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Review

Recent Progress in 3D Printing of Polymer Materials as Soft Actuators and Robots

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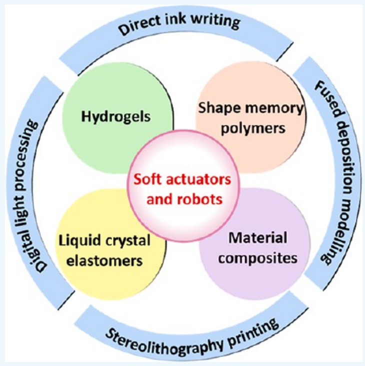
ABSTRACT: With inspiration from natural systems, various soft actuators and robots have been explored in recent years with versatile applications in biomedical and engineering fields. Soft active materials with rich stimulus-responsive characteristics have been an ideal candidate to devise these soft machines by using different manufacturing technologies. Among these technologies, three-dimensional (3D) printing shows advantages in fabricating constructs with multiple materials and sophisticated architectures. In this Review, we aim to provide an overview of recent progress on 3D printing of soft materials, robotics performances, and representative applications. Typical 3D printing techniques are briefly introduced, followed by state-of-the-art advances in 3D printing of hydrogels, shape memory polymers, liquid crystalline elastomers, and their hybrids as soft actuators and robots. From the perspective of material properties, the commonly used printing techniques and action-generation principles for typical printed constructs are discussed. Actuation performances, locomotive behaviors, and representative applications of printed soft materials are summarized. The relationship between printing structures and action performances of soft actuators and robots is also briefly discussed. Finally, the advantages and limitations of each soft material are compared, and the remaining challenges and future directions in this field are prospected.



KEYWORDS: *3D printing, soft actuators, soft robots, soft materials, stimulus responses*

1. INTRODUCTION

With the rapid advancement of technology, significant strides have been made in the field of robotics, showing promising applications from biomedical surgery and health care to industry machine assembly and environment protection.[1] For conventional hard robots, metals or other rigid materials are manufactured into structured elements and assembled into robotic machines. These hard robots usually have electric motors as the driving systems and multiple joints for controlled deformations, affording them with formidable strength as well as high preciseness and durability.[2] However, robots or actuators made of rigid materials usually have fixed physical properties and limited flexibility, making it difficult to adapt to the dynamically changing environments and task requirements. Especially, the poor interactive capabilities of hard robots with human bodies may lead to biotissue damage and safety accidents.[3] When we look back to the prototypes of soft actuators and robots, i.e., the living organisms with dexterous morphing and motion capacities, the components are usually in a soft and wet state with the features of high compliance, abundant response, and good adaptability. Inspired by the invertebrates, scientists have explored and utilized soft active materials to devise soft actuators and robots.[4−7] When compared to rigid materials such as metals, soft materials have high flexibility and multiple responses to stimulations, affording high degrees of morphing and adaptive capacities to environments.[8] The softness and compliance of soft actuators and robots enable better interactions with biological tissues and humans with improved safety.

In the recent two decades, a series of soft robots and actuators have been developed, greatly expanding the applications in biomedical and engineering fields.[9−12] The prosperity of this emerging area is inseparable from the innovations in new soft materials, advances in manufacturing techniques, and popular interdisciplinary research. In recent years, various soft materials have been developed by chemistry and materials scientists, providing abundant options to devise advanced soft actuators and robots through appropriate manufacturing technologies. Their basic mechanical properties, processability, and biocompatibility are studied and compared with biological tissues.[3] These soft materials with a high degree of design flexibility and rich stimulus-responsive characteristics

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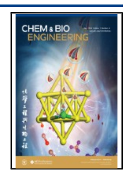

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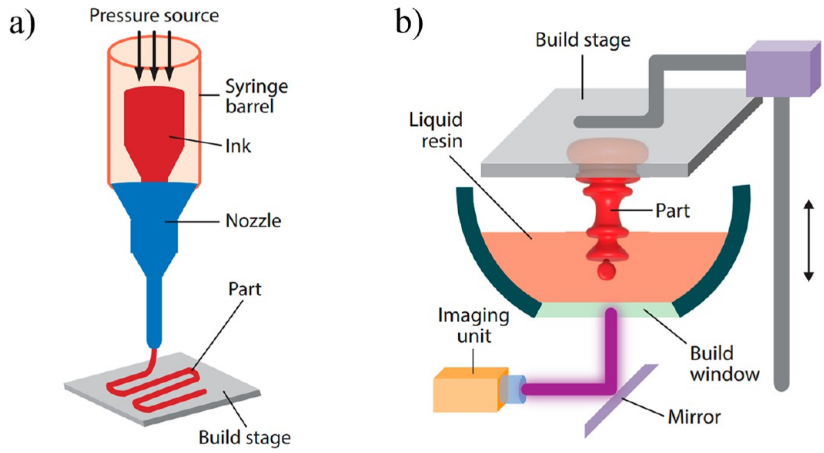

Figure 1. 3D printing of different processing techniques. (a) Extrusion-based printing. (b) Vat photopolymerization-based printing. Reproduced with permission.[13] Copyright 2023, The Authors.

favor the fabrication of soft robots to better mimic the structures of living organisms and perform a variety of complex actions.[13−17] Among these soft materials, hydrogels, shape memory polymers, and liquid crystalline elastomers have received increasing attention due to the versatile properties and functions.[3,9,13,18,19] These polymeric materials not only enable flexible design at macroscopic scales but also offer tailored functionalities by design at molecular and network levels.[20−23] Moreover, some specific functionalities, such as self-healing ability and degradability that hard materials rarely have, may increase the lifetime and sustainability of the soft robots and actuators, making them more close to biological organisms.[24−27]

Besides active soft materials, fabrication of soft actuators and robots requires advanced techniques. For example, soft actuators developed by conventional molding usually have simple structures and relatively low resolutions, limiting their morphing, sensing, and motion capacities.[28−30] Traditional manufacturing techniques including casting and molding cannot meet the increasing demands of refined architectures for the development of soft robots.[31] In recent years, several advanced manufacturing techniques have been developed and applied to devise soft robots with sophisticated architectures and improved robotic functions.[32] Specifically, the rapidly developed additive manufacturing techniques provide a viable solution for crafting biomimetic structures. The printing techniques suitable for engineering polymeric materials include fused deposition modelling (FDM), direct ink writing (DIW), selective laser sintering (SLS), ink jetting, stereolithography (SLA), digital light processing (DLP), etc.[3] In all of these techniques, the starting material (filament, ink, powder, or resin) is converted from a highly mobile state to a solid object during the processing process. The essence of 3D printing soft materials mirrors the growth pattern of biological organisms as the materials continuously stack and differentiate into predetermined shapes until the growth process is completed. This scenario boasts several advantages, such as high precision, flexibility, and customization, enabling the fabrication of soft actuators and robots with intricate shapes and gradient structures. The advent of 3D printing techniques has revolutionized the manufacturing of soft actuators and robots.[28]

These printing techniques are discussed in detail in several excellent reviews and will be briefly introduced in this paper with an emphasis on the printed constructs and resultant robotic functions and applications. We limit the contents of commonly used active soft materials for soft actuators and robots. This paper is structured as follows. First, we give a brief introduction to several 3D printing techniques commonly used in this field. Then, we summarize the printing of hydrogels, shape memory polymers, liquid crystalline elastomers, and their hybrids, focusing on the material's properties, morphing and motion principles, robotic functions, and applications with representative examples. The advantages, disadvantages, and optimization strategies of each soft material are discussed. The relationship between the printed structures and the robotic functions is also discussed for a better understanding of the design principles of soft actuators and robots. Finally, concluding remarks are provided to highlight the remaining challenges and future directions of this emerging field.

2. 3D PRINTING TECHNIQUES FOR SOFT ACTUATORS AND ROBOTS

3D printing, also termed additive manufacturing, has emerged as a versatile and powerful technique to engineer materials into structured elements with expanded applications in tissue engineering, electronic devices, soft machines, and high-performance metamaterials. Since most soft actuators and robots are constructed by using materials with active matrices or responsive fillers, we provide here a brief introduction to several 3D printing techniques commonly used for soft materials. Comprehensive introduction and discussion of printing techniques can be found in several excellent review papers.[33−35]

2.1. Extrusion-Based 3D Printing Techniques. The most widely used printing is extrusion-based methods (Figure 1a), including FDM and DIW.[36] Both methods form 3D objects in a line-by-line manner; the difference is that FDM extrudes a solid material such as thermoplastic through a heated nozzle to melt, deposit, and fuse, which solidifies during cooling, whereas DIW deposits a viscous liquid that can be cured or solidified during post-printing treatment such as ultraviolet (UV) light irradiation. By moving the printhead that holds the viscoelastic material along a substrate in the x and y directions, objects can be built up line-by-line with a resolution of >100 μm. The extrusion-based 3D printing techniques allow processing of viscoelastic materials with optional post-printing treatment/curing step such as UV exposure, cooling, or solvent exchange to obtain 3D solid structures.

