabrication of submicron features that were previously outside our capabilities [11,27,28]. Moreover, some AM technologies enable the construction of mixed material components (or multi-material AM) [29–33], which provide a much wider design space than traditional manufacturing approaches. Recent developments in AM also allow stimuli-responsive materials to be fabricated, which create structures that can transform their geometry, property, or functionality. This is often referred to as 4D printing, with the 4th dimension being time [34–37]. 4D printing is also used to fabricate active mechanical metamaterials (or stimuli-responsive mechanical metamaterials), whose architectures, and thus properties, can be adjusted autonomously based on changing environmental conditions. Active mechanical metamaterials have been fabricated that can respond to a variety of stimuli, such as temperature [38–40], magnetic field [41–45], electric current [46–48], and chemicals (water and pH) [49–52]. Active mechanical metamaterial research is an exciting field that holds the potential to create stronger, smarter, and more versatile materials that will serve as the building blocks for next generation of engineering structures.

In this review, we will cover the major AM techniques currently used in mechanical metamaterial research, including fused filament fabrication (FFF), direct ink writing (DIW), inkjet printing (IJP), vat photopolymerization, and powder bed fusion (PBF). For each of these

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techniques, we will review applications within in the broad field of mechanical metamaterials with a focus on active mechanical metamaterials. We will also cover several other emerging AM approaches that can further expand the mechanical metamaterial design/fabrication space. The third section will introduce some of the unprecedented structures and designs that are enabled by AM. In fourth section, the use of stimuli-responsive materials to achieve active mechanical metamaterials are summarized. Finally, we discuss the current limitations and the future of the fabrication of mechanical metamaterials. It should be noted that mechanical metamaterials are a subarea of the broader term of metamaterials, which also include optical metamaterials. This review will focus on mechanical metamaterials; therefore, for the rest of the paper, we will refer mechanical metamaterials as metamaterials.

2. AM techniques for metamaterials

The ever-growing palate of AM techniques provides a wide array of capabilities to produce intricate metamaterials that are beyond the capabilities of traditional subtractive fabrication methods. Depending on how raw materials are processed into products, AM technologies are classified into seven groups by International Organization for Standardization (ISO Technical Committee 261) and American Society for Testing and Materials (ASTM) International (Committee F42) [53]: binder jetting, directed energy deposition, material extrusion, material jetting, powder bed fusion, sheet lamination, and vat photopolymerization. While many techniques are decades old, there are some significant improvements that continue to push the limits of their manufacturing capabilities. These improvements include the consistency, resolution, speed, and versatility of printable materials. On the other hand, many new printing methods are still being developed. Some examples include direct bubble writing [54], capacitor edge effect [55], acoustophoretic printing [56], and electrohydrodynamic jet printing [57]. While techniques such as sheet lamination, direct energy deposition, and these new AM approaches have many unique applications, we will reserve the limited space below for discussions of the techniques that have seen the most utilization for metamaterials in recent years. Most stimuli-responsive materials are polymers due to their diversity of possible stimuli, easy synthesis, and low cost. As a result, the following sections will predominantly discuss polymer-related AMs.

2.1. Material extrusion

Material extrusion methods include FFF (also known as Fused Deposition Modeling (FDM)) and DIW. They owe much of their popularity to their simplicity. In the FFF process, a spool of solid polymer filament is fed through a hot nozzle, which draws a 2D slice of the desired shape as the filament is continuously deposited onto a build plate. This process repeats one layer at a time until a full 3D part is completed. Similarly, in DIW, a viscous liquid ink is deposited through a nozzle usually by a pressure regulator as the print head traces out each 2D slice (Fig. 1**a**).

FFF is widely used to print engineering thermoplastics, such as acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), and polyether ether ketone (PEEK), as well as fiber or particle-embedded composites. Consequently, FFF is popular for prototyping applications where structural integrity is important due to the excellent mechanical properties of these thermoplastics [58,59]. It is most suitable for relatively simple geometries and where high precision is not paramount. However, preparing high-quality FFF filaments with cutting-edge custom materials is typically a difficult endeavor, so FFF is less frequently used to implement newly designed material compositions. By contrast, DIW printing is a very common technique to employ specialized polymers with interesting functionalities because there are few restrictions on ink composition. These materials include conductive [60,61], cellulose-based [62,63], magnetic [41,64], fiber embedded [40,50,65], liquid crystal elastomers [39,66–68], vitrimers [69], epoxy thermosetting composites [65,70–72], and self-healing materials [73,74]. Researchers have also been able to DIW print biocompatible lattice structures that can provide structural support and provide scaffolding for cell growth [75–78].

DIW has seen several major advancements in recent years. For example, conformal printing brings the ability to print DIW shapes on non-planar substrates [60,79]. Skylar-Scott et al. [80] used a DIW printing method in combination with a sintering laser to fabricate free-standing metallic traces. More recently, Robertson et al. [81] used frontal polymerization to create free-standing polymer traces (Fig. 1**b**). Without the need for any supporting architecture, these technologies could vastly expand the metamaterial design space and increase print speeds. Extrusion printing on axially rotating substrates is another technique receiving attention recently for the rapid fabrication of complex metamaterials [82,83]. Fugitive physical gels have been

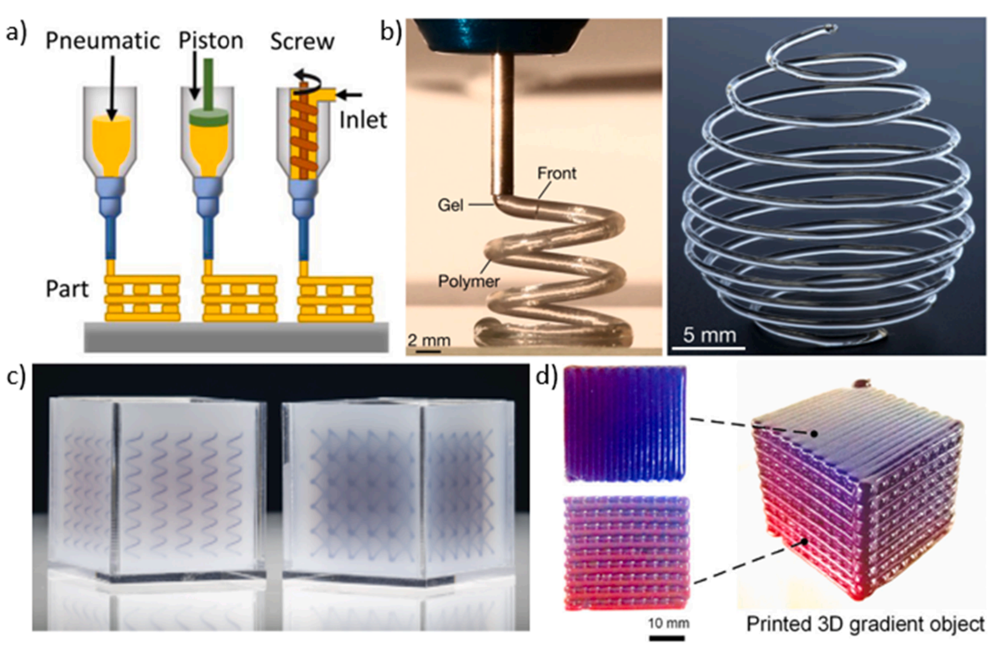

Fig. 1. Recent advances in DIW printing have broadened the palate of achievable structures. (a) Schematic of common DIW setups featuring multiple extrusion methods [13]. Copyright (2019) John Wiley & Sons, Inc. (b) The gel precursor is solidified by a propagating curing front while it is suspended in air, allowing for the writing of material traces in 3D space without the use of supports [81]. Copyright (2018) Springer Nature. (c) DIW has also been used to print directly inside other media, allowing for the creation of complex embedded structures [87]. Copyright (2018) American Chemical Society. (d) New DIW mixing techniques enable the creation of complex functionally graded metamaterials [94]. Copyright (2018) Elsevier B.V.