Materials for extrusion-based printing generally require a high shape-holding ability before curing. Typical extrusion 3D printers have printheads with nozzles that are 100 μm to 1 mm in diameter. The nozzle size can be used to control the dimensions of the deposited molten filaments or viscoelastic inks. The printheads can be driven mechanically or pneumatically. Pneumatic setups using compressed air for extrusion are suitable for printing materials with moderate viscosities. Mechanical systems with a piston or screw are needed to print highly viscous materials. Because the printing platform is the place to solidify or gelatinize the printed structure, it is often equipped with heating or cooling devices and sometimes with light sources for photopolymerization and cross-linking reactions. FDM is commonly used to print thermoplastic materials, which become printable at elevated temperatures and solidify at room temperature after printing. In contrast, DIW uses viscoelastic inks to print structures under ambient conditions and often needs post-treatment to stabilize or toughen the printed constructs. For extrusion-based 3D printing, the materials or precursor inks should have viscosity in the range of 6×10^7 to 30×10^7 mPa•s, which is higher than other printing techniques. The viscosity of the inks can be tailored by the molecular weight and concentration of polymers. At optimum viscosity and extrusion force, the inks are able to flow continuously without disruption of the printed filaments. The upper limit of the viscosity is determined by avoiding nozzle clogging. Too high viscosity hampers continuous extrusion of the filaments and leads to defective printed structures; too low viscosity leads to deliquescence of printed structures, low printing resolution, and poor structure fidelity. Besides the appropriate viscosity, the ideal ink for DIW should have prominent shear-thinning behavior, which favors a high shape fidelity of the printed structures. Owing to the shear-thinning property, the viscosity of the ink decreases at least one order of magnitude during the printing and readily recovers original high viscosity after being printed on the platform.[37] If these properties are well met, continuous flow of the ink through the nozzle will be achieved to produce a long filament with programmable printing path.

As described above, a wide range of polymeric materials can be manufactured by extrusion-based printing techniques into sophisticated architectures. Specifically, various thermoplastics can be engineered by FDM, whereas viscoelastic inks can be printed by DIW. The shear-induced flow can also be harnessed to align macromolecules or particular fillers, affording the printed structures with unique mechanical/optical properties or anisotropic responses.[38] The resolution of the structures printed by FDM and DIW is limited by the high viscosity of the printing materials and typically ranges from 100 μm to 1 mm. Another limitation of the extrusion-based printing techniques is the relatively low manufacturing speed, although it can be sped up by using multiple nozzles.[14] Although extrusion-based printing has been extensively used to devise soft actuators and robots, how to cure or solidify quickly after printing is challenging yet crucial for the high fidelity of printed structures.

2.2. Vat Photopolymerization-Based 3D Printing Techniques. Another popular method for 3D printing of soft materials is vat photopolymerization including stereolithography (SLA) and digital light processing (DLP) (Figure 1b). Compared with extrusion-based printing techniques, vat photopolymerization-based 3D printing techniques produce architectures with higher resolution and speed. The inks used for printing contain photosensitive monomers, and a laser beam or UV light is used as the light source to induce photocuring. The resolution limitation of printed structures is determined by the digital micromirror device (DMD) embedded in the projector. A typical SLA 3D printer consists of a container for the precursor, a printing platform on movable stage inside the container, and micromirror array to control the path of the light beam. A bath of liquid precursor is selectively exposed to light through a scanning laser, which induces photocuring and solidification. A typical DLP printer includes a fixed light projector, vat of liquid precursor, and build platform with a mobile Z axis. Objects can be printed by both techniques in a layer-by-layer manner; SLA constructs one layer by sweeping polymerization with a laser beam, and DLP creates one layer by polymerization at patterned regions. Therefore, DLP has higher printing efficiency than SLA. Once a layer has been printed, the platform moves vertically with a certain distance and continues to locally cure the precursor by using dynamic pattern or scanning beam. This process is repeated layer-by-layer until the desired structure is constructed.[39]

According to the moving direction of building platform, DLP-based 3D printing is divided into "bottom-up" form and "top-down" forms.[40] In the "bottom-up" DLP printing, solidification occurs at the bottom of the vat and the printed object hangs upside down on the build platform. The advantages of this method include less resin consumption and a higher leveling rate of liquid resin. However, this method requires the printed structures to have high mechanical properties to avoid gravity-induced shape change during the printing process. Regarding the "top-down" DLP printing, when the liquid resin is photocured into a solid layer, the printed structure is translated downward into the vat, the resin recoats the interface, and the next layer is similarly cured into a solid with different patterns. The height of the printed object depends on the vat depth. If the printed structure has low swelling in the precursor, the printed object will have relatively high resolution and fidelity because the bottom vat can provide buoyant force to support the printed construct. In addition, there are two ways for vertically moving the printing platform: continuous rise and intermittent rise.[41] For continuous rise, the thickness of each slice is usually $\leq$20 μm with a short light-exposure time. Therefore, it can print very fast, and the staircase effect on the surface is significantly eliminated. The disadvantage is that each layer cannot be fully cured; such printed structures may require post curing. For the intermittent rise, the thickness of each slice can reach a value of $\geq$100 μm and the curing time is longer. After curing one layer, the printing platform rises and then falls to a certain height for the next curing. Although post-curing can be omitted, this method is time consuming, and the staircase effect is obvious, leading to relatively low fidelity.

The intensity and exposure time of the light are key factors affecting the resolution of the printed structures. Besides, the efficiency of photoinitiators is also essential for the control of polymerization time, because sufficiently rapid curing is necessary for the vat photopolymerization-based printing techniques. Several commonly used and efficient photoinitiators are briefly introduced here. According to the solubility, these photoinitiators are divided into water-soluble and oil-soluble ones. Oil-soluble photoinitiators with a high

Table 1. Printing Manner, Resolution, Starting Material Requirements, and Characteristics of Different 3D Printing Methods[a]

Printing method		Printing manner	Resolution (μm)	Starting material requirements	Characteristic	Ref
Extrusion-based printing	FDM	Line by line	>100	Thermoplastic filament (6×10^7−30×10^7 mPa•s)	Low printing efficiency; poor precision	42
	DIW	Line by line	>100	Viscoelastic ink (6×10^7−30×10^7 mPa•s)	Low efficiency; poor precision; wide-range printing materials	43
Vat photopolymerization based printing	SLA	Layer by layer	<50	Low viscosity (<5 Pa•s); photopolymerizable	Medium efficiency; high resolution	44
	DLP	Layer by layer	<50	Low viscosity (<5 Pa•s); photopolymerizable	High efficiency; high resolution	32,40

[a]Abbreviations: FDM, fused deposition modeling; DIW, direct ink writing; SLA, stereolithography; DLP, digital light processing.

efficiency include 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TPO) and phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (Irgacure 819), while water-soluble photoinitiators include 2,2′-azobis(2-methylpropionamidine) dihydrochloride (V-50) and lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP). In addition, photoabsorbers are also particularly important for vat photopolymerization-based printing, which are used to control the curing depth of the precursor and prevent excessive solidification in preset sections.[32] High-resolution (at micro- and nanoscales) structures can be fabricated by these vat photopolymerization-based 3D printing techniques. Multimaterial printing is also achieved in recent years by these techniques using switchable vats or grayscale light.[3] A comparison of starting material and resolution of constructs between different printing techniques is shown in Table 1.

To date, the material systems for DLP printing are mainly limited in resins that have fast curing speed and high stiffness to avoid gravity-induced shape change during the printing of elaborate and high-fidelity architectures. Most-existing soft actuators and robots developed by DLP printing have relatively low resolution;[40] it is still a big challenge to print active soft materials into high-resolution constructs.

2.3. Other 3D Printing Techniques. The techniques described above are the most commonly used and highly developed ones for 3D printing of soft materials. In addition to these techniques, there are several printing methods for specific material manufacturing, such as inkjet 3D printing and two-photon and multiphoton laser lithography 3D printing. Unlike extrusion-based printing, inkjet printing is developed as a technology that allows constructing 3D structures using low-viscosity inks (3.5−12 mPa•s), which are deposited as small volume droplets.[45] Thermal or piezoelectric modules in the printhead split the bulk ink into droplets with a picoliter volume. The resolution of the printed structures is between 50 and 500 μm. While inkjet printing is useful to construct thin structures on solid substrates, this technique has limitations on the fabrication of self-standing structures. Due to their low viscosity, the ink droplets may spread out, which limits the resolution and the height of printed structures. Inject 3D printing with reactive droplets is also useful for the design of soft actuators and robots to create anisotropic patterns on an isotropic material substrate. The composition of printed droplets can be tuned to apply in different patterns, affording diverse responsiveness of the whole structure.

Two-photon lithography is a further variation of photopolymerization.[46] The corresponding setup is more complex and expensive. The light source of this technique is a pulsed femtosecond laser operated in the visible or near-infrared range with a wavelength of 780−800 nm; the precursor is highly transparent. Due to the high intensity of the laser pulses and the narrow focal volume (60 nm), two or more photons are absorbed simultaneously on the same atom, similar to the chemical process of UV photopolymerization in the focal volume. The target structures are built up voxel-by-voxel. Two-photon and multiphoton photopolymerization 3D printing gives access to constructs more than one order of magnitude smaller than conventional photopolymerization-based printing. So far there are few soft actuators and robots developed by this advanced technique,[33] which has much space to be explored by future studies.

Although the aforementioned printing technologies have been widely used in the molding of polymer structures, the printing requirements of soft actuators and robots are more stringent. The printing soft actuators or robots compared to printing inactive polymers has several challenges: (i) Balance of mechanical properties of printing materials. After curing, the soft actuator requires appropriate strength and stiffness to ensure the ability to perform the action and load capacity without reducing the flexibility of actions. (ii) The precision of the printing process. Soft actuators or robots require more complex and fine structures to achieve higher degrees of freedom and complex actions. (iii) Precise control of nonuniform structure. Many actuators have gradient or multimaterial heterogeneous structures, which require precise control of parameters and material feed during the printing process.

3. 3D PRINTED SOFT ACTUATORS AND ROBOTS

During the advancement of additive manufacturing techniques, printing of polymeric materials has often been used as a test bed. The 3D printing techniques have been widely used to engineer passive materials such as resins into architectured elements with static morphologies or topologies. If responsive materials are manufactured by 3D printing, then the printed constructs should change their architectures under external stimulations, which are important for the robotic functions of soft actuators and robots. These active materials can be generally classified into two categories: polymeric matrix-rooted responsiveness and functional filler-afforded responsiveness. In this Review, we will mainly focus on the former type of active soft materials, with applications such as soft actuators and robots. Soft actuators and robots execute their functions through the dynamic morphing of the active materials or structures. Although there is no clear boundary between soft actuators and soft robots, we limit the scope of soft actuators to soft grippers and manipulators and soft robots to locomotive soft machines. In addition, by design of the printed structures, passive soft materials can also be driven by pneumatic or hydraulic pressure. In the following sections, soft actuators and

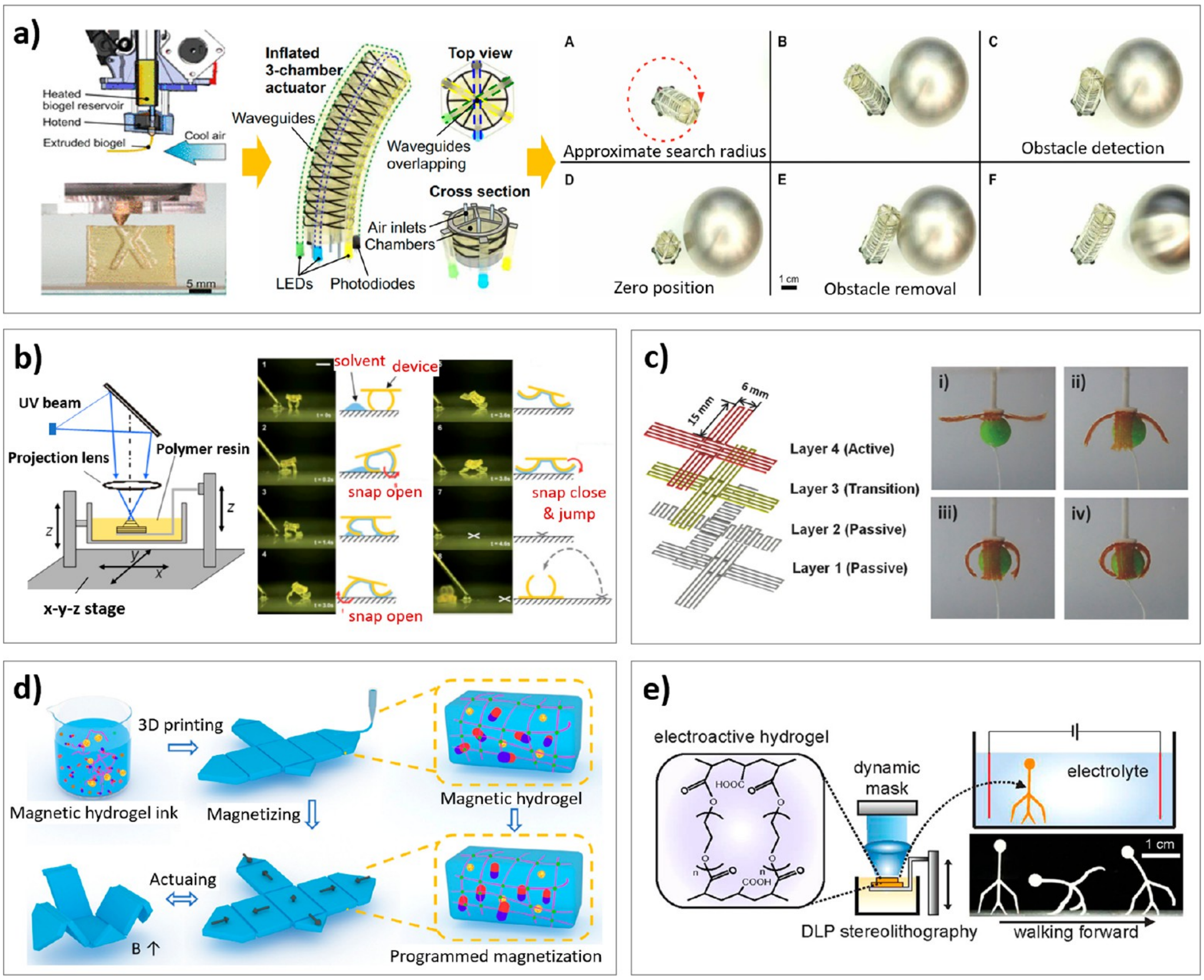

Figure 2. (a) 3D printed gelatin hydrogel-based pneumatic actuator with omnidirectional morphing capacity and sensing ability after incorporation of optical waveguides. Reproduced with permission.[59] Copyright 2022, AAAS. (b) 3D printed hydrogel jumper based on swelling-induced snapping of the legs with a double-curved structure. Reproduced with permission.[70] Copyright 2010, RSC. (c) Tough gel gripper by extrusion-based printing of different gels showing a high response speed and large output in a concentrated saline solution. Reproduced with permission.[14] Copyright 2018, Wiley-VCH. (d) Magnetic arthropod millirobot by DIW printing of hydrogel ink with magnetic particles programmed through a template-assisted magnetization strategy. Reproduced with permission.[5] Copyright 2022, Wiley-VCH. (e) Polyelectrolyte hydrogel walker fabricated by SLA printing and activated by an electric field. Reproduced with permission. Reproduced with permission.[62] Copyright 2018, American Chemical Society.

robots based on hydrogels, shape memory polymers, liquid crystalline elastomers, and their hybrids through appropriate 3D printing techniques are discussed in sequence.

3.1. Printed Hydrogels as Soft Actuators and Robots.

Hydrogel is a three-dimensional polymer network containing a large amount of water.[47−51] Due to its similarities to soft biological tissues, good biocompatibility, and operational capabilities in moist or wet environments, hydrogels hold significant potential in biomedical and underwater engineering fields.[52,53] Hydrogels offer a versatile design space, allowing the incorporation of various functional components to meet diverse requirements.[30,54,55] More importantly, hydrogels exhibit rich responsivenesses to external stimuli and have been recognized as an ideal candidate to devise soft actuators and robots.[4,8] Especially, the developments of various tough hydrogels with remarkable strength and stretchability significantly expand the application scope of hydrogels as soft robots and actuators.[56] Hydrogels can be engineered through extrusion-based printing and photocuring printing techniques.[30] The ink for extrusion-based printing should have shear-thinning behavior or sol-gel transition, which can be achieved through solvent exchange, charge shielding, temperature variation, and post-curing.[57−60] While extrusion-based printing has been extensively used in various hydrogel systems, it suffers low printing efficiency, relatively poor accuracy, and challenges in printing small and high-precision structures.[7] In contrast, photocuring printing, especially voxel printing achieved by precise light source control, offers high precision and efficiency and favors printing more complex structures.[3,55,61,62] The most widely used hydrogel systems for printed soft actuators and robots include polyacrylic acid (PAAc) gels,[62] polyacrylamide (PAAm) gels,[55] poly(*N*-isopropylacrylamide) (PNIPAm) gels,[60,63] hyaluronic acid gels,[63] chitosan gels,[64] and alginate gels.[65]

According to the mechanical properties and responsiveness of hydrogels, hydrogel actuators or robots can be divided into three categories with different actuation principles: external-pressure-driven actuation, solvent swelling actuation, and matrix stimulus response actuation. Pneumatic or hydraulic pressure is the simplest and fastest actuation way, which does not rely on the stimulus response of hydrogels but takes advantage of the softness and stretchability of the passive

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materials. Such pressure-driven hydrogel actuators require delicate internal and external structure designs to produce different actions. 3D printing can meet high manufacturing requirements. For instance, Heiden et al.[59] utilized melt deposition printing to develop gelatin gel-based pneumatic actuators, which was also embedded with stretchable optical waveguides for proprioception. These hydrogel actuators exhibited omnidirectional deformations within 1 s, accurately sensing their bending state and collisions with surrounding objects (Figure 2a). Hydraulic actuators can also take advantage of the stimulus responsiveness of the materials to achieve specific functions. Mishra et al. employed multimaterial stereolithography to print fluidic actuators with a PNIPAm body and a microporous polyacrylamide (PAAm) dorsal layer. When the actuator clamps a high-temperature object, the main body material shrank and the micropores on the dorsal expanded, allowing liquid to flow out and cool the object. Their sweat-like actuators demonstrated a 600% increase in cooling rate compared to conventional actuators.[61,66] Hydrogel pressure-driven actuators can also combine with bionic structural design to achieve more complex actions and functions. For example, Wang et al.[55] employed DLP processing to print octopus tentacle-mimicking pneumatic hydrogel suckers, and integrated into a biomimetic gripper for effective grasping in both underwater and aerial environments. However, pressure-driven actuators require the driving equipment and non-detachable pipelines, limiting the application scenarios of this kind of hydrogel actuators.[67]