developed to act as green support materials for complex geometry DIW printing [84–86]. Similarly, Grosskopf et al. [87] studied DIW printing inside of a soft silicone matrix to create complex patterns (Fig. 1**c**). The supporting matrix material allows for omnidirectional printing, which greatly increases the printable geometries.

Material extrusion setups are simple and versatile, but there are several crucial drawbacks. Since each layer must be created from 1D lines, these processes tend to be slow. These setups are also usually limited to just a few materials at one time, making it hard to print functionally graded structures. To this end, mutli-nozzle extrusion [33,88–92], microfluidics [93], and co-extruders with micromixers [29,94–96] have been developed for multi-material printing (Fig. 1**d**). The technique of static material mixers has even been recently adapted for use in FFF printing of thermoplastics [97].

2.2. Inkjet printing

Inkjet printing (IJP) is well known for its capability of multi-material (or digital material) printing. IJP uses rows of piezoelectric nozzles with their size on the order of 20–40 μm to deposit ink drops as the print head pans across the build plate (Fig. 2**a**). In this way, a few quick passes of the print head can create a complete layer of the target structure. The inks used in IJP are photocurable, so a pass with a UV lamp quickly cures each newly deposited layer. The PolyJet technology developed by Stratasys is an advanced form of IJP enabling digital printing of multi-materials. In the PolyJet system, two or more resin inks (typically one rigid and one soft) are deposited side-by-side in a predetermined ratio that determines the final macroscopic properties of the printed material. In this way, PolyJet allows the creation of the so-called digital materials, *i.e.*, a set of materials whose properties can be digitalized within a certain range.

IJP is popular for the construction of acoustic metamaterials since both the geometry and modulus can be easily altered in order to tune the frequency response [98–100]. PolyJet technology provides the means for realizing advanced topology optimized structures designed with multiple materials [101] or specially designed particle-embedded composite systems [102] (Fig. 2**b**). PolyJet has been used to induce simultaneous buckling modes using defect patterning [103] (Fig. 2**c**). The availability of digital materials also facilitates the creation of tunable energy dissipation structures via bi-stable beams [104] or Coulombic friction [105]. The versatility of PolyJet has also been leveraged to create physical logic gates [106] (Fig. 2**d**) and composites with tunable toughness (Fig. 2**e**) [107,108].

Despite its many advantages, IJP also has some limitations. Because droplets of ink are deposited individually, even the smallest overhangs require support materials, making it an inefficient way to create lattices or highly porous structures. Also, IJP has a stringent requirement on the ink properties, such as low viscosity (usually below 20 cP), which limits the ability to use new functional materials or fabricate parts with embedded particles.

2.3. Vat photopolymerization

Currently, vat photopolymerization is another widely studied AM technique, which shows great potential for the fabrication of metamaterials. Vat photopolymerization is a general term used to describe approaches that use light of various wavelengths to selectively cure photo-sensitive polymer resins. Several techniques fall into this category, including stereolithography (SLA), digital light processing (DLP), and two-photon polymerization (TPP). These procedures all begin with a reservoir, or vat, of photopolymer resin, and each employs a different technique to create a hardened part from the liquid resin.

SLA is an early 3D printing method that employs a focused UV laser beam to rapidly scan and cure the resin. This gives it the advantage of a large printing area. But since it uses a scanning laser, its printing speed can be slow, especially when the part is large. In addition, most SLA printers are commercial ones, which limits their compatibility with customized polymers.

DLP printing can be considered as an extension of SLA and has become popular in recent years due to its low cost, simple setup, and high printing speed. In DLP, a projector shines a 2D light pattern into the resin vat, curing one layer at a time. The top-down approach (depicted in

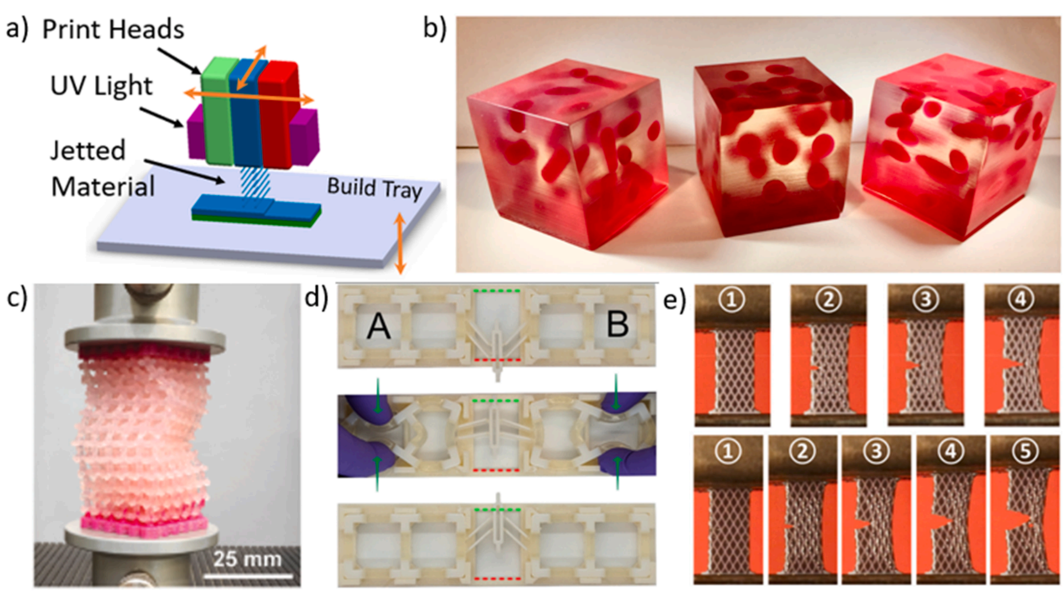

Fig. 2. IJP is popular in cases where multiple materials are incorporated into a single structure. (a) Schematic of the typical inkjet setup. Three different heads are used to print two different structural materials and a support material. The volume ratio of the two materials can be adjusted to tune the material properties (adapted from [109]). Copyright (2017) American Association for the Advancement of Science. (b) PolyJet can be used to create particle composites with tailorable particle shape, size, and distribution [102]. Copyright (2020) Springer Nature. (c) Using PolyJet technology to place rigid defects in a periodic lattice can produce complicated buckling phenomena [103]. Copyright (2019) Royal Society of Chemistry. (d) The ability to locally control material properties can lead to interesting responses such as this physical AND gate [106]. Copyright (2020) Elsevier B.V. (e) By varying the ratio of the digital materials in a 2D composite structure, the fracture properties can be tuned [107]. Copyright (2018) Elsevier B.V.