One general characteristic of hydrogels is the responsiveness, which allows hydrogels to change their volumes under different environments.[30,68] To achieve 3D deformations such as bending, folding, and twisting, hydrogels need to undergo asymmetric swelling.[20] Differential swelling ratios in the structure can be encoded by choosing two or more gels with different compositions and capacities to absorb different amounts of solvent.[54,69] By 3D printing techniques, especially multimaterial printing, in-plane and through-thickness gradients can be created in the constructs. An example is the hydrogel-based soft actuator with the multilayer structure developed by multimaterial printing. This hydrogel actuator is composed of an expandable top layer and a non-expandable bottom layer in response to water.[54] This gripper successfully captured live goldfish underwater. Shape morphing can also be realized in a single hydrogel with regions of different swelling capacities, due to different cross-linking densities or different alignments of nanofillers.[48,49,61] For example, Gladman et al.[38] developed a morphing hydrogel by extrusion-based printing of an ink containing nanocellulose fibers that are oriented during the extrusion process. The resultant gel fibers had anisotropic stiffness and anisotropic swelling, enabling the printed constructs to morph and form complex configurations. Fang et al.[70] fabricated a hydrogel jumper with microgroove-containing double-curved structure as the "leg" (Figure 2b). Upon solvent stimulation that swelled the gel near the grooves, the double-curved gel snapped and generated a thrust to make the device jump off the ground. Next-round jumping required other stimuli to restore the original shape and trigger a new snap-through transition of the "leg".

Besides swelling-driven shape morphing, responses to stimuli such as temperature, pH, ionic strength, and light are also harnessed to devise hydrogel-based soft actuators and robots by 3D printing techniques. PNIPAm gel is most commonly used for the construction of soft actuators. Below its lower critical solution temperature (LCST) of ~32 °C, PNIPAm chains are hydrated and become dehydrated when the temperature is above the LCST, resulting in drastic contraction of the gel. This volume transition is reversible, which can also be triggered by light after incorporating photothermal agents into the PNIPAm matrix, enabling remote and local stimulation for specific functions. For example, Bakarich et al.[71] printed a multimaterial valve with an active PNIPAm gel. At elevated temperatures, the hydrogel contracts and closes the valve. Besides the temperature, the PNIPAm gel is also responsive to the ionic strength. Zheng et al.[14] created tough gel-based soft gripper by multimaterial printing. The Fe^{3+}-reinforced poly(acrylic acid-*co*-*N*-isopropylacrylamide) gel fibers served as the active layer, while the Fe^{3+}-reinforced poly(acrylic acid-*co*-acrylamide) gel fibers acted as the passive layer. When immersed in a concentrated saline solution, the active gel contracted its volume, leading to bending of the printed gel construct along the active fibers (Figure 2c).

To devise hydrogel-based soft robots with continuous motions, the interactions between printed gel robots and the surrounding environments should be dynamically controlled. Cyclic actuations are usually applied for dynamic deformations and thus locomotion of the printed gels. For example, the electromagnetic or magnetic field is used to dynamically stimulate the shape morphing of the hydrogel after loading of soft or hard magnetic particles.[5] The magneto-actuated gel robot can be by direct ink writing of a viscous precursor containing nanoclays and neodymium iron boron (NdFeB) microparticles (Figure 2d). The magnetic domains of the printed gel robot were programed by the template-assisted magnetization strategy. Under magnetic fields, the gel robot was actuated to show programmed deformations. Recently, Cheng et al.[60] fabricated soft robotic devices by DIW 3D printing of multiple hydrogels with different driving mechanisms. A hydraulic artificial tentacle was made of PAAm hydrogel and actuated by injecting water through embedded channels; a "robotic heart" was made of poly(vinyl alcohol) gel with embedded pneumatic cavity mimicking cardiac pulsation, and an artificial seta was made of carbon nanotube-containing PNIPAm gel by printing on a polydimethylsiloxane (PDMS) substrate to form a light-activated bilayer structure.

Electroactive hydrogels are also used to devise soft robots by 3D printing. For example, polyelectrolyte hydrogels are responsive to the electric field, which results in the directed migration of mobile ions and creates differential osmotic pressure within the gel. Therefore, the polyanion gel strip bends toward the cathode and the polycation gel bends toward the anode. Continuous and programmed motions can be realized by 3D printing to control the structure of the gel robot and using an electric field for dynamic actuations. For instance, Han et al.[62] devised soft robot by stereolithography printing of PAAc gel, which was activated by an electric field and showed bidirectional walking motions in an electrolyte solution (Figure 2e).

As described above, hydrogels have been widely used to devise soft actuators and robots due to their similarity to soft tissues and rich responses to stimuli. 3D printing, especially the multimaterial printing, provides powerful tools for fabrication of hydrogel machines with sophisticated architectures. The printed gel actuators and robots have promising applications in the biomedical field. However, the action speed and output force are relatively low, which require more efforts to improve

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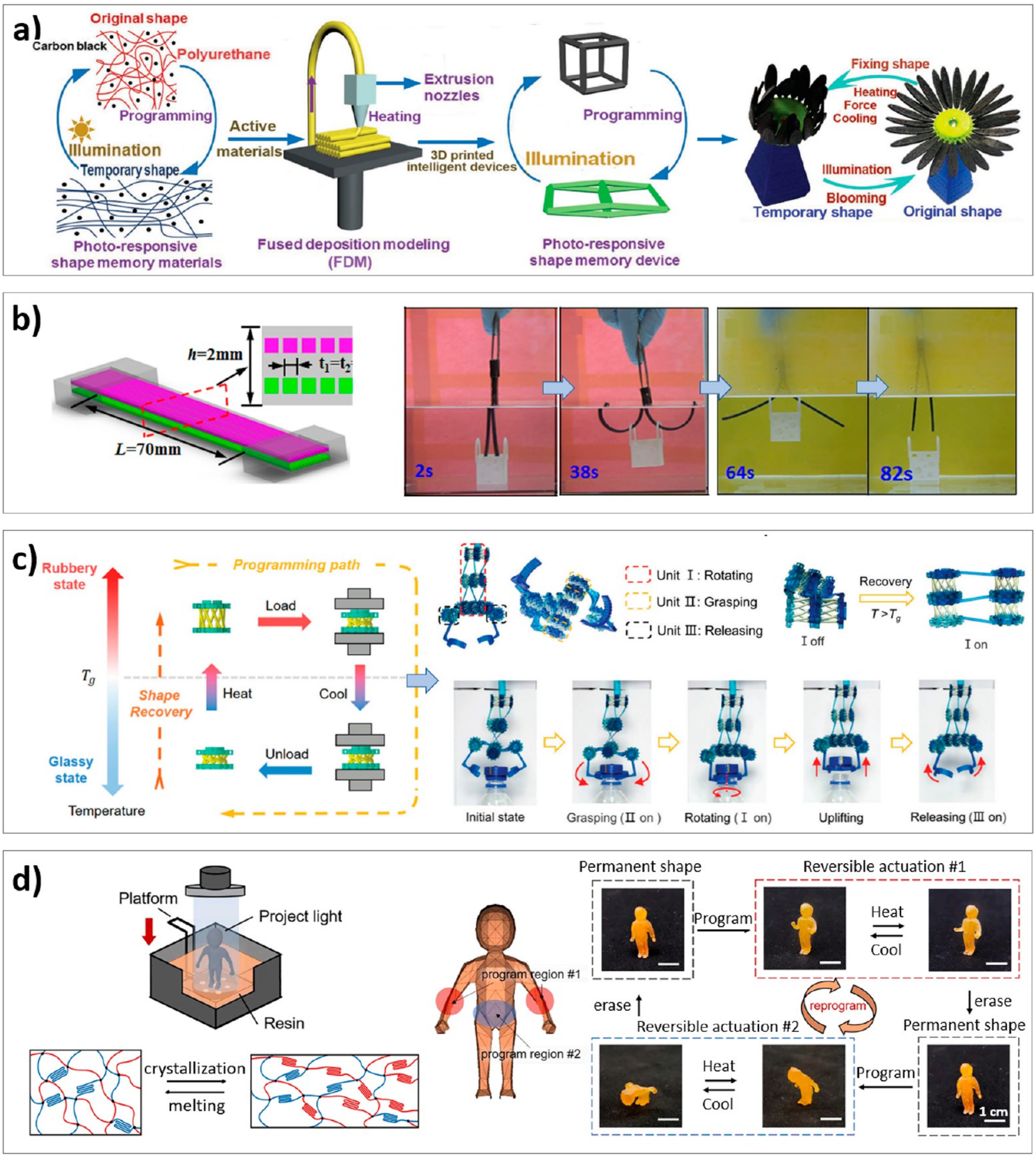

Figure 3. (a) FDM printed flower composed of SMP and carbon black particles that can be actuated by visible light. Reproduced with permission.[80] Copyright 2017, Wiley-VCH. (b) Printed actuator by 3D printing of multiple SMPs with different T_g values that can grasp and release an object on demand. Reproduced with permission.[82] Copyright 2016, Springer Nature. (c) 3D printed SMP-based pressure-twist coupled units and modularly assembled multimode soft gripper. Reproduced with permission.[77] Copyright 2023, Wiley-VCH. (d) DLP printing of two-way SMP to devise a cartoon character capable of performing multiple reversible actions. Reproduced with permission.[89] Copyright 2021, Elsevier.

the gel properties and robotic performances. In addition, the stimulus sensitivity poses a hidden problem for the stability of hydrogel machines during practical operations.

3.2. SMP-Based Actuators and Robots. SMPs are another kind of smart material that can remember and recover the initial shapes upon stimulations.[28,72] Shape programming of the SMPs usually consists of two processes: temporary shape assignment and permanent shape recovery. In the process of "writing-in" temporary shapes, the plastic polymer is heated above the thermal transition temperature (glass transition temperature T_g for amorphous polymers or melting temperature T_m for semi-crystalline polymers), which increases the mobility of the chains and results in a soft rubbery material.[73] The application of external stress at this temperature deforms the material, causing the orientation of the polymer chains at a specific region. In this process, the external force is converted into entropic energy and is stored in the polymer chains. By cooling below T_g or T_m, the oriented chains are locked in the material to fix the temporary shape,[74] because the vitrified or crystalline phase limits the movement of chain segments. Recovery to the original shape can be triggered by heating above T_g or T_m, which enables the motion of chain segments and entropy elasticity of the material.[72,75] At this point, the material can be reprogrammed to create a new temporary shape.[75,76] Besides the one-way SMPs, two-way SMPs capable of reversibly shifting between two distinct shapes have received increasing interest in recent years and have become an ideal material to devise soft actuators and robots.

The SMPs can be engineered by 3D printing techniques to form complex structures, which morph upon heating or light irradiation. The combination of shape morphing and 3D printing of materials is also termed as 4D printing.[72,75,77] One-way SMPs have been well explored and used to devise soft actuators and robots.[75] For example, Zarek et al.[78] used methacrylate modified polycaprolactone (PCL) as a raw material and applied SLA printing technology to create thermally-driven shape memory objects, which can be used flexible circuits. Another example is that Ren et al.[79] fabricated SMP-based soft robots by 3D printing, showing simultaneous changes of shape and color upon stimulations. By incorporation of thermochromic pigments into the SMP, biomimetic color-shifting flowers and camouflaging octopuses were constructed by 3D printing. Chen et al.[80] have also reported on the design of shape memory devices by combining the FDM printing technique and photoresponsive composites consisting of SMP and carbon black particles as photothermal agents. The printed SMP-based device showed excellent shape memory behavior triggered by natural sunlight (Figure 3a).

Although most one-way SMP can only remember a temporary shape, some multiSMPs can remember two or more temporary shapes, which rely on multiple phase transition temperatures[76,81] or have a wide range of phase transition temperature.[73] The seminal example is the perfluorosulfonic acid ionomer, which has one broad phase transition and exhibits dual-, triple-, and at least quadruple-shape memory effects.[73] A multiple shape memory effect can also be afforded by multimaterial printing of SMPs. For example, Wu et al.[82] achieved sequential changes of the printed construct into different shapes by 3D printing of multiple SMPs with a multilayer structure; these SMPs had different T_g. After the thermomechanical programming process, the strip bent when the temperature rose to a value between the two T_g values; when it continued to rise above the two T_g values, the structure returned to the initial state. Taking advantage of this characteristic, the 3D printed hook can grab and release objects on demand (Figure 3b). Ma et al.[83] obtained a shape memory composite with highly tunable T_g by adding polycaprolactone (PCL) to PLA with different proportions. A bilayer flower was prepared by FDM printing of the hybrid materials with different T_g. Sequential opening of the petals was achieved during the heating process. The morphing direction of the SMP can also be controlled by embedding oriented fibers. For instance, Ren et al.[84] deployed short steel fibers with specific orientations in different regions of the printed construct by magnetic-assisted 3D printing technique; the printed flower and robotic hand showed sequential deformations upon stimulations.

Another strategy to achieve multiple shape memory behaviors is to design the geometry of local locations of the printed constructs,[85] because the recovery or thermal response time depends on the thickness of the material. Liu et al.[86] developed SMP structures with different thickness by jet printing and studied the effect of thickness on the response time of the printed constructs. They found that by controlling the thickness of each component in the structure, the response sequence can be precisely controlled. The recovery speed of SMPs is not only a function of temperature but also a function of prestress or prestrain. The process of producing plastic deformation under high stress at room temperature is called cold programming. Qi et al.[87] controlled the light intensity of each pixel during the DLP printing process and obtained printed structures with different T_g values at different locations. By cold programming of different parts at room temperature, the printed construct formed various global configurations during the shape morphing process. The robotic functions can also be enriched by the design and fabrication of 3D structures. Recently, Qian et al.[77] reported compression torsion coupled components with embedded chirality, which were developed by DLP printing of multiple SMPs (Figure 3c). Each chiral unit can be individually programmed through mechanical compression at a selected temperature. With these building blocks, lattice like architectures were constructed in planar and layer-to-layer assemblies that exhibited different deformation modes. An untethered multimodal soft gripper was printed with the ability to unscrew bottle caps given by the module level programming functionality.

The limitation of one-way SMPs is that they cannot reversibly change between the temporal and permanent shapes, which limits continuous robotic functions of the printed constructs.[88] This issue has been addressed by the development of two-way SMPs, which can be reversibly actuated between two different shapes.[74,89−91] Detailed features and mechanisms of two-way SMPs have been omitted here. More information can be found in the literature.[74,89−91] Another important feature of two-way SPMs is that the shape transformation can be reprogrammed in the same material.[74,90,92] The two-way SMP has been applied for the design of a twisted actuator that can reversibly turn an arrow sign between three positions in the hand of a manikin.[93] This function of materials can also be combined with manufacturing techniques to develop advanced soft actuators and robots. For example, Xie et al.[89] devised an actuator by DLP printing of a two-way SMP with two crystalline phases via thiol−acrylate chemistry. A set of special geometric patterns can be obtained by digitally defined exposure regions with a specified time, allowing for 3D kirigami or origami reversible actuation of the printed structures. On the basis of reprogrammable and reversible shape shifting of two-way SMP, the printed gripper and a cartoon character can perform multiple reversible actions (Figure 3d). When compared to hydrogels, SMP actuators and robots have a high output force, good stability, and a high degree of commercialization for applications in biomedical and engineering fields.

3.3. LCE-Based Soft Actuators and Robots. LCE is an integrated body of liquid crystal medium and a polymer network. The mesogens can be incorporated into the network as part of the main chain or attached as the side chain.[13] The liquid crystal media plays a role in regulating the internal structure of the material, while the polymer network provides elasticity of the material.[86,94] As mentioned earlier, an anisotropic structure can lead to the macroscopic performance of anisotropy. When the liquid crystal medium is aligned in one direction (nematic phase), LCEs have enormous potential to generate anisotropic responses.[95] The LCE with unidirectional alignment of mesogens is also known as single domain LCE, which changes to isotropic phase (i.e., multidomain LCE) without long-range orientation of the mesogens at elevated temperatures (e.g., above the nematic-to-isotropic

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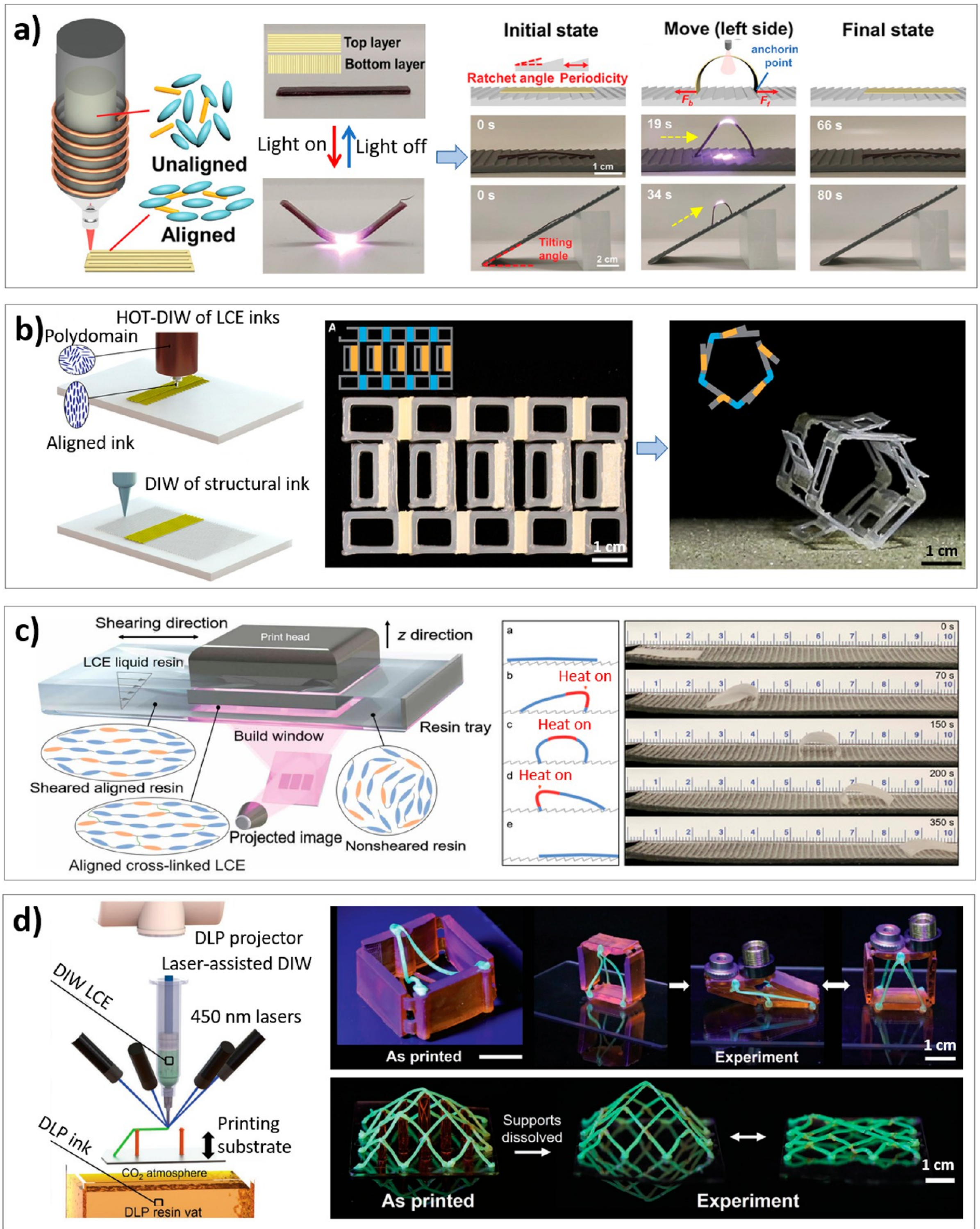