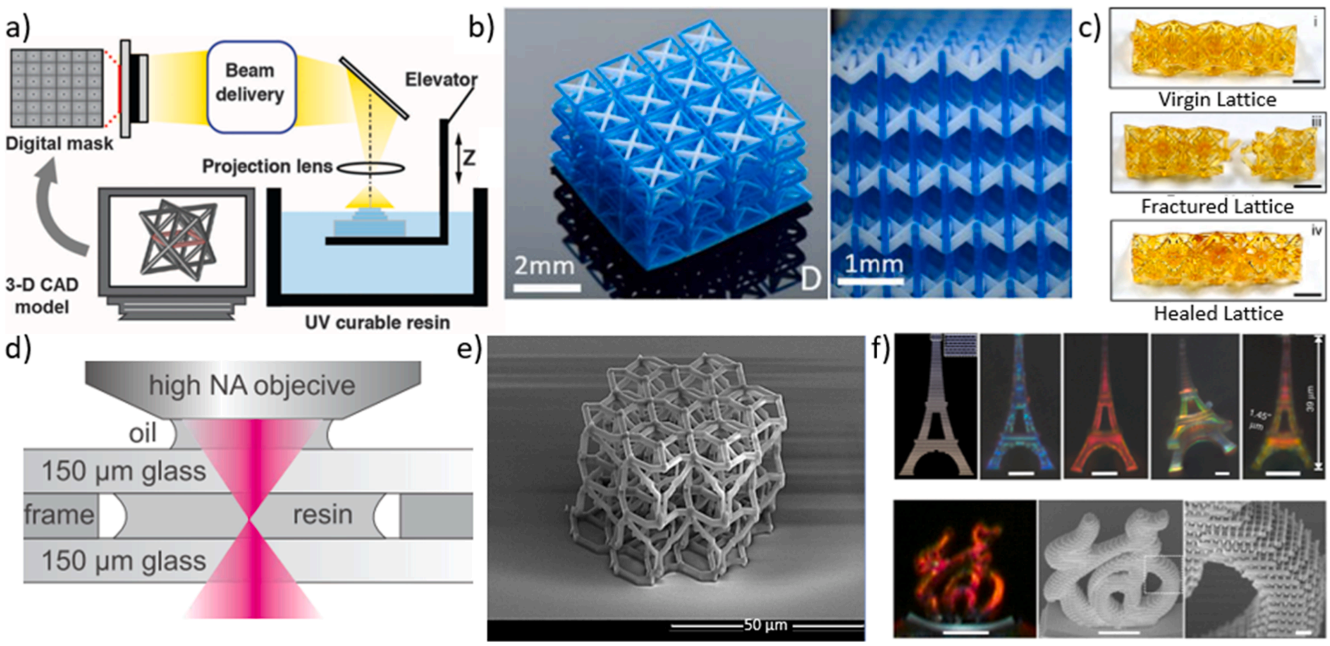

Fig. 3. Vat photopolymerization techniques have been employed to create a plethora of unique metamaterials. (a) Schematic of the typical DLP process. 3D models are sliced into 2D images, which are sent to the DMD device and projected into the vat [12]. Copyright (2014) American Association for the Advancement of Science. (b) A multi-material μDLP process can be used to locally vary the material properties throughout a structure to create metamaterials with widely tunable Poisson's ratio [119]. Copyright (2018) Springer Nature. (c) The flexibility of vat polymerization can lead to the creation of parts with specialized functionality such as healability [123] (scale bars: 4 mm). Copyright (2020) Springer Nature. (d) Schematic of the TPP process. A precisely focused laser is shone into a small pool of resin, and the focal point is tightly controlled to draw microscopic sculptures in the resin [139]. Copyright (2004) The Optical Society. (e) The buckling properties of microscopic lattices can be widely controlled using TPP [136], Copyright (2019) Elsevier B.V. (f) Structures can be shrunk after TPP printing to achieve even tighter lattice spacings, allowing the structures to exhibit photonic phenomena [137] (scale bars: 10 μm, bottom right: 1 μm). Copyright (2019) Springer Nature.

Fig. 3**a**) features a light source facing downwards into the vat to cure the resin. The light source can also be projected upwards through a transparent window in the bottom-up approach. The projectors typically employ a digital micromirror device (DMD) which uses an array of tiny mirrors to independently control the on/off state of each pixel. This means DLP methods typically have a resolution of 50–100 μm. Larger print sizes are possible but at the price of lower resolution. A variant of DLP called micro-DLP (μDLP, or projection micro-stereolithography PμSLA) can print finer features down to 0.6 μm [110] by significantly decreasing the DMD focal distance. But this approach results in much smaller printed parts [110–112]. A significant enhancement to bottom-up DLP is the continuous liquid interface production (CLIP) [113]. The CLIP technique takes advantage of the photoinhibition effect of oxygen and uses an oxygen permeable window to create a very thin layer of uncured resin (or the dead zone), which eliminates the possibility of window adhesion and vastly increases the print speed up to ~500 mm per hour [113]. A more recent high-area rapid printing (HARP) method developed by Walker et al. [114] utilizes an immiscible oil layer to prevent adhesion, which also increases the print speed to ~430 mm per hour. In addition, volumetric projection approaches, in which liquid resin is illuminated from multiple directions or with an evolving image into a rotating resin vat, are able to rapidly form a complex structure in minutes [115–117]. DLP printing of multiple materials has also been achieved using various techniques. Kowsari et al. [118] employed an accurate and efficient multi-material DLP process to create metamaterials with sharp property transitions. A similar technique was applied to μDLP by Chen et al. [119] (Fig. 3**b**). Wang et al. [120] employed a multi-material PμSLA approach to print a metamaterial with negative thermal expansion. Another recent improvement is grayscale DLP printing, which uses the light intensity to locally control the degree of cross-linking in the cured regions [31,78,121,122]. When grayscale is combined with the two-stage curing (photocuring (3D printing) followed by the thermal curing), parts with large property difference (modulus ranging from 1 MPa to 1 GPa) can be created [31], which greatly expands the application scope of the DLP printing method. An advantage of DLP printing is its easy setup, which also permits the usage of customized functional inks. For example, Yu et al. [123] have used DLP to create healable metamaterials that can be put back together and reused after fracture (Fig. 3**c**) with only minimal degradation after multiple healing cycles. Many other new materials and resins have been developed to enable resilient mechanical properties and functional properties, which can greatly enhance the research of printed metamaterials [124–134].