Figure 4. (a) LCE-based walker constructed by FDM printing capable of morphing and walking on a ratchet substrate upon cyclic light irradiation. Reproduced with permission.[104] Copyright 2023, Wiley-VCH. (b) Printed construct with LCE-based hinge actuators showing self-propelled rolling motion on a hot plate. Reproduced with permission.[106] Copyright 2019, AAAS. (c) DLP printing of LCE with shear alignment of mesogens to devise an LCE robot capable of locomotion on a ratchet plate. Reproduced with permission.[100] Copyright 2021, AAAS. (d) LCE-based tensegrity structures based on combined DIW and DLP printing techniques showing reversible morphing and robotic functions upon stimulations. Reproduced with permission.[103] Copyright 2022, Wiley-VCH.

transition temperature). During this process, the LCE shows anisotropic deformation, accompanied by conformation change of polymer chains from the stretched to coil state. This anisotropic response is reversible, upon heating or light irradiation, depending on the types of LCEs.[75,96] Generally speaking, LCEs are a typical kind of two-way SMPs. During the material preparation process, the LCE is usually in an isotropic (multidomain) state; an additional step is required for long-range orientation of the mesogens such as by using surface template, electric/magnetic field, microfluidic technology, electrospinning, mechanical stretching, etc.[96−99] However, these methods are limited to producing unidirectional LCE sheets or fibers, and cannot set different director alignments at specific regions.[100] In recent years, 3D printing has been used to engineer LCEs with arbitrary 3D shapes and controllable mesogen orientation fields.[98,101] The printed LCEs capable of robotic morphing and motion upon stimulation can be considered soft actuators and robots.

Various 3D printing techniques have been applied for the manufacturing of LCEs. During the extrusion-based printing, the mesogens are oriented by the shearing force and aligned along the moving direction of the printing nozzle.[102] Further cross-linking immobilizes the ordered structures of the mesogens; each fiber exhibits reversible and anisotropic contraction elongation along the longitudinal direction.[97,98,103] For example, Kotikian et al.[97] demonstrated the creation of programmable oriented LCEs via FDM-based printing. By taking advantage of the shear-induced alignment of mesogens and the control of printing path, localized orientations of the mesogens were encoded in the printed constructs. Another example is the fabrication of LCE-based actuator by FDM printing of photoresponsive LCE into bilayer strip with orthogonal alignment of printed fibers.[104] This bilayer structure showed a reversible bending deformation upon light stimulation. Under cyclic light irradiation, the printed LCE strip can walk along a specific direction on a rachet substrate, which regulated the friction and converted cyclic bending deformation of the LCE into direction motion (Figure 4a). LCEs can also be integrated with other passive materials to design soft actuators and robots. This task by multimaterial printing, such as to fabricate a self-propelling robot with multiple hinge actuators, can be accomplished. As shown in Figure 4b, the hinge actuator was constructed by DIW printing of LCE into a bilayer structure with orthogonal alignment of the mesogens at each layer. When heated above the actuation temperature, the printed LCE hinge exhibited a large, reversible bending response. The flat printed structure with multiple hinge actuators deformed into a pentagonal prism when placed on a hot plate, leading to bending of the hinges. The pentagonal prism continuously rolled on the plate, because the hinge was actuated when contacted and heated by the hot plate, which rolled the prism over the neighboring vertex with the next hinge on the plate. Successive actuation and action of the hinge actuators accounted for the self-propelled rolling motion of the printed construct.

For DIW-based printing of LCEs, the manufacturing time is limited by the size and resolution of printed constructs. Smaller extrusion nozzles are needed for higher orientation order, and longer path lengths are required for larger constructs.[3] By contrast, DLP-based printing is more efficient for the fabrication of LCE-based soft actuators and robots. For example, Li et al.[100] applied DLP printing to fabricate LCE with assistance of shear alignment of mesogenic resin in each thin layer before the photocuring step. LCE actuators with spatial control of director alignments were thus fabricated with high resolution. The printed LCE-based actuators showed versatile robotic performances, such as grasping, crawling, and weight lifting (Figure 4c). Other external fields can be used for better control of the local alignment of the mesogens during the DLP printing process. For example, Tabrizi et al.[99] exploited anisotropic magnetization of liquid crystal monomers under a redirectable magnetic field and thus achieved voxel-precise director orientations during DLP printing for the manufacturing of LCE into 3D architectures.

Although various printed LCE actuators and robots have been developed by DLP printing, the structures are still relatively simple, and spatial lattices or levitation structures are rarely reported in the literatures. This is because the soft LCE cannot maintain its shape when it is printed and suspended in air. As a consequence, the drive to print LCE structures is limited to planar contraction, simple bending, or twisting. In engineering, structures can have two or more steady states by means of special mechanical design, such as tensile monolithic structures. During the steady state transition, the structure has a great degree of deformation in space.[105] According to these considerations, Peng et al.[103] develop a novel hybrid manufacturing system for the construction of freestanding LCE on-the-fly of 3D structures. DLP and DIW printing techniques were combined in this system with an in situ laser curing module. The curing module quickly solidified the LCE ink as it was extruded out and stretched by the moving nozzle, while the DLP printing system provided optional structural or removable supports (Figure 4d). After dissolving the DLP-printed supports, a DIW-printed LCE architecture was obtained. The initiation wavelengths for DLP printing and LCE curing should be reasonably selected to avoid the interference. The printed LCE structures, including a hybrid lattice and tensegrity, showed reversible shape morphing abilities.

Owing to the molecular-scale anisotropic arrangement of the mesogens, LCEs possess reversible actuation capability and fast response speed and are thereby recognized as an ideal artificial muscle to devise soft actuators and robots. However, LCE requires a relatively high temperature for actuations, limiting the applications of LCE actuators/robots having interactions with biological tissues. To better compare the printing materials and printing strategies for the development of soft actuators and robots, corresponding appropriate printing ink, advantages, and disadvantages of different printing methods are summarized in Table 2.

3.4. Material Composite-Based Soft Actuators and Robots. As we introduced in the above sections, different kinds of soft materials have their unique properties and responses, as well as advantages and disadvantages. For example, hydrogels have rich structure and function designability, but the driving force is an order of magnitude lower than that of SMPs. To combine the advantages of different materials for the design of soft actuators and robots, one straightforward way is to integrate them into soft composites with programmable architectures and responses. Multimaterial 3D printing provides a powerful manufacturing tool to target this target, in which different materials should have strong interfacial bonding. For example, Ge et al.[108] used multi-material 3D printing system to devise miniature pneumatic robots with a combination of soft and stiff materials. Qi et al.[109] printed hydrogel and SMP into a bilayer structure. The responses of both the hydrogel and SMP enriched the shape changing abilities of the printed construct. As shown in Figure 5a, reversible deformations of the soft actuator were achieved by cooperatively controlling the temperature and water environment. Dunn et al.[110] printed composite structures composed of SMP and elastomer with built-in compressive strain during the photopolymerization. When heated, the printed SMP was softened, releasing constraints on the

Table 2. Printing Strategy, Appropriate Printing Ink, Advantages, and Disadvantages of Different Materials to Devise Soft Actuators and Robots

Materials	Printing strategy	Appropriate printing ink	Advantage	Disadvantage	Ref
Hydrogels	Extrusion-based printing	High-viscosity ink	Applicable to various hydrogel systems	Low printing efficiency and relatively poor accuracy	38,107
	Vat photopolymerization-based printing	Low-viscosity ink, photopolymerizable, excellent mechanical properties, and resistance to swelling	Precise light source control, high precision and efficiency and printing complex structures	Applicable to limited hydrogel systems	40
Shape memory polymers	Extrusion-based printing	High-viscosity ink	Applicable to various shape memory polymers systems	Low printing efficiency and relatively poor accuracy	80
	Vat photopolymerization-based printing	Low-viscosity ink, photopolymerizable	Printing complex structures	Big challenge to print high-viscosity ink	89
Liquid crystalline elastomers	Extrusion-based printing	High-viscosity ink containing the liquid crystal media	Shear-induced alignment of mesogens and controllable printing path, localized orientations of the mesogens	Low printing efficiency, relatively poor accuracy	106
	Vat photopolymerization-based printing	Low-viscosity ink, photopolymerizable	Shear alignment of mesogenic in each thin layer and efficient and high-resolution fabrication	Big challenge to control local alignment of mesogens without the help of external fields	100

strained elastomer and allowing the printed construct to transform into a new permanent shape, which can be reprogrammed into multiple subsequent configurations. Lendlein et al.[111] imitated the geometric change of cactus stems (from star to circle) by printing a composite material with soft elastomer and hydrogel as the actuation components. The bionic structure exhibits controllable motions upon stimulations.

During the printing of soft materials, the addition of fibers also affords the material with anisotropic response and mechanical properties, leading to shape change of the printed composite under stimulations.[37] For example, Wu et al.[37] used extrusion-based 3D printing technology to embed microfibers with specific orientations within the hydrogel. In these composite materials, the microfibers were distributed in the upper and lower layers of the hydrogel, enabling programmed deformations. Siqueira et al.[112] introduced cellulose nanocrystals (CNCs) into LCE and used DIW printing to construct soft actuator with simultaneously oriented CNCs and mesogens.

To further broaden the applications, the soft actuators and robots need to have sensing and control functions.[117,118] Achieving this goal often requires a combination of functional elements. In this regard, 3D printing processes have a natural advantage over traditional manufacturing processes. Its integrated manufacturing process, customizability, embedded sensing capability, enhanced performance, and cost-effectiveness provide significant advantages for a wide range of applications. Currently, some efforts are devoted to fabricating soft actuators with complex external geometries and internal functional areas (such as self-sensing units) by multimaterial printing. For example, Cui et al.[113] developed a sequential multimaterial embedded 3D printing technique that can fuse and print soft elastomer, conductive ink, and fiber-reinforced elastomer into a hybrid structure (Figure 5b). Taking the printing of a self-sensing composite actuator as an example, we found the printing technique involved several separate printing stages. First, the inflating body was printed on the matrix with an elastomer ink. Second, sensing units were printed into the inflating body with conductive ink. During this stage, the first printed structure functioned as the matrix for embedded 3D printing. Finally, the reinforced composite was conformally printed onto and into the inflating body to limit undesired deformations. The composite actuator with an embedded resistance sensor can monitor the bending angle and direction in real time. Boley et al.[119] added various materials such as carbon fiber and carbon nanotubes into the polymer matrix to develop a new heterogeneous polymer composite for 4D printing. The printed bilayer structure had programmable and predictable thermal and mechanical responses and, thus, enabled self-sensing functionality.

Besides the robotic modes, large morphing amplitude and high action speed are the goals of soft actuators and robots. Compounding drive units into soft materials through 3D printing can greatly increase the action speed and morphing amplitude of soft actuators and robots. For example, Gong et al.[120] printed liquid metal (LM) and LCE to form a composite construct, in which the conductive LM had response to a magnet field. Except for the traditional bending deformation mode, the asymmetric magnetic actuator also exhibited a folding deformation mode due to the presence of a gap structure. Zhao et al.[115] also reported an LCE-LM composite actuator, which showed ultrafast and programmable actuations by eddy current induction heating. The composite consisted of

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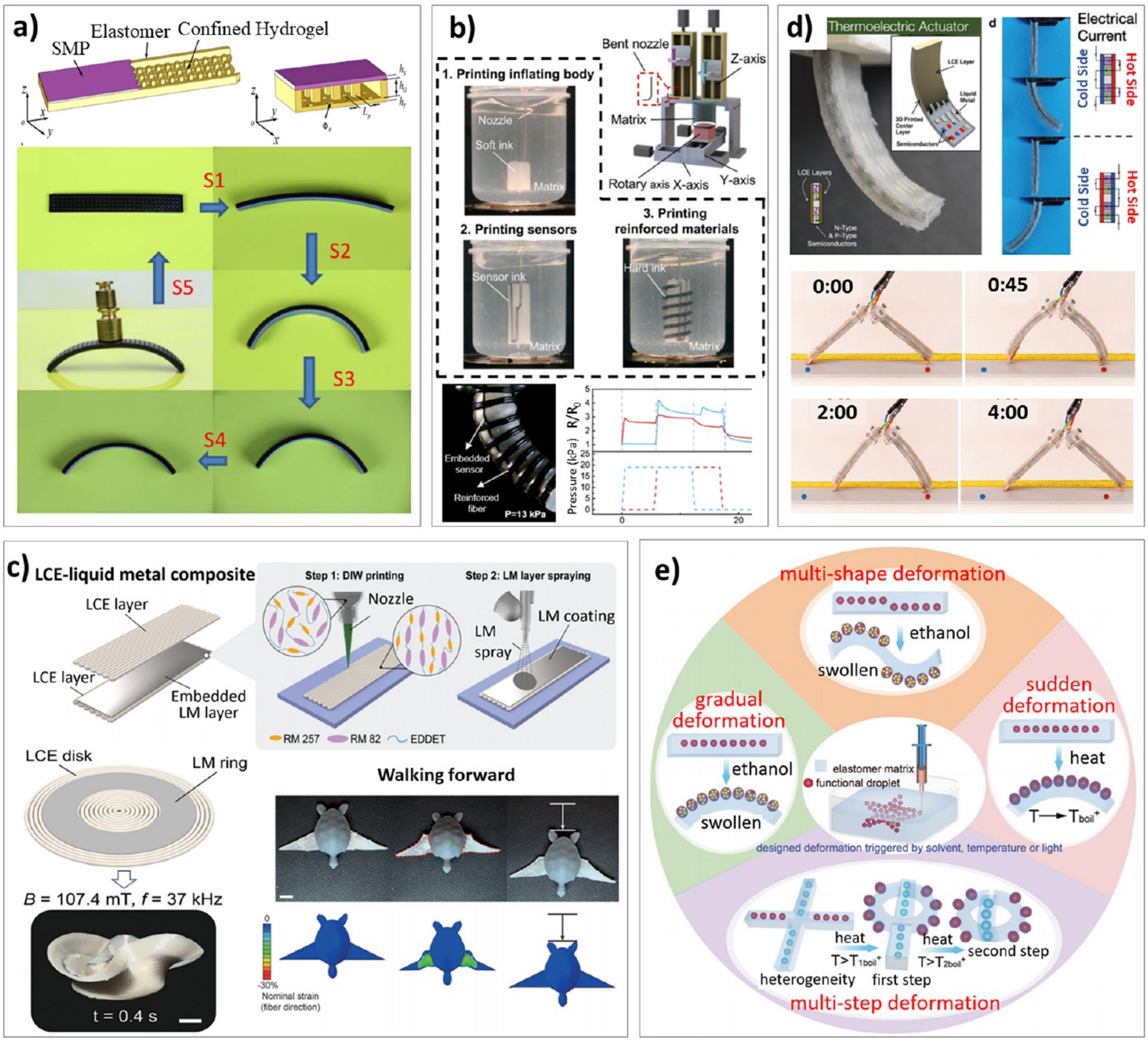

Figure 5. (a) 3D printing of the hydrogel and SMP into a bilayer composite showing reversible deformation with large output force. Reproduced with permission.[109] Copyright 2016, Springer Nature. (b) Embedded 3D printing of multiple materials into fiber-reinforced soft actuator with self-sensing ability. Reproduced with permission.[113] Copyright 2023, Elsevier. (c) Printed LCE-LM composite capable of crawling ultrafast under cyclic actuations with an electromagnetic field. Reproduced with permission.[114] Copyright 2022, Wiley-VCH. (d) Printed LCE-LM composite with thermoelectric layer capable of walking and harvesting energy driven by voltage. Reproduced with permission.[115] Copyright 2023, Wiley-VCH. (e) Microfluidic printing of droplets within an elastomer to form the composite actuator capable of shape morphing into various configurations. Reproduced with permission.[116] Copyright 2023, Wiley-VCH.

LM sandwiched between two LCE layers constructed by DIW printing. When subjected to a high-frequency alternating magnetic field, the composite actuator was actuated in milliseconds. By moving the magnetic field, the eddy current can be spatially controlled for selective actuation. The printed construct was even capable of omnidirectional crawling, to mimic the motion of a sea turtle, upon cyclic actuations of the printed "fins" (Figure 5c).