TPP is an approach similar to SLA and utilizes a laser beam to draw the desired shape in the resin (Fig. 3**d**). Here, curing only occurs due to the simultaneous absorption of two photons, which is a rare event that only happens in very high intensity focal point of the laser. In this way, the beam can penetrate into the resin vat without curing the upper regions. TPP can print structures with submicron resolution typically around ~100 nm [27] with some techniques decreasing the achievable feature size to ~40 nm [135]. Using this approach, lattice structures can be printed with a total size of ~50 μm (Fig. 3**e**) and exhibit a tunable buckling response [136]. More recently, by employing a thermal shrinkage process after TPP fabrication, Liu et al. achieved structures with a lattice constant as small as 280 nm [137]. These structures have optical stopbands in the visible wavelength range, enabling them to reflect certain colors based on their geometry alone (Fig. 3**f**). Gross et al. [138] were able to decrease the achievable feature size by coupling TPP with a subtractive etching procedure in which printed features were manually eroded after fabrication. This was applied to lattice structures to create architectures with extremely thin struts 19 nm thick as well as more complicated structures, such as a microscopic flower.

2.4. Powder bed fusion

Another technique for the 3D printing of polymers and metals is powder bed fusion (PBF), which includes techniques such as selective laser melting (SLM), electron beam melting (EBM), and Multijet Fusion (MJF). In these techniques, a thin layer of powder is deposited on a print bed, and a high-powered laser or light source can generate high energy to heat the power layer according to desired 2D pattern, which leads to the local sintering of the materials. This technique can be used to make complicated components that cannot be easily machined or injection molded. Researchers have used PBF to construct hollow lattices [140], lattices with tapered walls [141], and even difficult pentamode metamaterials [142]. Interesting polymer-based structures with widely tunable Poisson's ratio [143], high energy absorption capacity [144], and novel auxeticity mechanisms [145] have also been achieved using the same techniques.

3. AM fabrication of metamaterials with complex structures

The aforementioned improvements to printing techniques have unlocked access to complex architectures that enable the creation of an array of new designs and structures. This increase in structural complexity has led to metamaterials with improved properties such as chiral metamaterials that twist under compression [2,4,5,146–149] and acoustic metamaterials that deftly manipulate sound waves [98,99,150]. While there are many exciting metamaterial structures, here we will focus on multi-stable, hierarchical, and graded

Fig. 4. AM advances have allowed for the creation of complex metamaterial structures. (a) While most multistable metamaterials exhibit a snapping phenomenon in one direction, these novel structures exhibit independent snapping in all three directions [104]. Copyright (2020) Elsevier B.V. (b) These origami-inspired multistable metamaterials can transform into multiple stable states as opposed to the two states of most snapping metamaterials [158]. Copyright (2019) Springer Nature. (c) IJP can be used to create complex hierarchical metamaterials that have improved energy absorption [164]. Copyright (2018) Elsevier B.V. (d) Printed metamaterials combining two auxetic patterns exhibit significant transformations under tension [2]. Copyright (2018) Springer Nature. (e) An advanced non-linear optimization procedure can be combined with PolyJet printing to create lattice structures with tailored response profile [167] (scale bar: 20 mm). Copyright (2019) Elsevier B.V. (f) Grayscale DLP printing can be used to fabricate lattice structures that exhibit simultaneous buckling in two directions and sequential buckling in the third direction [31]. Copyright (2019) American Association for the Advancement of Science. (g) SLA is used for the fabrication of complex graded metamaterials with the porosity tuned in such a way that the degrees of freedom can be pre-determined [169]. Copyright (2019) John Wiley & Sons, Inc. (h) Directionally compliant metamaterials can be fabricated with TPP, and they will exhibit tunable deformations under certain loads. These structures are modular, so they can take a variety of shapes and achieve the same deformation [170] (scale bar: 50 μm). Copyright (2019) Springer Nature.

metamaterials.

3.1. Multi-stable metamaterials

A commonly studied metamaterial is the multi-stable snapping structure. In these structures, local energy minima are utilized to achieve recoverable energy absorption unlike the permanent losses seen due to damage, plasticity, friction, or viscosity. These materials are extensively researched due to their considerable potential for energy trapping [151,152] or wave guiding [153]. Many such structures are 2D patterns extruded into 3D space, therefore, IJP is often employed [154–156]. Moreover, the amount of energy absorption is dependent on small changes in the geometry or the modulus, which can both be easily tuned using digital materials offered by IJP. Yang and Ma [104] demonstrated that these 2D snapping structures could be extended into three dimensions for increased energy absorption and versatility using FFF. They were also able to produce complicated 3D multi-stable metamaterials shown in Fig. 4**a** using a combination of FFF and IJP [157]. The ability to construct these structures in 3D configurations is an important step to employing these designs in more applications. More recently, Iniguez-Rabago et al. [158] used FFF to explore a different kind of 3D multi-stable metamaterial inspired by origami (Fig. 4**b**). These prismatic metamaterials use FFF-printed cell walls as building blocks connected by thin, laser-cut mylar hinges. These structures feature multiple stable states as compared to the two stable states displayed by most snapping metamaterials, enhancing their utility as energy absorbing structures. Similarly, Zhang et al. [159] employed FFF to create a multistable hexagonal metamaterial that uniquely exhibited stability in some tilting directions.

3.2. Hierarchical metamaterials

An exciting area of research is to use common architectures as a base to create hierarchical metamaterials [12,160,161]. A simple 2D geometry prevalent in many engineering applications is the honeycomb [162]. Inspired by nature and highly regarded for their low weight and energy absorption capabilities, honeycombs are compliant in the planar directions and stiff in the out-of-plane direction. IJP has been utilized to create hierarchical honeycomb structures that exhibit tunable stiffness and Poisson's ratio [163] or that have better energy absorption and recoverability in compression [164] (Fig. 4**c**). Other hierarchical metamaterial designs have also been investigated using IJP. Jiang and Li studied combining chiral shapes and reentrant shapes [2], which are both common patterns to achieve auxeticity. In this work, the combination of the two patterns enabled significant tunability across a wide strain range, as shown in Fig. 4**d**.

While these structures exhibit interesting properties, most designs are 2D patterns and the size of the unit cells are on the order of millimeters. To overcome this first limitation, Yang et al. [143] employed SLM to create polymer lattices that combined several different 2D geometries to create several distinct 3D unit cells. These structures exhibited widely varying porosity, Young's modulus, and Poisson's ratio. The second limitation, namely the scale of the metamaterials, can be addressed by TPP. Meza et al. [165] employed TPP to construct metamaterials with three levels of structural hierarchy. The precision of the TPP process allowed for the creation of nanolattices with unit cell scales below 10 μm. These structured metamaterials showed improved structural toughness and damage tolerance, but Meza et al. [165] also pointed out that the use of hierarchy beyond two levels may not further improve structural properties.

More recently, Moore et al. [166] combined DLP printing procedure with phase separating resins that allows for tunable multi-level hierarchy. The resins contain a mixture of a pre-ceramic polymer and an organic polymer that are hardened into a bi-continuous structure during photocuring. The DLP procedure allows for the creation of complex geometries, then a pyrolysis step removes the organic polymer, leaving behind a porous substructure. Because the phase separation reaction is time-dependent, the substructure can be locally tuned by varying the light intensity. Other novel techniques such as direct bubble writing (DWB) [54] can be used to tailor both the macroscopic shape and microstructural properties of metamaterials to evoke nuanced mechanical properties.