Soft robotic systems with more comprehensive and advanced functions, such as energy recovery and multistep mode transformation, can also be implemented with the assistance of 3D printing of multiple soft materials. For example, Zadan et al.[114] combined LCE with soft and stretchable thermoelectricity to form transducers capable of electronically actuating, active cooling, and thermoelectric energy conversion. The thermoelectric layers were composed of semiconductors embedded within a 3D printed elastomer and wired together with LM interconnects. These thermoelectric layers were covered by LCEs, which reversibly triggered bending deformation of the printed composite based on voltage-controlled Peltier activation. Moreover, the thermoelectric layer can harvest energy from thermal gradients between the two LCE layers through the Seebeck effect, allowing for regenerative energy harvesting. As demonstrated in Figure 5d, a flexible robotic walker can move toward the heat source and collect energy. Recently, Cheng et al.[121] proposed a novel photoresponsive liquid−vapor phase transition composite with integrated actuating and sensing performances. The composite actuator was operated on the principle of piezocapacitive sensing and liquid-vapor phase transition caused by photothermal effect of the embedded graphene plate. Yang et al.[116] also developed a microfluidic droplet printing platform to fabricate composite elastomers architected with patterned arrays of functional droplets. The

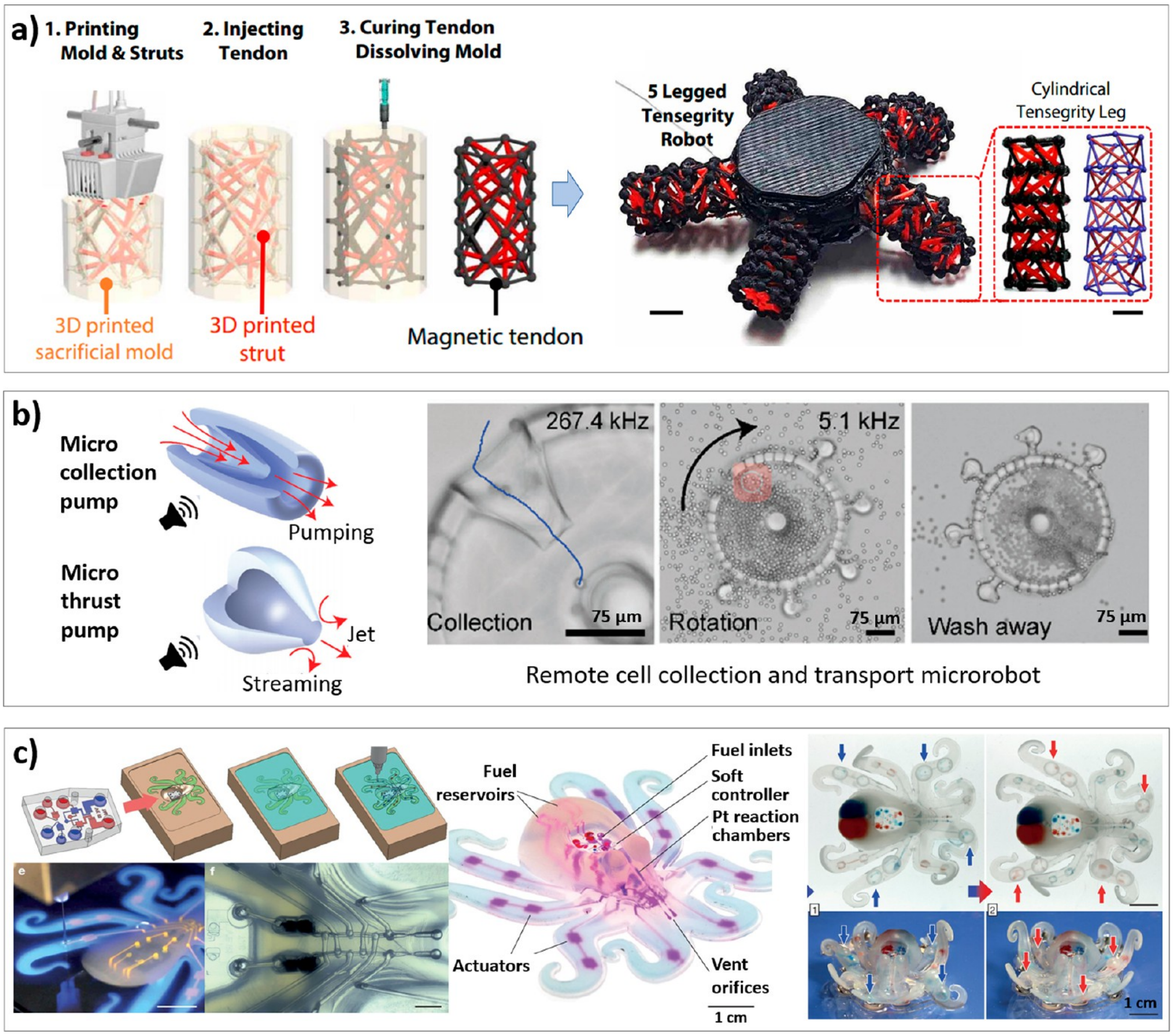

Figure 6. (a) Printed soft robot with a tension monolithic structure with programmable system-level mechanics and robotic performances. Reproduced with permission.[125] Copyright 2020, AAAS. (b) Ultrasonic-driven miniature robot of printed gel capable of locomotion, collecting, and transporting cells by acoustic pumping. Reproduced with permission.[67] Copyright 2020, Wiley-VCH. (c) Soft and autonomous robotic systems with self-regulated reaction to generate gas for actuations. Reproduced with permission.[2] Copyright 2016, Springer Nature.

composite elastomers were sensitive to stimuli, such as solvent, temperature, and light, capable of shape morphing to from serial configurations (Figure 5e).

As mentioned before, interfacial bonding between different materials is crucial for the overall mechanical and robotic performances of the printed composite actuators and robots. Here we have not provided details on this point, which can be found in several excellent literature sources.[122−124] With the integration of different kinds of materials, the responses and functions of the resultant soft machines can be enriched for broad applications in diverse fields. However, the integration of different materials is usually limited by the high contrast properties and processabilities. How to merge and process these materials to form advanced soft actuators and robots still needs efforts to explore new design principles and printing techniques.

4. CONCLUSION AND OUTLOOK

In this Review, we have summarized the developments of soft actuators and robots that are fabricated by various 3D printing techniques. We limit the scope to several responsive soft materials, including hydrogels, SMPs, and LCEs. The responses of these materials to external stimuli afford soft machines with adaptivity to environments and embodied intelligence. Since the morphing ability and robotic functions of soft machines are closely related to the geometries and gradient structures, 3D printing provides a powerful tool to devise soft actuators and robots. Considering the unique properties and processability of each kind of soft material, the printing technique with series of printing parameters should be carefully selected and optimized. The emergent printing of multiple materials with a combination of different printing techniques should further advance the fabrication of soft actuators and robots with complex architectures. Incorporation of fillers with a controlled distribution and orientation also greatly increases the functionalities and performances of printed soft actuators and robots. Although various 3D printed soft actuators and robots have been developed with versatile robotic performances and applications, this field is still in its infancy, especially considering the huge gap of performances between artificial machines and living organisms. It also offers many opportunities for materials scientists and engineering

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researchers to develop novel soft materials and explore new printing techniques. In the future, efforts should be devoted to solving several fundamental and application-related issues in this emerging field.

4.1. Creative Structural Designs. Structural designs are critical to increasing the functional diversity and physical intelligence of soft robotic systems. The current structural designs of soft robots are still dominated by simple multilayer or block fashions, far behind natural organisms. It is hampered by an understanding of working principles of living organisms and the manufacturing techniques to create sophisticated biomimetic architectures. We believe that the combination of new materials, 3D printing techniques, and creative structural designs will afford soft robots with rich robotic functions and application opportunities. A preliminary example is shown in Figure 6a, in which Kim et al.[125] applied the 3D printing technique and sacrificial molding to fabricate a flexible tension monolithic structure. The robotic performances can be tailored through the soft structure to program system-level mechanics.

4.2. Development of Miniature Robots. Soft actuators and robots exhibit promising applications in the biomedical and engineering fields. For biomedical applications such as drug delivery and thrombus removal, the soft machines should be miniaturized to submillimeter size. Although 3D printing has superiority to develop miniature structures with high resolution and fidelity, submillimeter-sized soft actuators and robots have rarely been reported when compared to highly explored big ones. The practical biomedical applications also require appropriate actuation and control means such as by near-infrared light, sonication, and magnetic field. One proof-of-concept example is the design of the micrometer-sized ultrasonic-driven robot. As shown in Figure 6b, Sakar et al.[67] harnessed the principle of fluid mechanics and created this miniature robot by 3D printing of hydrogels. This robot can move forward, turn, and collect-and-transport cells actuated through pumping with acoustic streaming inside the robot, which has application potentials in diagnosis and therapies.

4.3. Fully Soft and Autonomous Robotic Systems. So far, most soft robots require dynamic stimulations for actuations and lack efficient strategies for perception and self-control.[126] It is still a great challenge to devise soft robots with autonomous motions. In contrast, living organisms can achieve completely autonomous movements with self-regulation mechanisms. Such physical intelligence (e.g., actuation and control) should be implemented by integration of different systems with the assistance of 3D printing techniques. One seminal work is from collaborative teams at Harvard University.[2] They reported an untethered robotic system composed entirely of soft materials (Figure 6c). This soft robot was contrasted by 3D printing of multiple materials and controlled by microfluidic logic, which autonomously regulated the fluid flow to catalytically decompose the propellant fuel supply. The gas generated from the decomposition inflated fluidic networks and resulted in autonomous actuations.

In summary, recent years have witnessed rapid progress in soft actuators and robots based on 3D printing techniques. The prosperity of this field relies on the collaboration of scientists from different disciplines, such as bionics, chemistry, materials, and mechanics. Especially, understanding the typical structure and kinematics of living organisms, as well as the innovations of designs, materials, and manufacturing techniques, should be crucial for the advancements of this area. In addition, practical applications of printed soft actuators and robots also need many efforts for transformation and commercialization. We hope that this Review has provided an overview to this field and will inspire worldwide scientists to engage in this emerging area.

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