3.3. Graded metamaterials

Digital materials enabled by PolyJet technology can provide both geometric and property versatility, allowing material gradient designs that were previously unachievable. The flexibility and convenience of this technology was utilized by Weeger et al. [167] to print graded lattice structures (Fig. 4**e**). These structures were designed with a nonlinear optimization workflow incorporating Rhinoceros®, Grasshopper™, and IntraLattice to achieve certain deformation responses. Fig. 4**e** shows a shoe sole where radius gradients in the lattice could be employed to locally tune the energy absorption under certain regions of the foot. Kuang et al. [31] reported the grayscale DLP printing combined with a two-stage curing resin to create functionally graded lattice structures that demonstrate vastly different compression properties in two directions (Fig. 4**f**). In the direction normal to the gradient, the foam is uniform in the compression direction, so simultaneous buckling occurs. In the gradient direction, however, buckling occurs layer-by-layer, which could lead to energy absorbers with greatly improved performance.

In addition to locally varying the material properties of a part, structural variation can also be utilized to produce a gradient in stiffness. Yuan et al. [168] used 3D printed molds to press graded origami shapes into metallic sheets. Varying the characteristic angle of the Miura architecture affects the stiffness of the structure, effectively producing a property gradient. A more common method to structurally control the stiffness is by tuning the porosity. This is preferred method for creating functionally graded foams (FGFs) since locally controlling the modulus is difficult during foam fabrication. Goswami et al. [169] employed SLA to create lattice structures with the porosity tailored to make certain degrees of freedom more compliant than others. Using this approach, they were able to create grippers, crawling robots, and a biomimetic hand (Fig. 4**g**) with predetermined deformation modes defined by the printed lattice structure. Directionally compliant metamaterials (DCMs) [170] (Fig. 4**h**) are another class of structures that are designed to deform only in certain degrees of freedom. These unique structures are modular, so they can take a wide variety of shapes while retaining their desired compliance properties. This gives DMCs great potential in fields such as robotics or biomedicine.

4. Active metamaterials

Metamaterials have been shown to exhibit a wide range of desirable properties from ultra-high specific stiffness to tunable auxeticity. Still, these properties typically remain unchanged after fabrication, limiting their functional applications. For this reason, active metamaterials (or stimuli-responsive metamaterials), which can exhibit geometric transformations under external stimuli to modify the metamaterial properties after fabrication, are actively pursued in recent years. Creating these advanced structures has been facilitated by AM of stimuli-responsive materials, also referred to as 4D printing (the fourth dimension being time) [34,36,37,171–177]. Various stimuli-responsive materials, including hydrogels [49,50,178,179], shape memory polymers [1,180–183], liquid crystal elastomer [39,184–186], and magnetoactive soft materials [41,44,187–189] can be exploited to fabricate active metamaterials.

4.1. Active metamaterials by swelling/deswelling

The shape shifting induced by swelling/deswelling is a widely used mechanism for active metamaterials. The most common example is to use composite hydrogels or anisotropic hygroscopic composite materials, which can uptake and release water [50,190–193]. For example, Mao et al. [194] have demonstrated using PolyJet to produce sequential self-folding structures by using the swelling mechanism of hydrogels. Zhang et al. [49] utilized this capability to further produce bilayer metamaterials with an active hydrogel layer and an inactive polymeric layer. When placed in water, the hydrogel undergoes swelling, leading to the shape shifting of the lattice (Fig. 5**a**). By tuning the initial lattice geometry as well as the hydrogel distribution, they were able to achieve programmable, reversible deformations. Liu et al. [195] have employed a PμSLA approach to create 2D metamaterials with 100 μm wall thickness that can exhibit negative swelling ratios when immersed in acetone. This is accomplished by inducing a buckling effect caused by a swelling mismatch between the inner core and outer layers of the printed structures. After printing, the top and bottom of the metamaterial are irradiated by another dose of UV light, which gives the outer layers a higher stiffness and lower swelling ratio than the less-cured core of the structure. When immersed in acetone, these outer regions will tend to deform less, forcing the core to buckle and leading to the shape changes (Fig. 5**b**). DLP enables location specific material swelling, which can be used to achieve local shape shifting [173,196–199]. For example, Kim et al. designed responsive buckled surfaces by halftone gel lithography [198]. Two photomasks were exploited to locally control a highly cross-linked dots region embedded in a lightly cross-linked matrix to access nearly continuous, and fully two-dimensional, patterns of swelling. With this method, complex surfaces with constant Gaussian curvature (spherical caps, saddles, and cones) or zero mean curvature (Enneper's surfaces) as well as more complex and nearly closed shapes can be easily fabricated. Swelling due to lithiation can also be used to create a controlled shape change. Xia et al. [46] used TPP to fabricated lattice structures (Fig. 5**c**) then coated the lattices with a thin layer of nickel and silicon. The metamaterial lattice deformed into predetermined buckling modes due to lithiation under an electric current. Because the active mechanism is lithiation, the deformation is held constant when the electrical stimulus is removed, which is highly desirable for acoustic bandgap structures and deployable or pop-up metamaterials. Moreover, the buckling is almost completely reversed after a delithiation procedure. Recently, Huang et al. [51] reported a graded active metamaterial using grayscale TPP procedure to tune the crosslinking density on the microscale. When the printed structures swelled, the tailored crosslinking differences caused controllable buckling to occur. Small 2D building blocks were linked together to make active tubular lattice-like structures. These tubes were then connected in long rows to make active strips (Fig. 5**d**). The active metamaterial strips were used to create a 500 μm transforming structure that could alternate between a car and a humanoid configuration.

4.2. Thermally active metamaterials

Heat induced shape-shifting has been widely utilized for active structures [34,36,200,201]. Hu and coworkers used FFF to print PLA for thermally triggered pattern transformation due to heat-induced shrinkage of the structure [202]. Moreover, local and inhomogeneous shrinkage for complex shape shifting can be achieved by controlling the porosity and thickness of the constructs as well as through bilayer design [203]. Shape memory properties of FFF filaments have also been used to produce shape recovery metamaterials that could return to their initial states [1,204,205]. Additionally, when the filament cools after deposition during FFF, some volume shrinkage is observed, which introduces residual stresses in the part. The magnitude of residual stress can be controlled by varying the temperature of the deposited filament. These internal stresses can be designed to drive a shape change above the glass transition temperature [206]. Naify et al. [47] used a conductive PLA (cPLA) filament to print acoustic membranes with controllable resonance frequencies. Passing a current through the conductive membrane induced a change in temperature, which acted to alter the membrane's frequency response. Incorporating rationally placed nonconductive PLA regions allowed for a non-symmetric temperature change, which introduced further adaptability of the metamaterial's frequency response. This is a promising technique to introduce active frequency control in acoustic metamaterials.

DIW printing causes high shearing on the resin within the small nozzle tip, which acts to align fibers or long polymer chains within the ink. This is highly beneficial to 4D printing applications in which fiber alignment is critical. Recently, Boley et al. [40] reported DIW-printed 3D

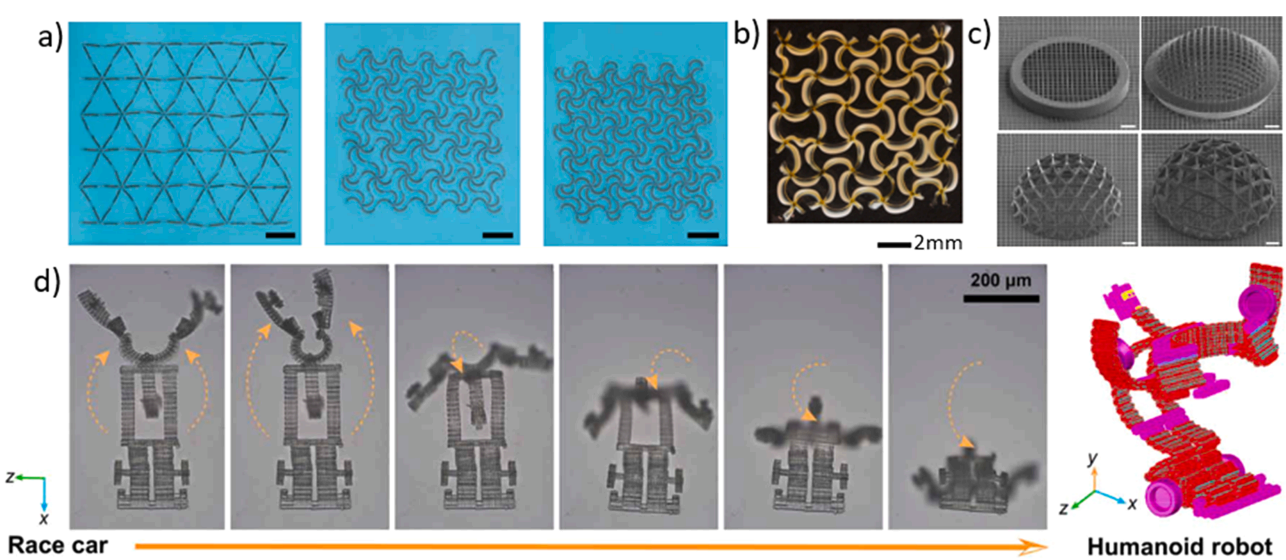

Fig. 5. By tuning the swelling ratio of constituent materials, competing eigenstrains can be leveraged to realize complex deformations. (a) Multi-material inkjet printing allows for the creation of large metamaterials composed of hydrogels and inactive materials to achieve drastic swelling configurations [49] (scale bars: 40 mm). Copyright (2018) American Society for the Advancement of Science. (b) Micro-stereolithography allows for the creation of tiny metamaterials that exhibit negative swelling ratios [195]. Copyright (2016) John Wiley & Sons, Inc. (c) TPP-printed structures are given extra coatings of nickel and silicon, which causes buckling during lithiation. This makes the deformation electrically controllable [46] (scale bars: 15 μm). Copyright (2019) Springer Nature. (d) A grayscale TPP process is employed to locally tune the cross-link density on the microscale. Small building blocks are combined for form larger shape-shifting structures [51]. Copyright (2020) American Association for the Advancement of Science.

shape-shifting lattices using thermal expansion mismatch of glass fiber-reinforced poly(dimethylsiloxane) (PDMS) multi-materials (Fig. 6**a**). The thermal expansion coefficients of the printing inks were controlled by varying the mixing ratios of the PDMS components and adjusting the loading of glass fibers. In Boley's work, four distinct ink recipes were used to create bilayer patterns in the two directions normal to the printing direction, which allowed for both in-plane and out-of-plane buckling. This additional direction of bending control makes this technique more versatile than previous works, vastly increasing the design space for active structures. For example, structures as complicated as a human face were achieved after transforming an initially planar 2D structure. In addition to fibers, DIW printing is used to align long polymer chains within the ink. For example, the DIW nozzle can align mesogens, the active component of LCE, which exhibits large shrinkage upon heating. Roach et al. [39] used this principle to create metamaterials that combined the active LCE with thermally inert materials to achieve shape transformation (Fig. 6**b**). DIW printing of shape memory composites can also be implemented for active metamaterials [73,207]. For example, Chen et al. [207] reported a printed method called dynamic photo mask assisted DIW to print multi-material-based lattices with controlled buckling and crack propagation pathways.

IJP of SMP and composites has been widely investigated for active metamaterials [1,183]. PolyJet technology enables direct 4D printing by which the desired transformation can be programmed during printing as opposed to afterwards [109]. Wagner et al. [208] leveraged the shape memory effect (SME) of IJP materials to create metamaterials with

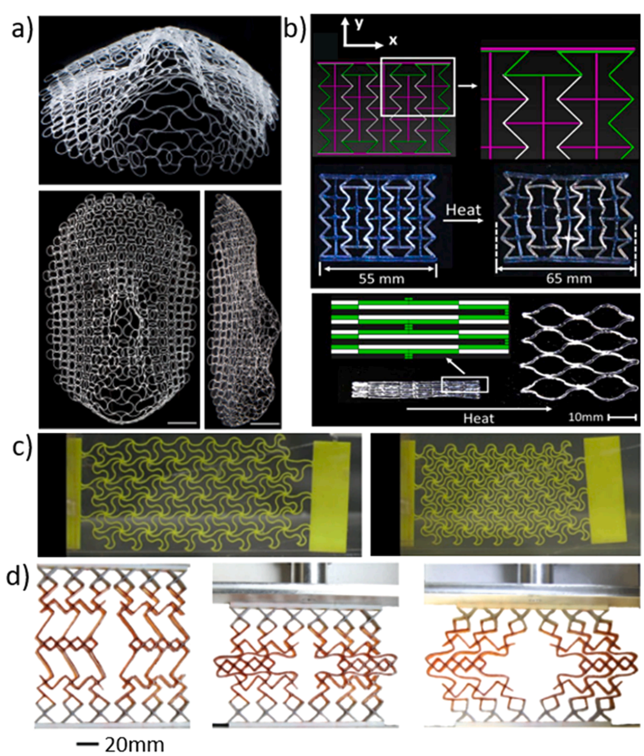

Fig. 6. Metamaterials have been created that can deform under thermal stimuli. (a) These 2D patterns are printed with four materials to cause in-plane and out-of-plane buckling modes. This allows them to achieve topologically complex deformations such as a human face [40]. Copyright (2019) National Academy of Sciences. (b) LCE can be combined with thermally inactive materials to exhibit interesting metamaterial deformations [39]. Copyright (2018) IOP Publishing. (c) The shape memory effect can also be observed in inkjet materials, which can exhibit larger deformations under thermal stimulus [183]. Copyright (2020) American Chemical Society. (d) Inkjet-printed molds can be used to create thermally responsive metamaterials like this smart window that will automatically open or close as the temperature changes [38]. Copyright (2018) John Wiley & Sons, Inc.

programmed shape transformations. More recently, Wang et al. [183] demonstrated the substantial thermal transition of horseshoe metamaterials as shown in Fig. 6**c**. Digital materials can also be used to locally tune the glass transition temperature of a structure in a voxel-like manner. Under this principle, some regions can be active and others inactive at certain temperatures. Hamel et al. [209] utilized this concept and demonstrated the ability to use machine learning to design active/inactive voxel patterns to achieve a desired deformation. This capability could be an effective tool for the future design of voxel-printing based active metamaterials. PolyJet can print glassy polymers and elastomers, which have a large difference in thermal expansion coefficient. This feature was used by Li et al. [210] to create shape shifting structures. In addition, polymers change their modulus dramatically as the temperature crosses their glass transition temperature. This can also be used to evoke a shape change. For instance, Yuan et al. [38] employed IJP to create a mold to fabricate metamaterials consisting of a glassy polymer and an elastomer. By choosing a glassy polymer whose rubbery modulus was lower than the elastomer, a transition of buckling patterns could be achieved under a combination of mechanical and thermal stimuli. In Fig. 6**d** this principle was used to create a smart lattice with a window that opened as the temperature increased.

Vat polymerization can also be used to create SMPs. Pandini et al. [211] demonstrated that SLA printing could be used to fabricate 2D SMP-based metamaterials that exhibited controllable out of plane deformations. Yang et al. [212] employed a DLP process to realize 3D shape memory metamaterials that can be reconfigured into new geometries. In this way, the printed metamaterials can be designed to serve multiple unique applications. Tabrizi et al. [213] demonstrated a method to locally control polymer alignment by combining permanent magnets with DLP printing. This method has a much higher programming resolution that previous extrusion-based alignment techniques. These printed structures can exhibit shape transformations due to competing eigenstrains due to stimuli such as heat or light. Fang et al. [214] used a DLP process to create modular metamaterials that were fused together via interfacial bond exchange, providing more flexibility than as-built structures.

4.3. Magnetoactive metamaterials

Hard-magnetic soft active materials (hmSAMs) are exciting stimuli-responsive materials that have recently been explored. Hard-magnetic particles, in contrast to their soft magnetic counterparts, have high magnetic remanence and coercivity, which exert micro-toques on the material under an applied magnetic field. This can be used to drive the shape change of the soft matrix material to achieve untethered, rapid, and reversible actuation. These advantages can be exploited to create reprogrammable active metamaterial structures. Kim et al. [41] employed a DIW printing approach that aligns magnetic particles to the printing direction. Under an applied magnetic field, the magnetic particles will drive the shape change of the printed structure to produce complex but predictable deformations (Fig. 7**a**). Recently, Wu et al. [44] employed this material system to create metamaterials with asymmetric joints that can achieve distinct deformation modes under an opposite magnetic fields as seen in Fig. 7**b**. In addition, Wu et al. [64] used the DIW printing process to achieve voxel-level magnetization control and combined this new capability with the evolutionary algorithm to design the proper magnetic orientations for complicated active structures. This new capability can be used in the future to design and construct highly complex magnetoactive metamaterials. Ze et al. [187] developed a magnetic shape memory polymer (M−SMP) that responds to both thermal and magnetic stimuli, which was then utilized by Ma et al. [215] to DIW print multi-material, multi-responsive metamaterials. The asymmetric joints in Wu et al. [44] were exploited by Montgomery et al. [45] to create rapidly actuating metamaterials with tunable stiffness, Poisson's ratio, and bandgap response. Roh et al. [188] also used a DIW process to print magnetoactive metamaterials. In this work, the printed

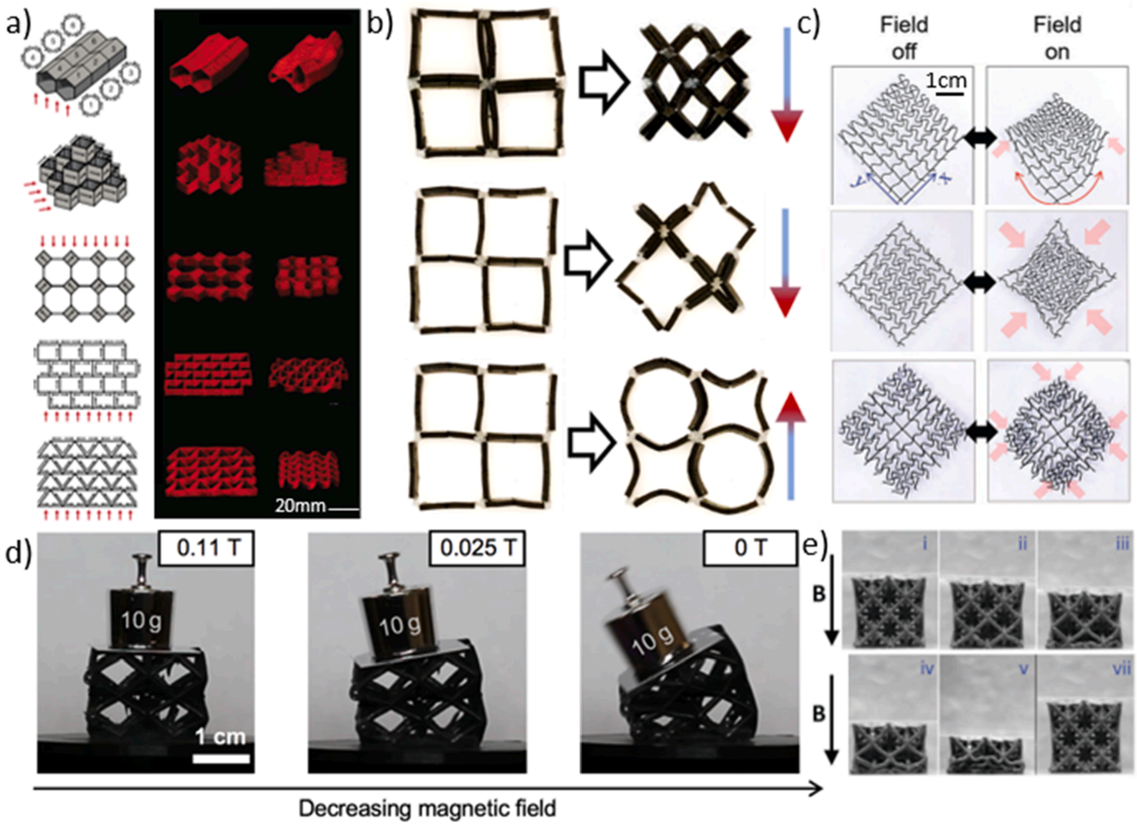

Fig. 7. An emerging mechanism for active metamaterials is magnetism. (a) A novel DIW approach is used to tune the magnetic pole orientation of different regions during printing. This leads to intricate deformations that can be well-predicted [41]. Copyright (2018) Sringer Nature. (b) Metamaterials that use an asymmetric folding joint can achieve drastically different configurations under opposite magnetic fields [44]. Copyright (2019) American Chemical Society. (c) A DIW printed metamaterial that floats on water harnesses magnetic and capillary forces to achieve interesting deformations [188]. Copyright (2019) John Wiley & Sons, Inc. (d) An SLA-printed hollow lattice is filled with a magnetic ink that can be used to adjust the lattice stiffness under a magnetic field [217]. Copyright (2018) American Association for the Advancement of Science. (e) A 3D printed scaffold allows for the injection of a magnetic ink followed by the dissolution of the scaffold. Applying a magnetic field changes the acoustic absorption properties [218]. Copyright (2018) John Wiley & Sons, Inc.

material was composed of iron particles embedded in PDMS microbeads. The printed structures were placed on the surface of water and would contract in the presence of a vertical magnetic field due to a combination of magnetic forces and capillary forces from the water (Fig. 7**c**). DIW has also been used by Pierce et al. [216] to produce tunable acoustic metamaterials, which demonstrates the ability to use DIW to produce effective tunable acoustic metamaterials.

Vat polymerization can also be used to create molds for novel magnetic materials that have not been optimized for 3D printing. In these situations, DLP and SLA remain the preferred method to construct porous or lattice-like molds. Jackson et al. [217] employed SLA to create hollow lattices infilled with magnetic ink, which imbues the lattices with tunable mechanical properties under a magnetic field (Fig. 7**d**). Similarly, Yu et al. utilized DLP printed scaffolds to create lattices with hollow struts (Fig. 7**e**) comprised of a magnetoactive ink [218]. These structurally complex metamaterials can exhibit widely tunable acoustic properties using a remote magnetic field. Xu et al. [219] exploited selective exposure of UV light to encode hard magnetic particles in planar materials with arbitrary 3D orientation at micrometer scale. 3D magnetization profiles were also achieved by rotating the magnet during photocuring, allowing for higher-order and complex bending and torsion for microrobotic locomotion. Similarly, Shinoda et al. [220] used SLA to directly print hmSAM structures by rotating a nearby magnet to control the local magnetic dipole orientation.

Cui et al. [221] employed an electron beam lithography process to deposit nanomagnets on a soft/stiff silicone membrane. Rigid members were connected by softer members which acted as hinges. This work utilizes multiple types of magnetic particles with unique hysteresis loops, which allows the different particle directions to be programmed independently. This freedom allows for the creation of interesting morphing shapes on a small scale.

5. Outlook & perspectives

Recently, metamaterials have seen a surge in research focus, especially in the realm of stimuli-responsive materials. This has led to the development of unique structures that can control the propagation of waves or mechanical properties by transforming between multiple complex configurations. New advances in 3D printing technology have also led to improvements in fabrication times and printable resolution so that metamaterials can be printed faster and more accurately than before. Although significant progress has been made, there are still many challenges and opportunities to be explored.

First, the size and shape of active metamaterials has thus far been limited. Most active metamaterial structures tend to be confined to the millimeter scale since many of the typical actuation mechanisms have not yet been introduced to micro- and nano-scale printing techniques. Some works have addressed this by adding an active coating to a TPP printed structure [46,222] or by grayscale TPP [51,223]. In addition, very large active metamaterials are also rare due to the need for special materials and fabrication procedures. More scalable AM techniques are needed for 3D-printed structures to compete with traditional engineering materials. An expanding area of research is in volumetric projection approaches in which liquid resin is illuminated from multiple directions to rapidly form the structure. The two main approaches are computed axial lithography (CAL) [115,116], which projects an evolving image into a rotating resin vat, and holographic volumetric fabrication [117], which employs three overlapping holograms. Interference-based techniques, such as five beam holographic lithography [224] and self-propagating polymer waveguides [225], also show some potential. In addition, a modular printing approach via the assembly of individual printed parts can provide an alternative solution [215,226].

Another challenge facing metamaterial AM is balancing printing speed, size, and quality. Usually, the printing size is sacrificed for improvements in resolution and quality. For example, in μDLP, a very high resolution can be achieved, but the projection area is decreased significantly compared to typical DLP setups. There have been several recent advances to increase print sizes without sacrificing resolution. One solution is the large area projection micro stereolithography (LAPμSL) [160], which combines the scanning lens of SLA with a μDLP projection to allow for the fabrication of larger scale parts with microscopic features. Additionally, Wang et al. [227] manipulated the focal length of a DLP setup to create both large and very fine features with one projector. In this way, large structures with some fine details can be fabricated. These techniques that bridge multiple length scales are promising for the fabrication of next-generation mechanical metamaterials. As metamaterials become more complex, involving smaller building blocks and units, the more susceptible they become to small defects during production. This can be detrimental to metamaterial performance [165]. Even at a larger scale, since final quality is tightly related to printing parameters, it often takes many attempts to achieve a defect-free product. To remedy this, the convergence of machine-vision and machine leaning has enabled real-time feedback controls to increase the success rate on AM systems [116,228,229]. Further work in this area is necessary to ensure that even the most complicated structures are printed with minimal defects on the first try.

Advanced designs are desirable to enhance the unique functional properties of metamaterials. There are several promising areas of mechanical design that warrant more arduous exploration. Although unintentional defects can be the bane of metamaterials, precisely positioned defects can be desirable in some instances. This is useful in wave guiding [230], pattern transformation [46], rare buckling phenomena [103], and failure property enhancement [231]. Another exciting area of research is material property gradients. Coupling the advances in metamaterial structure design with new printing capabilities such as PolyJet and grayscale DLP printing could lead to more resilient structures than have been achieved so far. The addition of predesigned defects or material property gradients will greatly increase the metamaterial design space, so recent advances in machine learning-based design tools should be leveraged to properly study these vast spaces. The use of active materials to fabricate hierarchical metamaterials has not been well explored, nor has their use in interesting designs such as graded lattices, chiral metamaterials, or multi-stable energy absorbers.

Lastly, innovation in materials is critical for enhancing functional applications of metamaterials. Printed structures with extreme properties, such as high or low stiffness or high toughness [232], can be further enhanced by incorporating more robust materials. But it remains a challenge for AM to expand into these material realms. To further harness the programming capability of active metamaterials, the intelligent coordination of the active mechanism with the underlying metamaterial properties is required. A wise choice of stimuli-responsive materials for shape programming also needs to be considered for specific applications. For example, light and magnetic field can enable remote actuation in aerospace and biomedical applications, while water responsiveness may be particularly suitable for some biomedical devices. Therefore, the proper selection of both smart material and printing technique must be carefully investigated as these applications become more widespread. More work must also be done to ensure that new material advances are available on all AM platforms, especially those as ubiquitous as FFF. There is no doubt that novel stimuli-responsive materials in combination with improved printing techniques can be further leveraged to achieve multi-functionality of active metamaterials.

6. Conclusion

The extensive research into metamaterial AM-based fabrication has led to significant improvements in manufacturing technologies that provide researchers more options than ever before to realize their novel designs. New advances in stimuli-responsive materials have also led to the rapid expansion of the active metamaterials field. These nascent fields have great potential to create the next generation of functional materials. Despite the encouraging progress, there are still many fabrication challenges that must be overcome in order for AM to be efficient tools for many engineering applications. With the parallel advances in printing techniques, design, and materials, we envision that active metamaterials will find exciting applications in a myriad of application including electronics, optics, aerospace, and biomedical devices.

Author contributions

S.M.M and X.K. performed the review and wrote the manuscript. S.M.M. gathered and organized the figures. C.A. proofread the document and assisted with figures. H.J.Q. revised and organized the document and provided guidance on the structure and content of the review.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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